DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE INVESTIGATION OF SLUDGE DISINTEGRATION USING OXIDATION PROCESSES

by
Gülbin ERDEN

January, 2010
İZMİR

THE INVESTIGATION OF SLUDGE DISINTEGRATION USING OXIDATION PROCESSES

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled "THE INVESTIGATION OF SLUDGE DISINTEGRATION USING OXIDATION PROCESSES" completed by **GÜLBİN ERDEN** under supervision of **PROF. DR. AYŞE FİLİBELİ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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ABSTRACT

In this thesis, the feasibility of oxidation techniques as biological sludge disintegration purpose was investigated to improve anaerobic digestion performance, to increase stabilization degree and to increase biogas production with experimental studies. Fenton process, ozone oxidation and ultrasonic treatment as advanced oxidation processes were applied to biological sludge samples preceding anaerobic sludge digestion. Biological sludge was sampled from the municipal wastewater treatment plant in Izmir, Turkey, which has extended aeration activated sludge plant with nutrient removal facilities.

In the first stage of the study, experiments were carried out to optimize the process conditions for floc disintegration. All applied methods allowed to destruction of microbial sludge cells resulting in an increased biodegradability. Among the methods, ultrasonic treatment gave the maximum disintegration degree.

In the second stage of the study, sludge digestion studies were carried out using lab-scale anaerobic reactors. Reactors were operated both as batch and as semi batch system. The reactors were operated in mesophilic conditions for thirty days. Experimental results showed higher volatile solids reductions and higher biogas productions for the digesters fed with disintegrated sludge. All applied method showed a positive effect on anaerobic sludge biodegradability. When comparing the applied methods in terms of sludge digestion performance, ozone oxidation and ultrasonic treatment gave much closed results and ultrasonic treatment gave the best results in terms of methane production. Fenton process had lower efficiencies then the other two methods in terms of methane production. When comparing the operation types in terms of sludge digestion performance, semi batch systems had better digestion performance than batch system. On the other hand, disintegration processes had no positive effect of sludge dewatering properties.

Key words: Anaerobic digestion, biological sludge, Fenton process, filterability, floc disintegration, ozone oxidation, ultrasonic treatment

İLERİ OKSİDASYON PROSESLERİ KULLANILARAK ÇAMUR DEZENTEGRASYONUNUN ARAŞTIRILMASI

ÖZ

Bu tez kapsamında, biyolojik çamurların anaerobik çürüme performanslarının geliştirilmesi, stabilizasyon derecesinin ve biyogaz oluşumunun arttırılmasına yönelik olarak oksidasyon tekniklerinin çamur dezentegrasyonu amacıyla kullanılabilirliği yapılan deneysel çalışmalar ile araştırılmıştır. Biyolojik çamur örnekleri anerobik çürüme öncesinde Fenton prosesi, ozon oksidasyonu ve ultrasonik arıtma işlemlerine tabi tutulmuştur. Biyolojik çamur, İzmir'de bulunan nutrient giderimi gerçekleştiren bir uzun havalandırmalı aktif çamur sistemi içeren bir evsel atıksu arıtma tesisinden temin edilmiştir.

Çalışmanın ilk bölümünde deneyler, uygulanan oksidasyon proseslerinin koşullarının çamur dezentegrasyonu için optimizasyonuna yönelik olarak yürütülmüştür. Dezentegrasyon amacıyla uygulanan yöntemler çamur içerisindeki hücrelerin parçalanmasına olanak sağlayarak çamurların biyolojik olarak parçalanabilirliğini arttırmıştır. Yöntemler içerisinde en yüksek dezentegrasyon derecesi ultrasonik arıtma uygulaması ile elde edilmiştir.

Çalışmanın ikinci bölümünde, laboratuvar ölçekli reaktörler kullanılarak çamur çürüme çalışmaları yürütülmüştür. Reaktörler kesikli ve yarı kesikli olarak işletilmiştir. Reaktörler mezofilik sıcaklık koşulunda otuz gün süre ile işletilmiş; çamur çürüme performansları laboratuvar ortamında yürütülen deneyler ile tayin edilmiştir. Deneysel çalışma sonuçları, dezentegre edilmiş çamurla beslenen reaktörlerde daha fazla organik madde indirgenmesi ve daha fazla biyogaz oluşumu olduğunu göstermiştir. Uygulanan tüm dezentegrasyon yöntemleri çamurların anaerobik parçalanabilirliği üzerinde olumlu bir etki göstermiştir. Uygulanan üç yöntem çamur çürüme performansı açısından karşılaştırıldığında ozon oksidasyonu ve ultrasonik arıtma uygulamaları çok yakın sonuçlar vermiş olmakla birlikte ultrasonik dezentegrasyon uygulaması metan gazı oluşumları dikkate alındığında daha etkili olmuştur. Fenton prosesi diğer iki yönteme kıyasla metan gazı oluşumu

açısından daha düşük verim sağlamıştır. İşletim türüne bağlı olarak yapılan değerlendirmede kesikli olarak işletilen sistemlerin yarı kesikli olarak işletilen sistemlere göre çok daha düşük bir çürüme performansına sahip olduğunu söylemek mümkündür. Diğer yandan, dezentegrasyon yöntemleri anaerobik yöntemle çürütülmüş çamurların su verme özellikleri üzerinde bir etki göstermemiştir.

Anahtar kelimeler: Anaerobik çürüme, biyolojik çamur, Fenton Prosesi, filtrelenebilirlik, flok dezentegrasyonu, ozon oksidasyonu, ultrasonik arıtma

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CHAPTER ONE
INTRODUCTION

1.1 The Problem Statement

Municipal and industrial wastewater treatment plants produce large amounts of sludge. The type of sludge produced depends on a number of factors, such as the type of sludge separation and the treatment processes employed, which are really a function of the size of the treatment plant and wastewater characteristics. They are generally in the form of a liquid or semisolid, which typically contains from 0.25 to 12 percent solids by weight (Spinosa et al., 2001). The sludge should be processed and disposed of in accordance with the environmental health criteria for environmental reasons (Metcalf & Eddy, 2003). The main objectives of sludge treatment and disposal are as follows (Scholz, 2006):

- Stabilization of the organic matter contained in the sludge;
- Reduction in the volume of sludge for disposal by removing some of the water;
- Destruction of pathogens;
- Collection of by-products, which may be used or sold to off-set some of the costs of sludge treatment; and
- Disposal of sludge in a safe and aesthetically acceptable manner.

For many authorities and engineers, the effective sludge management is still a big challenge since the investment and operational costs (Metcalf & Eddy, 2003). Treatment and disposal of excess sludge in a biological wastewater treatment system requires enormously high cost, which has been estimated to be 50–60% of the total expense of wastewater treatment plant (Egemen et al., 2001). Although processing of the sludge depends on the characteristics and quantities, the core methods used for processing are thickening, stabilization, conditioning, dewatering, and final disposal-incineration, land application (Spinosa et al., 2001).

Sludge stabilization is an important issue in sludge management field for effective reduction of organic matter, removal of pathogen and odor potential. For this purpose, alkaline stabilization, aerobic and anaerobic stabilization, aerobic thermophilic digestion, and composting are introduced. Among the methods, anaerobic digestion has been widely used with its many advantages. The main advantages of anaerobic digestion in comparison with other processes are; the lower energy requirement, the production of biogas and the lower production of excess sludge including efficient degradation of biodegradable particulate organic matters in sludge (Speece, 1996).

Anaerobic digestion process is achieved through several stages: hydrolysis, acidogenesis, and methanogenesis. Anaerobic digestion of waste activated sludge (WAS) is often slow due to the rate limiting cell lysis step which results in long residence times of 20 or more days and the requirement of a large tank volume (Li, et al., 1992). Biogas considered as the clean energy source is produced in the anaerobic digestion process depending on the stabilization degree. Nevertheless the highest degree of degredation reached, amounted to about 40 % for excess sludge at the most (Kapp, 1984). In order to improve hydrolysis and anaerobic digestion performance, floc disintegration was developed as the pretreatment process of sludge to accelerate the anaerobic digestion and to increase degree of stabilization (Bougrier et al., 2005; Weemaes et al., 2001).

Sewage sludge disintegration can be defined as the destruction of sludge by external forces. The forces can be of physical, chemical or biological nature. Because of the disintegration process, numerous changes of sludge properties have been occurred (Muller et al., 2004). The changes may be summarized as disruption of microbial cells in the sludge, thereby destroying the cell walls and releasing the cell content; breaking up or disrupting the cell walls, so that substances protected by the former are released and dissolved; opening up the cell walls of organisms, so that the substances contained in the cell are solubilized (Vranitzky et al., 2005). Increased stabilization degree of sludge with disintegration process provides less sludge production, more stable sludge and more biogas production comparing the classical anaerobic digestion (Wang et al., 2005). Ultrasonic treatment (Biyu et al., 2009;

Lafitte-Trouque et al., 2002; Nickel et al., 2007; Pham et al., 2009; Tiehm et. al., 2001; Xin et al., 2009; Zawieja et al., 2008), ozone oxidation (Bougrier et al., 2006; Magdalena et. al., 2007; Weemaes et. al., 2000), mechanical disintegration (Lehne et al., 2001, Nah et al., 2000), alkaline treatment (Chang et al., 2002; Lin et al., 1997), thermal treatment (Barjenbruch et al., 2003) and biological hydrolysis with enzymes (Ayol et al., 2007; Lai et al., 2001) were investigated for sludge disintegration purpose by several researchers in half-scale and lab-scale plants.

This thesis examined the feasibility of some advanced oxidation techniques of Fenton Process, ozone oxidation, and ultrasonic treatment for biological sludge disintegration purpose and overall fate and effects of these processes on anaerobic sludge digestion performances.

The Scientific and Technical Council of Turkey- TUBITAK financially supported this research under award #105Y337 “Sludge Disintegration Using Advanced Oxidation Processes”. Experimental study was done at the Department of Environmental Engineering, Dokuz Eylul University.

1.2 Purpose of Research

The scope objective of the thesis was to investigate the feasibility of advanced oxidation techniques as biological sludge disintegration purpose and the improvement of anaerobic degradation of sludge with these techniques. The objectives were therefore:

- To investigate the feasibility of Fenton Process, ozone oxidation, and ultrasonic treatment for biological sludge disintegration purpose,
- To optimize the process conditions for biological sludge disintegration in terms of sludge and sludge’s supernatant characteristics,
- To compare the effects of applied methods on disintegration performance of biological sludge,
- To determine dewatering characteristics of disintegrated sludge,

- To investigate the effects of applied disintegration methods on accelerated hydrolysis of the organic matter content of sludge,
- To compare the effects of applied methods on the hydrolysis and anaerobic degradation of biodegradable particulate organic matter in biological sludge,
- To investigate dewatering capacity of anaerobically digested sludge for final disposal purpose,
- To determine the effects of disintegration methods on dewatering characteristics of sludge in anaerobic digestion units.

CHAPTER TWO
BACKGROUND INFORMATION & LITERATURE REVIEW

2.1 Introduction

Water/wastewater treatment processes have produced sludge in different characteristics and quantities (Metcalf & Eddy, 2003). Sludge is generally in the form of a liquid or semisolid, which typically contains from 0.25 to 12 percent solids by weight (Spinosa et al., 2001).

Sludge suspensions include different types of water that can be categorized according to their physical bonding to the sludge particles. These are:

- free water, which is not bound to the particles;
- interstitial water, which is bound by capillary forces between the sludge flocs;
- surface water, which is bound by adhesive forces;
- intracellular water (Spinosa & Vesilind, 2001).

Figure 2.1 shows the schematic diagram of a sludge floe showing the association of the sludge particles with the available water.

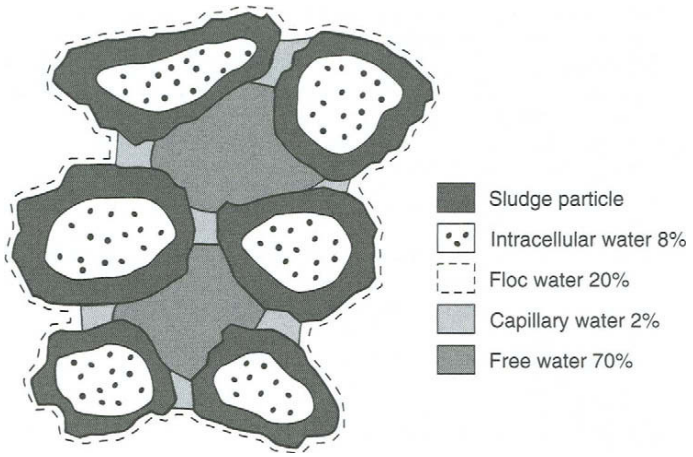


Figure 2.1 Schematic diagram of a sludge floe showing the association of the sludge particles with the available water (Gray, 2005).

The free water content represents the largest part (70-75 %) of sewage sludge that can move freely between the individual sludge particles is not adsorbed by them and is not influenced by capillary forces. It can be separated by gravity and mechanically, for example by centrifugal forces or filtration. Spinosa and Vesilind (2001) defined the interstitial water is kept in the interstice of the sludge particles and microorganisms in the sludge floc while the surface water covers the entire surface of the sludge particles in several layers of water molecules and is bound by adsorptive and adhesive forces. The important point is that the surface water is physically bound to the particles and cannot move freely. Similarly, the intracellular water contains the water in cells and can only be determined together with the surface water. This type of water fraction namely bound water can be removed by thermal processes (Spinosa; Vesilind, 2001, p. 24-25).

Sludges are very complex materials to be characterized and they should be handled using appropriate environmental technologies. The problem of dealing with sludge is complex because;

- they largely contain the substances of untreated wastewater,
- the portion of sludge produced from biological wastewater treatment contains the organic matter contained in the wastewater and will decompose and become more offensive,
- it contains only a small part of solid matter

The sludge should be processed and disposed of in accordance with the environmental health criteria for environmental reasons. In principal, sludge management targets to reduce the water and organic content of sludge and to render the processed solids suitable for reuse or final disposal. For many authorities and engineers, the effective sludge management is still a big challenge since the investment and operational costs of sludge processing have an important part of overall plant's costs (Metcalf & Eddy, 2003).

Sludge treatment and disposal at any particular location may comprise any or all of the following steps:

- Concentration: reduction in the volume of sludge to be treated by encouraging the sludge to compact to higher solids content.
- Treatment to stabilize organic matter: destruction of pathogens and/or yield of by-products.
- Dewatering and drying: removal of water, thus reducing the sludge volume. Sludge with ≤80 % moisture content is usually spadeable.
- Disposal: the only places where sludge can be disposed of are into the air, onto land or into water.

The receiving environment is legally, aesthetically and ecologically acceptable, depends on both the degree of treatment provided and the method of dispersing the sludge into the environment (Scholz, 2006).

Chapter two gives the commonly used processes in sludge treatment and disposal focuses on the stabilization processes especially anaerobic stabilization process regarding the research study.

2.2 Sludge Treatment

2.2.1 Thickening

Untreated sludge from the primary and secondary sedimentation tanks have high water contents and in order to reduce the volume of sludge handled in the stabilization or dewatering processes the sludge needs to be concentrated or thickened. Thickening is achieved by physical means, such as flotation, centrifugation, lagooning but most commonly by gravity settlement. Gravity thickeners can increase the sludge concentration in raw primary sludge from 2.5 % to 8.0% resulting in a three-fold decrease in sludge volume, while a five-fold decrease in the volume of wasted activated sludge is not uncommon being thickened from

0.8% to 4.0% solids. 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 for either thickening or dewatering purposes (Gray, 2005; Metcalf & Eddy, 2003).

2.2.2 Sludge Stabilization

Raw sludge is biologically active and includes many biodegradable compounds. The objective of sludge stabilization is to reduce the problems associated with sludge odor and putrescence, as well as reducing the hazard presented by pathogenic organisms. Sludge may be stabilized using chemical, physical, and biological methods. The methods used for stabilization summarized as follows:

- biological sludge digestion- aerobic digestion, anaerobic digestion, composting,
- alkaline stabilization- usually with lime,
- thermal stabilization- pasteurization, thermal drying (Metcalf & Eddy, 2003; Weiner et al., 2003).

Sludge can be stabilized by an aerobic process. They are maintained in an aerobic condition by external aeration, through which organic material is oxidized. A basic goal of aerobic digestion is that the degradation of floc-forming microbes, pollutants or any organic material as reduction the mass of the solids for disposal. While a fraction of the organic material is used for the synthesis of new microorganisms, resulting in an increase in biomass, the remaining material is channeled in to metabolic energy and oxidized to carbon dioxide, water, nitrates sulphates and phosphates to provide energy for both synthesis and cellular functions. Figure 2.2 summarized the mechanism of aerobic digestion process. The final product should be a mineralized sludge with good settleability characteristics that can be easily thickened and dewatered. The process is most widely used at smaller treatment plants, as unlike anaerobic digestion there is no recovery of energy making aerobic digestion comparatively expensive to operate due to the high energy costs associated with aeration and mixing, although in capital terms it is relatively cheap and easy to

operate. The process is inserted between the activated sludge tanks and dewatering processes, so that it also provides a degree of sludge equalization giving a more uniform product and allowing better control over sludge production. It is a low odor process while aerobic conditions are maintained producing a supernatant that is largely oxidized, although often with a high-suspended solids concentration, that is returned to the inlet of the plant. There is a decrease in pH during aerobic digestion due to nitrification that can inhibit digestion so that pH control to 6.5 may be necessary. Performance is directly related to microbial activity, which in turn is largely dependent on temperature (Gray, 2005; Metcalf & Eddy, 2003; Scholz, 2006; Whiteley et al., 2006).

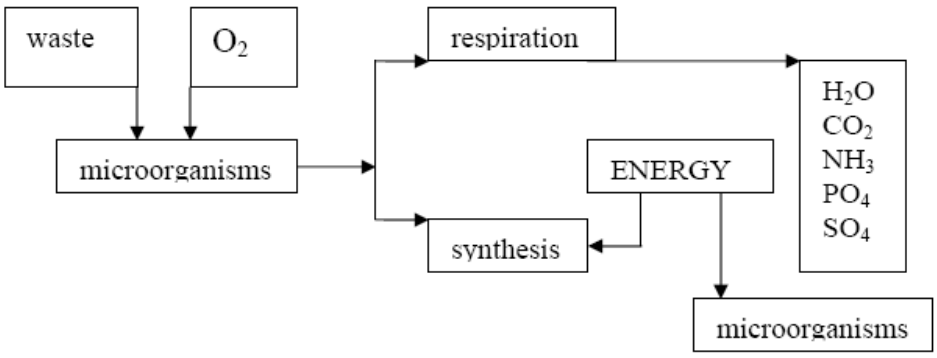


Figure 2.2 Aerobic digestion of waste containing microorganisms (Whiteley, C.G., Lee, D.-J., 2006)

Anaerobic digestion is one of the more commonly used stabilization processes in sludge management, providing effective pathogen destruction, reduction of volatile solids and odour potential and an energy source in the form of biogas (Novak et al., 2003; Speece, 1996). Many progresses have been made in the fundamental understanding and control of the anaerobic digestion process, design and the application of the equipment. This process is one of the dominant processes for stabilizing sludge because of the energy conservation and recovery. Anaerobic digestion of municipal wastewater sludge can in many cases, produce sufficient digester gas to meet most of the energy needs for plant operation (Metcalf & Eddy, 2003).

Anaerobic digestion breaks down the organic material of sludge into biogas in the absence of oxygen. During anaerobic digestion, a complex microbial community consisting of many interacting microbial species like acetic acid-forming bacteria (acetogens) and methane-forming archaea (methanogens) degrades natural polymers such as polysaccharides, proteins, nucleic acids, and lipids, in the absence of oxygen, into methane and carbon dioxide. The final electron acceptor in anaerobic digestion mechanism is different from oxygen, for example, sulphate-reducing bacteria transfer electrons to sulphate (SO_4^{2-}) reducing it to H_2S, while others (nitrate reducers) transfer the electrons to nitrate (NO_3^-) reducing it to nitrite (NO_2^-), nitrous oxide (NO) or nitrogen gas (N_2) (McInerney, 1999; Metcalf & Eddy, 2003; Whitely & Lee, 2006). This process has four distinct stages given below and schematized in Figure 2.3:

(a) Most waste compounds have non-degradable properties so it is not possible to treat directly by microorganisms. Because of that, hydrolysis of these complex and insoluble organics are very important in order for them to be used by bacteria as an energy and nutrient source. In hydrolysis stage, complex organic matter is decomposed into simple soluble organic molecules using water (hydrolysis) and hydrolase enzymes (glycosidase, lipases, proteases, sulphatases, phosphates) During hydrolysis, stabilization of the organic material is not possible. In this stage only, transformation of the organic material to a structure that can be used by microorganisms is accomplished. Enzymes produced and given to the environment by bacteria groups carry out hydrolysis stage.

(b) In the acidogenesis stage, chemical decomposition of these single monomeric unit molecules (monosaccharide, amino acids, fatty acids, and glycerol) into volatile fatty acids by a process termed.

(c) In this stage, products formed as a result of acidoge Increase in nesis stage, are oxidized to H_2 and acetate. After this formation, hydrogen is used as an energy source by some bacteria for acetate production and for the reduction of carbon dioxide to methane. However, hydrogen sulphur in the system carries inhibitory properties for acid forming bacteria. As a result, organic acid concentration decreases and methane production is inhibited (Öztürk, 1987). Consequently, hydrogen can be

used as an efficiency indicator because of its regulating effect in acid production and consumption.

(d) Stabilization of wastewater is completed during methane production phase. In methane production stage, two different groups of organisms are active. These are methane bacteria that use molecular hydrogen to form methane and methane bacteria that produce methane and bicarbonate by acetate dicarboxylation. This stage prevents accumulation of acids and alcohol and as a result prevents reduction of system efficiency. (Filibeli et al, 2000; Metcalf & Eddy, 2003; Whitely & Lee, 2006).

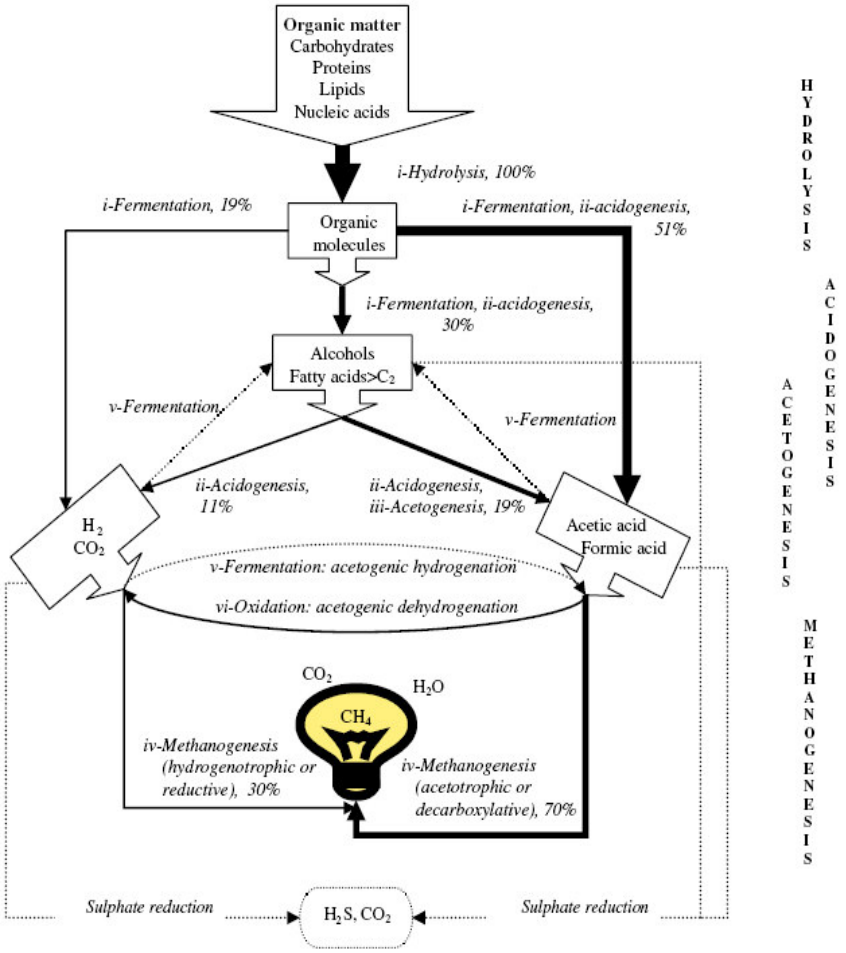


Figure 2.3 Schematic of the different metabolic steps and microbe groups involved in the complete degradation of organic matter to methane and carbon dioxide (Aiyuk, S., Forrez, I., Lieven, D.K.,Haandel, A.V., & Verstraete, W., 2006).

The efficiency of an anaerobic digester depends on the dynamics and kinetics of the microbial populations within the reactor and on the narrow limits that thermodynamics places on the ensuing reactions (McInerney, 1999). Solids retention time, hydroulic retention time, temperature, alkalinity, pH, the presence of inhibitory substances, i.e., toxic materials and the bioavailability of nutrients and trace metals are the important environmental factors for this process (Metcalf & Eddy, 2003).

Anaerobic digestion, although slow, offers a number of attractive advantages in the treatment of strong organic wastes. The advantages and disadvantages of anaerobic digestion are outlined in Table 2.1.

Table 2.1 Advantages and disadvantages of anaerobic digestion compared to aerobic digestion (Filibeli et al., 2000; Gray, 2005)

Advantages	**Disadvantages**
Low operational costs	High capital costs
Low sludge production	Generally require heating
Reactor sealed giving no odor or aerosols	Low retention times required (>24 h)
Sludge is highly stabilized	Corrosive and malodorous compounds produced
Methane gas produces as an end product	Not as effective as aerobic stabilization for pathogen destruction
Low nutrient requirement due to lower growth rate of anaerobic bacteria	Hydrogen sulphide also produced
It is appropriate for seasonal and batch operation	Reactor may require additional alkalinity
Rapid start-up possible after acclimation	Slow growth rate of anaerobic bacteria can result in long initial start-up of reactors and recovery periods
Digestion is not limited with oxygen transfer	Anaerobic degradation is a highly sensitive process to the presence of some chemical compounds such as $CHCL_3$, CCI and CN^-
Reactor need small area	Anaerobic degradation process is mainly a pretreatment method. Consequently, before giving the treated water to the receiving media an appropriate final treatment is required
It can be apply both for big and small scales	Methane bacteria reproduce very slowly and they are very sensitive to environmental conditions

Alkaline stabilization is used to eliminate the nuisance conditions in sludge with alkaline material. Lime is generally used as alkaline material. Lime stabilization is achieved by adding lime, either as hydrated lime ($Ca(OH)_2$) or as quicklime (CaO) to the sludge, which raises the pH to 11 or above. This significantly reduces the odor and helps in the destruction of pathogens. The major disadvantage of lime stabilization is that its odor reduction is temporary. Within days the pH drops and the sludge once again becomes putrescible (Metcalf & Eddy, 2003; Weiner et. al., 2003).

Thermal or heat treatment is a continuous process that both stabilizes and conditions sludge by heating them for short periods like 30 min under pressure. This releases bound water allowing the solids to coagulate, while proteinaceous material is hydrolyzed resulting in cell destruction and the release of soluble organic compounds and ammonical nitrogen. The Zimpro process heats the sludge to 260 °C in a reactor vessel at pressures up to 2.75 MN/m^2 The process is exothermic which results in the operating temperature rising. The solids and liquid separate rapidly on cooling with up to 65 % of the organic matter being oxidized. The process sterilizes the sludge, practically deodorizes it and allows dewatering to occur mechanically without the use of chemicals. Owing to the disadvantages of capital and operating costs, operational difficulties and the large volume of very strong waste liquor produced, there are very few such plants operating in Europe. There are many improved designs becoming available. Thermal drying is normally now combined with anaerobic digestion. The digestion process produces the biomass and energy to run the drier, and the energy recovered from the drying process is used to heat the digester. Modern thermal drying units produce small quantities of final product in the form of a stable granular material similar in size to artificial fertilizer allowing it to be easily handled by standard agricultural spreading equipment. With a dry solids content of between 90 % and 95 % it can be bagged and stored for long periods without problems. The product is odorless and can be used for a wide range of disposal options primarily as a fertilizer but also as a low sulphur (0.5 %) and greenhouse gas neutral (0.5 % CO_2) fuel. The main disadvantages are the high capital cost of thermal drying and the risk of combustion if operating conditions are not carefully controlled (Gray, 2005).

2.2.3 Dewatering

Raw sludge contains high amounts of water, usually more than 95 % by weight. It is only possible to remove a certain proportion of free, adhered and capillary water with the technology (European Commission, 2001; Metcalf& Eddy, 2003). Dewatering is a mechanical unit operation used to reduce the water content of sludge to obtain a solid concentration of at least 15 %, usually much more. It is normally preceded by thickening and conditioning, which is the addition of chemicals to aid flocculation and water separation, and may be followed by further treatment. This reduces the total volume of sludge even further so reducing the ultimate transportation cost of disposal. The resultant sludge is a solid, not a liquid, and so can be easily handled by conveyers or tractors although experience has shown that the dried sludge, known as cake, is more easily handled at solids concentrations of >20 %. Its solid nature makes it suitable for many more disposal options than liquid sludge. The ratio of primary to secondary sludge is a major factor controlling dewatering, with primary sludge on its own capable of being dewatered to 35-45 % DS but when mixed with secondary sludge this falls to a maximum of 17-20 % DS (Gray, 2005). Different dewatering processes are available such as natural systems like drying beds and mechanical units like centrifuging, belt filter press, and filter press. All processes except for drying beds require the chemical conditioning. The water content of the sludge after dewatering depends on the treatment and can reach about 30 % (European Commission, 2001).

Sludge conditioning is used to improve sludge dewatering characteristics and to provide the separation of flocs from the liquid phase to achieve high solid content in sludge before final disposal (Metcalf & Eddy, 2003).

The conditioning of sludge involves pretreatment in order to facilitate water removal during subsequent thickening and/ or dewatering operations. During the conditioning process small and amorphous gel like particles are transformed into larger and stronger aggregates, thereby increasing the rate and/ or extent of water drainage and solid separation (Eckenfelder & Santhanam, 1981).

Eckenfelder et al. (1981) have reported that factors affecting conditioning effectiveness are pH, dissolved oxygen, redox potential, and the concentration of carbonates, detergents, oil and greases, and degradable organics. pH may be considered as the most important factor influencing the conditioning mechanisms. It affects the adsorption and ionization equilibrium of both the dispersed sludge particles and conditioning agent, pertinent solubility, the degree of the polymer's curl, the charges on sludge dispersions and conditioning agents, and the nature of the binding mechanisms. The dissolved oxygen and the redox potential have effects on the charging and solubility of both sludge and conditioning agents. Oil and grease, often present in raw sludge, may decrease cake permeability and bind filtering medium, consequently, presence of these interfere the dewatering of sludge. Bioactivity within the sludge will result in a change of composition, both in molecular weight and degree of charge, thereby altering absorbability and solubility and consequently affecting dewaterability.

S. K. Dentel (2001) determined the conditioning mechanisms considering the particle breakage and its role in conditioning. He has pointed out that:

- *Flocculation of the sludge*. Whether an inorganic or organic conditioner is used, sufficient dose provides initial attachment of a particles and a growth of flocs.
- *Breakage of sludge particles and floc*. Breakage of sludge or floc particles occurs during sludge mixing, during flow to the solid-liquid separation process, and then during thickening or dewatering. In a floc particle, the original particles are the weakest component, and are more likely to break than the metal hydroxide deposits or the polymer connections.
- *Presence of residual flocculant in solution*. When inorganic conditioner is added to sludge, deposition on the particle surfaces is due to precipitation. Larger doses do not increase the amount remaining in solution, but lead to additional layers of the precipitate. But when a cationic polymer is added to the sludge, deposition is governed by charge attraction. If it is added beyond the amount required for charge neutralization (or moderate charge reversal),

most of the excess remains in solution due to the lack of charge attraction (and even charge repulsion) between the polymer and the surfaces.

- *Reflocculation effects*. Breakage of sludge particles increases the amount of particle area and, consequently the amount of chemical required modifies these surfaces. As long as the sludge in a liquid state, any excess of flocculant chemical in solution can attach the newly exposed surfaces and thus reflocculate the sludge. This breakage and reflocculation process (sometimes termed 'pelletisation') decreases the 'reverse' of flocculant in solution and eliminates the weakest bound in the sludge matrix. The strength of the flocculated sludge increases.However if the remaining flocculant in solution is used up, any further floc breakage will decrease the floc size (but not the floc strength).
- *Resulting sludge properties*. At the culmination of these processes, the sludge will possess a particle size distribution, a particle strength distribution, and a perhabs a residual of flocculant in the lquid phase. These factors will determine the thickening or dewatering behaviour of the sludge. The preceding phenomena will also determine other measurable properties of the sludge such as electrokinetic and rheological characteristics which may be useful for monitoring or control purposes.

Conditioning methods may be divided into two basic groups: chemical conditioning, in which one or more additives are used to alter sludge properties; and physical conditioning, in which temperature or other physical properties are changed to affect the sludge properties.

In chemical conditioning, conditioners aid the dewatering process by improving the filtration characteristics of sludge by increasing the degree of flocculation of the sludge particles so that the absorbed water can be more easily removed (Gray, 2005). Conditioning chemicals can be categorized into two groups: *inorganic chemicals* such as ferric and ferrous salts, aluminum salts, and lime; and *organic chemicals* like high molecular weight polymers. The polymers have become a primary choice as a conditioning chemical for sludge dewatering operations in recent years. Inorganic

chemicals may be used in combination with polymers for specific purpose (Metcalf & Eddy, 2003).

Thermal conditioning, freeze-thaw conditioning and elutriation are used for physical conditioning. In thermal conditioning, sludge is heated to 150-200 ºC in 30 to 60 minutes. Heating to 40ºC or 50ºC is also possible and will give a partial thermal conditioning (Metcalf & Eddy, 2003). Freeze/thaw treatment can significantly improve certain sludge dewatering characteristics, transform the floc structure into a compact form and, reduce the sludge bound water content (Lee et al., 1994). The application of freezing as a conditioning process is energy insensitive and appears economically unfeasible unless a technological breakthrough decreases energy requirements. The capital cost, and space requirements are all considerably higher than for chemical conditioning of sludge (Eckenfelder & Santhanam, 1981). "Elutriation" is a process of improving filtration by washing the sludge. It reduces the alkalinity and, therefore, the lime coagulant demand of sludge by upgrading the biochemical quality of the sludge water before chemicals are added. It consists of two operation steps. In the mixing step, the sludge is mixed with a washing liquid, and in the settling step, the sludge suspended solids are recovered in their original volume. These two steps may be repeated and each such repetition is called a stage. Normally, elutriation systems have a mixing time of one minute and a gravity settling time of three to four hours (Nemerow, 2007).

2.3 Sludge Disposal

Even after treatment, we are left with a large volume of sludge that needs a final resting place. The choices for ultimate disposal of sludge are limited to air, water, and land (Weiner, 2003). There are several disposal methods for sewage sludge. In many countries for regarding to sustainable activities, agricultural use of sludge is becoming more attractive instead of land filling. Incineration is another option for sludge disposal whereas the end product is not suitable for beneficial use. In the following subsections, the disposal alternatives will be discussed.

2.3.1 Incineration

Sludge can be burnt to produce ash, which contains very little water and very little organic matter. The sludge is therefore reduced to the non-volatile fraction. A sludge containing 30% solids, of which 50% are volatile, would reduce to approximately 15% of the original wet sludge volume. Sludge contains more volatile combustible matter and less fixed carbon than coal, so once it is dried sludge will burn to generate considerable heat. Sludge solids have calorific values similar to conventional fossil fuels (e.g., coal and oil: 20 000–50 000 kJ/kg). Thus, dry sludge can be burnt with no additional fuel consumption. Incineration destroys the organic and volatile components of sludge including any toxic organic compounds, leaving a sterile ash in which all the toxic metals are concentrated. Although the weight of sludge cake is very much reduced, the ash that remains is a hazardous waste that must be disposed of at a regulated site. Alternatively it can be used as an amendment in cement or aggregate manufacture. If the solids concentration of sludge is <30 % then additional fuel is required to burn the sludge because the amount of energy released during combustion is less than that required to evaporate the water present. At solids concentrations >30 % the reaction is auto-thermal. This problem is generally overcome by mixing sludge with refuse to increase combustibility of sludge.

In practice, the fuel value is reduced considerably by the moisture in the sludge, so that effective dewatering is necessary prior to incineration. Designs are usually based on the production of sufficient heat to evaporate the associated water from the sludge. Sludge can be incinerated with municipal refuse.

The two types of furnace employed are the multiple hearths and the fluidized bed. Multiple hearth furnaces consist of a series of floors in a cylindrical tower; the cake is introduced at the top, and it gradually falls to the lower floors. The material is moved over floors by rabble arms. The major combustion occurs at lower levels, and heat from these levels dries out the sludge at the upper levels. In comparison, fluidized bed furnaces have a cylindrical chamber, which contains approximately 1.0 m of sand on a heat-resistant steel grid. The bed is fluidized by the injection of compressed air, and as sludge is injected into the sand under pressure through an air-cooled lance, water evaporates and the organic material burns.

Incineration requires a high capital cost, so is not widely adopted except for large cities where other disposal routes are not available or metal contamination is high (Gray, 2005; Scholz, 2006).

2.3.2 Sludge Barging

Sludge barging is the other method of final disposal of sludge. In this method, raw, precipitated, digested, or filtered sludge solids are pumped into a waiting barge and transported to a suitable site from the shore, where it is discharged, usually by pumping out deep under the water surface. The advantages of sludge barging are relatively lower operating costs and reduced land demands. However, experience has shown that this method of disposal results in several environmental concerns:

- long-term adverse effects on the ecology of the receiving water,
- sludge floating matter rising to the surface,
- public objection, and
- potential for sludge residues carried to the shore during tidal cycles and causing public health impacts.

Based on these concerns, this method of disposal has been discontinued and is not a recommended practice (Nemerow, 2007).

2.3.3 Land filling

The second method of disposal, land disposal, is becoming more popular, particularly in areas where there are restrictions on industrial contaminants entering the wastewater treatment. (Sludge contaminated with industrial chemicals may not be suitable for land application). The ability of land to absorb sludge and to assimilate it depends on such variables as soil type, vegetation, rainfall, and slope. In addition, the important variable of the sludge itself will influence the capacity of a soil to assimilate sludge. Generally, sandy soils with lush vegetation, low rainfall, and gentle slopes have proven most successful. Mixed digested sludge has been spread

from tank trucks, and activated sludge has been sprayed from both fixed and moving nozzles. Given enough time, and the absence of toxic materials, soils will assimilate sprayed liquid sludge. Most unsuccessful land application systems may be traced to overloading the soil (Weiner, 2003). The other risks of the disposal of sewage sludge to landfill sites may be summarized as - contamination of leachate with metals and organics, - pathogen transfer risks, - enhanced methane production on decomposition (Gray, 2005).

2.3.4 Disposal to Agricultural Land

Sewage sludge is rich in organic matter and nutrients, especially N and P. It is also rich in trace elements, so it is useful both as a soil conditioner and as a fertilizer. There is considerable variation in the agricultural value of sludge, which depends largely on the treatment it receives. The main problems are that a significant portion of the N is lost in the final effluent, and that sludge has a low K concentration, as the K present is mainly soluble and so is also lost in the final effluent. Therefore, when sludge is used as a fertilizer a supplementary source of K may be required. The content of phosphorus is unaffected by treatment as it is generally present in insoluble forms, and so retained in the sludge. It is constant at between 1.0 % and 1.8 % of DS, giving a low N: P ratio compared to artificial fertilizers. So sewage sludge is rather like a superphosphate fertilizer with 50-60 % of the P readily available. Phosphorus as a plant nutrient is less important than N, as most soils have adequate reserves, also the extent to which P is used is controlled by N availability. Phosphorus is a major eutrophication nutrient so the disposal of sewage sludge to agricultural land must be carefully managed to prevent surface-water pollution (Gray, 2005). Sludge also contain pathogenic organisms and can be a source of odors. Therefore, it is most common to recycle sludge only after digestion, and in some cases pasteurization or disinfection is required before the sludge can be used on agricultural land. The requirements for the pre-treatment of sludge before land application also depend on the crop to be grown. For agricultural use of sludge, approximately 1 ha is required for a population of 1000. Most sludge is produced in large urban areas, and the logistics of transporting it to agricultural land can pose problems. Additionally, there is usually a significant industrial component in

municipal wastewaters; certain toxic metals, for example, concentrate in the sludge and can restrict its land application. Land treatment can be regarded as recycling of organic materials back into the food chain (Scholz, 2006).

2.4 Sludge Disintegration

In this section, the objectives and mechanisms of disintegration process were summarized and then disintegration methods were evaluated.

2.4.1 Objective of Sludge Disintegration

The main by-product of municipal wastewater treatment of waste activated sludge (WAS) has been increasing worldwide as a result of an increase in the amount of wastewater being treated. Treatment and disposal of excess sludge in a biological wastewater treatment system requires enormously high cost which has been estimated to be 50–60 % of the total expense of wastewater treatment plant (Egemen et al., 2001). Anaerobic digestion is a common process for stabilization of treatment plant sludge. Compared with other processes, its advantages are less energy required, a better stabilized product, and usable gas. Anaerobic digestion process is achieved through several stages: hydrolysis, acidogenesis, methanogenesis. For waste activated sludge degradation, the rate-limiting stage is the hydrolysis. Biogas considered as the clean energy source is produced in the anaerobic digestion process depending on the stabilization degree. Anaerobic digestion is a slow process, which results in a long residence time and the requirement of a large tank volume. In order to improve hydrolysis and anaerobic digestion performance disintegration was developed as the pre-treatment process of sludge to accelerate the anaerobic digestion and to increase degree of stabilization (Bougrier et al., 2005). Disintegration process results in an improvement of velocity and degree of degradation. To increase of stabilization degree of sludge with disintegration process provides less sludge production, more stable sludge and more biogas production comparing the classical anaerobic digestion. Sewage sludge disintegration can be defined as the destruction of sludge by external forces. The forces can be of physical, chemical or biological nature. As a result of the disintegration process is numerous

changes of sludge properties (Muller et. al., 2004). Disintegration cause disruption of microbial cells in the sludge, thereby destroying the cell walls (Vranitzky et. al., 2005). The destruction of floc structure and disruption of cells results in the release of organic sludge components into the liquid phase. These components exist in a dissolved phase, e.g. components of intracellular water, or can be liquefied. Particle size or colloidal components may still be present within the solution because they cannot be separated from the liquid phase. Their minute particle size and only a slight difference in density of particle and surrounding water are the cause. But components are easily biodegradable on the other hand. Since they are already liquefied or offer a large surface in comparison their volume, the hydrolyzing process is simple. Released carbon compounds after disintegration are easily accessible and can be digested much faster in later biological process than sludge in a particular phase. The results are shorter degradation times and higher degrees of degradation during the aerobic and anaerobic stabilization. Besides, these compounds can further be used for carbon limited process steps within the wastewater treatment such as denitrification or the biologically enhanced phosphorus elimination. After disintegration, the liquid phase has to be cleaned from the released nitrogen and phosphorus compounds before leaving the treatment plant. If this happens by returning the water into the WAS process, additional capacities have to be taken into account. Disintegration within the sludge pre-treatment has advantages in combination with selective recycling processes due to the increased nitrogen and phosphorus concentrations (Muller et. al., 2004).

Table 2.2 is summarized the possible objectives of sludge disintegration.

Table 2.2 Possible objectives of using sludge disintegration (Muller, 2003)

Reduction of sludge	Improvement of sludge characteristics
Improvement of the anaerobic degradation performance of surplus sludge	Improvement of the settling performance of bulking and floating sludge
Halogen donor for the denitrification	Reduction of foam production
Improvement of the recycling options of phosphorus and nitrogen	Improvement of sludge conditioning
	Reduction of pathogens

2.4.2 Mechanisms of Sludge Disintegration

Sludge disintegration can be defined as the destruction of sludge by external forces. These forces can be of physical, chemical or biological nature. A result of the disintegration process is numerous changes of sludge properties, which can be grouped in three main categories:

- destruction of floc structures and disruption of cells
- release of soluble substances and fine particles
- biochemical processes

The applied stress during the disintegration causes the destruction of floc structures within the sludge and/or leads to the break-up of micro-organisms. If the energy input is increased, the first result is a drastic decrease in particle size within the sludge. The destruction of floc structures is the main reason for this behavior. The disruption of microorganisms is not as easily determined by the analysis of particle size because disrupted cell walls and the original cells are of similar size. Floc destruction and cell disruption will lead to the following changes in sludge characteristics:

- *Hydrolysis*: Disintegrated microorganisms are much more easily hydrolyzed than undisrupted ones. The reduction in particle size generally allows an easier hydrolysis of solids within the sludge due to larger surface areas in relation to the particle volumes. The result is an accelerated and enhanced degradation of the organic fraction of the solid phase.
- *Disinfection:* the disintegration process affects all microorganisms. Higher organisms are disrupted easiest because of their size and gram-positive bacteria are the most difficult organisms to be disrupted due to their strong cell wall. Depending upon the treatment a partial up to a complete disinfection of the sludge is possible since pathogenic micro-organisms are also disintegrated.

- *Settling and dewatering:* In case of a strong disintegration a large amount of organic solid material is transferred into the liquid phase (see later paragraph). The remaining solid sludge particles contain a higher percentage of inorganic substance. The result is a higher content of dry substance after dewatering (Muller, 2003). In case of a less intense disintegration combined with a partial disruption of floc structures the results in settling of well sediment sludge are worse. But the settling properties of filamentous sludge (bulking sludge) can be improved due to the destruction of voluminous floc structures.

- *Flocculation:* The reduction of particle size and therefore the increase of the specific surface because a higher amount of surface charges that need to be neutralized when the sludge is conditioned. Consequently, disintegrated sludge use more flocculent.

- *Viscosity, foaming:* Disintegration has an effect on other sludge parameters as well. The viscosity is severely decreased which simplifies mixing and pumping of sludge. Foaming problems can be controlled in case of sludge with a high content of filamentous microorganisms. The production of scum as well as the foaming within digesters is reduced.

The destruction of floc structures and disruption of cells result in the release of organic sludge components into the liquid phase. These components exist in a dissolved phase already, e.g. components of the intracellular water, or can be liquefied. Particle size or colloidal components may still be present within the solution because they cannot be separated from the liquid phase. Their minute particle size and only a slight difference in density of particle and surrounding water are the cause. But the components are easily biodegradable on the other hand. Since they are already liquefied or offer a large surface in comparison to their volume, the hydrolyzing process is simple. The influence of the released amounts of carbon, nitrogen and phosphorus compounds on sludge characteristics are:

- *Degradation:* Carbon compounds are easily accessible and can be digested much faster in later biological processes than sludge in a particular phase.

The results are shorter degradation times and higher degrees of degradation during the aerobic and anaerobic stabilization.

- *Carbon source:* Easily accessible compounds can further be used for carbon limited process steps within the wastewater treatment such as denitrification or the biologically enhanced phosphorus elimination.

- *Return-Flow-Pollution:* The wastewater has to be cleaned from released nitrogen and phosphorus compounds before leaving the treatment plant. If this happens by returning the water into the WAS-process, additional capacities have to be taken into account.

- *Recycling:* A separate treatment and recycling is possible as well, e.g. through ammonia stripping or phosphor crystallization. Disintegration within the sludge pre-treatment has advantages in combination with selective recycling processes due to the increased nitrogen and phosphorus concentrations.

During or immediately after the disintegration, biochemical reactions may appear. The influence of these reactions on the degradability of the sludge is contrary:

- Continuing formation or release of easily degradable compounds

- Formation of hardly degradable compounds

The formation of problematically biodegradable, humic-like reaction products if sludge is disintegrated at higher temperatures can be explained by the "Maillardreaction". At lower temperature ranges, this effect is less strong, but it is suspected that problematically biodegradable compounds are produced in any thermal disintegration process. Many times proven is the transformation of problematic compounds to easily degradable compounds by partial oxidation. This effect has been found especially in the treatment of industrial wastewaters, but it is not fully verified in sludge treatment through ozone or other oxidation partners. The formation of hardly degradable compounds was found as well and degradation

processes only performed well after an adaptation of the microorganisms (Muller et al., 2004).

2.4.3 Sludge Disintegration Methods

In recent years, for the purpose of waste activated sludge (WAS) minimization and more biogas production than classical anaerobic digestion, several disintegration methods have been investigated. The methods can be classified as following topics (Filibeli & Kaynak, 2006);

- Chemical disintegration (Fenton process, Ozone treatment, alkaline treatment etc.)
- Mechanical disintegration (Ultrasonic treatment, Stirred ball-mill, High-pressure homogenizer, Lysat centrifuge, Jet Smash Technique, The High Performance Pulse Technique etc.)
- Thermal disintegration
- Biological disintegration (High temperature sludge stabilization with thermophilic bacteria, Enzymatic lysis)

Since the thesis deals with the effects of Fenton process, ultrasonic pre-treatment and ozone oxidation process on anaerobic biodegradability of sludge, these disintegration methods will be given in details in this section of the thesis.

Fenton Process: Fenton's reagent is a mixture of H_2O_2 and ferrous iron. The ferrous iron initiates and catalyses the decomposition of H_2O_2, resulting in the generation of highly reactive hydroxyl radicals (Kitis et al., 1999).

Fenton's reagent was discovered about 100 years ago, but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s (Huang et al., 1993).

Iron catalyzed decomposition of H_2O_2 has been slowly occurring under alkaline conditions. This process is only effective at acidic pH level of about 2.8 (Pignatello, 1992) or acidic conditions (Bishop, 1968; Walling, 1975).

Fenton reaction are known to be very effective in the removal of many hazardous organic pollutants from water in wastewater treatment processes (Badawy et. al., 2006; Catalkaya et. al., 2007; Kang et. al., 2002). The main advantage is the complete destruction of contaminants to harmless compounds, e.g. CO_2, water and inorganic salts.

The following mechanism for the independent Fenton's Reagent activity has been accepted (Ashraf et al., 2006).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet \quad \text{(Eq. 1)}$$

The Fe^{3+} produced in this reaction reacts with H_2O_2 to regenerate Fe^{2+} as shown in the following equations:

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+ \quad \text{(Eq. 2)}$$

$$Fe(OOH)^{2+} \rightarrow Fe^{2+} + HO_2\bullet \quad \text{(Eq. 3)}$$

A similar mechanism for the Fenton-like reaction of hydrogen peroxide with ferric iron can be attributed. The initial rate of mineralization is faster with Fenton's Reagent (Fe^{+2}/H_2O_2) than the Fenton like reaction (Fe^{+3}/H_2O_2) due to the force of hydroxyl radicals, which is produced by Fenton's Reagent (Amiri et al., 1996).

Fenton process can effectively be used in WAS treatment. Pere et al., 1993 indicate that Fenton process of sludge enhances the dewaterability. The dewaterability of the sludge is strongly dependent on the concentration of hydrogen peroxide, the reaction temperature, the pH and the Fe^{2+}-concentration in the Fenton's peroxidation (Neyens et al., 2003). Neyens et al. 2003 were applied Fenton's oxidation to thickened sludge taken from a municipal sewage treatment plant at different conditions and they noted that optimum activity is the presence of 25 g H_2O_2 /kg DS, 1.67 g Fe^{2+} /kg DS, pH=3 and at ambient temperature and pressure. In

these conditions Fenton Process resulted in a considerable reduction of dry solids (DS) and organic dry solids (ODS) contents in the filter cake of approximately 20%, an improved dewaterability with a 30% reduction of the sludge volume, and a 30% increase of the cake DS-content when compared with the untreated sludge sample. In addition, a reduced CST-value by approximately 20 s when compared with the 'blank' sample was achieved.

Fenton's oxidation enhances cake dewaterability in two ways:

- it degrades EPS (extracellular polymeric substances) proteins and polysaccharides reducing the EPS water retention properties and
- it promotes flocculation which reduces the amount of fine flocs (Neyens et al., 2004).

Dewil et al. (2005) was investigated the influence of Fenton process on drying performance of waste activated sludge. Results demonstrated that the Fenton process positively influences the sludge cake consistency and hence enhances the mechanical dewaterability and the drying characteristics of the dewatered sludge. For the two sludge used in that study, i.e. obtained from the wastewater treatment plants (WWTP) of Tienen and Sint-Niklaas – the dry solids content of the mechanically dewatered sludge increased from 22.5 % to 40.3 % and from 18.7 % to 35.2 %, respectively.

In the other study, Fenton's reagent was applied to biological sludge samples as a chemical conditioner. Different concentrations of Fe^{2+} (1000–6000 mg/L) and H_2O_2 (2000–6000 mg/L) were used, and dewatering properties of sludges were evaluated based on capillary suction time (CST) and specific resistance to dewatering (SRF) parameters. Experimental results indicated that high Fe^{2+} and H_2O_2 concentration provides higher dewatering efficiency. Minimum SRF, 6.149×10^{9} m/kg, was achieved at 5000 mg/L Fe^{2+} and 6000 mg/L H_2O_2 concentration and minimum CST, 15.7 s, was obtained at dosage of 5000 mg/L Fe^{2+} and 6000 mg/L H_2O_2 (Buyukkamaci, 2004).

Tokumura et al. (2007) applied the similar advanced oxidation method of photo-Fenton reaction to WAS in a batch photo reactor for disintegration purpose. Soluble chemical oxygen demand (SCOD) was achieved at highest level in the presence of 4 g H_2O_2/L, 40 mg Fe(II)/L, 3000 mg MLSS/L, pH=3 for 6 h reaction time and effective disintegration was obtained. At longer times than 6 h, SCOD decreased and mineralization occurred.

Ozone oxidation: Ozone is an allotropic form of oxygen with the chemical formula: O_3. In high densities, ozone has a characteristics blue color. Ozone is unstable gas obtained by electrically exiting oxygen. This is achieved by applying the high voltage to generate an electrical field, under the influence of which oxygen undergoes partial dissociation into radicals. The electrical field increases the kinetic energy of free or dislodged electrons and causes them enter into successive collision, thus exciting the oxygen and producing dissociation. Ozone molecules form as the result of successive transition. An ozone-producing environment contains a huge amount of energy, which means that a number of transient forms are liable to occur: ions, atoms, free radicals, or energized molecules. Chemically speaking, these transient forms are highly reactive, which means that there is an increased tendency to for new stable products, which would be difficult, or even impossible, to produce using other types of excitation (Vranitzky et al., 2005).

The combination of anaerobic sludge digestion with disintegration using ozone is seen as one promising technical and economic method of enhancing the stabilization process.

For better understanding of ozone disintegration, it may be explained that inactivation of microorganisms by ozonation. A bacterium is schematically composed of a cell wall surrounded by exo-polysaccharides, then a cytoplasmic membrane, and finally the cytoplasm containing the genetic information-carrying chromosome. The cell liquid offers a near neutral pH and a high concentration of bicarbonate ions. It is therefore probable that the radical action of ozone is inhibited inside the cell. On the other hand, the cytoplasmic membrane can provide a site for ozone reaction, due to numerous proteins among its constituents. If residual ozone

crosses this membrane, the cytoplasm and the chromosome become preferred sites, since the nucleic acids are quickly degraded by ozone (Vranitzky et. al., 2005).

Thorough the implementation of sludge ozonation, refractory organic structures are oxidized and converted into biodegradable low-molecular compounds. Hence, a substantially increased degree of sludge stabilization can be achieved. Basically, the disintegration process is accomplished by the application of ozone to break down cell walls. Thus, cell walls are fragmented and intracellular compounds are released. The product can be utilized as a substrate in the anaerobic biological processes (Weemaes et al., 2000).

Altough there are several advantages of ozone treatment on improvement of anaerobic digestion as mentioned above, there are not too many studies in the literature.

Vranitzky et al. (2005) investigated the overall disintegration efficiency of ozonization at different ozone doses. Results showed that only 0.06 g O_3/ g DS was necessary to destroy the biological activity of treated biomass. The tests conducted provide evidence of an increase in the average degradation rate of organic matter to 65% as compared to 45% in the conventional system.

Weemaes et al. (2000a) studied on disintegration of municipal wastewater treatment plant sludge with ozone treatment in lab scale. In the study, 0.1 g O_3/g COD ozone dose was used by adjusting the ozonation time on the basis of the COD-content of the sludge. The ozonized and the non-ozonized sludge were subjected to a batch digestion test in Erlenmeyer of 2 L. To 750 mL of sludge, 250 mL of inoculum was added. The test was performed in mesophilic conditions at 35ºC. The biogas production was followed during 30 days. An ozone dose of 0.1 g O_3/g COD resulted in a 16 ± 6 % decrease of the total COD. The decrease in total TOC (16 ± 4 %) indicates that a part of the sludge is completely oxidized to CO_2. The increase in soluble COD (29 ± 6 %) and TOC (16 ± 4 %) indicates the release of soluble cell compounds and/or the hydrolysis of solid organic cell fragments. Both solubilization and oxidation led to a decrease of 40 ± 5% and 50 ± 6% in the SS, VSS-content, respectively. The batch digestion test of the ozonized and the non-ozonized sludge

indicated that pre-ozonation enhanced the anaerobic digestion of the sludge. The efficiency (calculated on the basis of methane production) increased from 33–41 % for untreated sludge to 45–51 % for the ozonized sludge. The initial rate of methane production increased from 8.3–15.1 mL CH_4/g COD. d to 22.8–32.5 mL CH_4/g COD. d. Besides sludge disintegration, results showed that the ozone treatment influences the sludge settling characteristics by stabilization of surface charges and the release of intercellular water.

In the other study of Weemaes et al. (2000b), the digestion of sludge treated at 0, 0.05, 0.1 and 0.2 g O_3/g COD was investigated in batch tests. During the course of the experiment, the COD soluble-concentration increased gradually. The disintegration of the sludge cells was also reflected in the decreasing SS and VSS-contents of the sludge. During the disintegration of the sludge cells, the pH dropped significantly from 7.8 to 4.9. Degradation efficiency of sludge was increased with ozonation. At the end of the experiment, the degradation (based on COD) of the untreated sludge was calculated to be 36 %. The ozonation treatment enhanced the degradation of the sludge to 54 % for the treatment with 0.05 g O_3/g COD and to 64% for the treatment at 0.1 g O_3/g COD. The dose of 0.2 g O_3/g COD increased the degradation to 47%. Results showed that the maximum methane production rate was achieved at the dose of 0.1 g O_3/g COD. The dewaterability was evaluated through CST-measurements and decreased drastically by ozonation. The CST increased strongly from 33 ± 44 s to 309 ± 373 s at the end of the experiment. On the other hand, the dewaterability was significantly enhanced after the anaerobic digestion. The CST for the ozonated samples decreased from 716 to 86 s, from 862 to 115.2 s and from 372 to 74 CST-s, respectively, for the sludge ozonated at a dose of 0.05, 0.1 and 0.2 g O_3/g COD. The dewaterability of the pretreated and digested sludge was comparable with the dewaterability of the untreated sludge (CST=80 s). The strong deterioration of the dewaterability can be explained by the changed structure of the sludge through ozone treatment. Microscopic observations (Fig. 2.4) indicated that the sludge flocs dispersed. This dispersion of flocs causes filter clogging which complicates the dewatering operation. Obviously, the treatment subsequent to ozonation has to be aim at coagulation and flocculation of the fine particles.

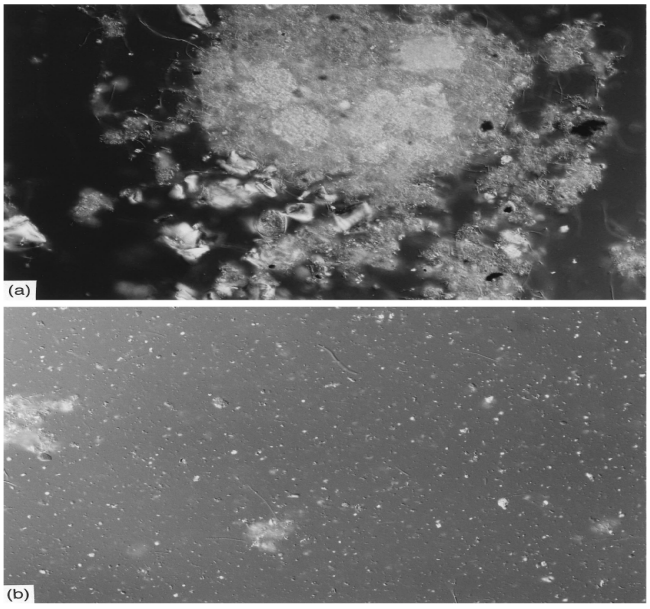


Figure 2.4 Microscopic observation of the sludge before (a) and after ozonation (b) (i.e. after an addition of 0.2 g O_3/g COD) (Weemaes et al., 2000).

Goel et al. (2003) studied on process performance and change in sludge characteristics during anaerobic digestion of sewage sludge with the combination of ozonation and solid liquid separation. The process performance with respect to solid reduction efficiency and other important process parameters like accumulation of inorganic solids, changes in sludge viscosity and dewatering characteristics were evaluated from the data of long-term pilot scale continuous experiments conducted using a mixture of primary and secondary municipal sewage sludge. Due to the ozonation and long SRT, high VSS degradation efficiency of approximately 80 % was achieved at a reactor solid concentration of 6.5 %. A high fraction of inorganic solid consisting mainly of acid insoluble and iron compounds was found to accumulate in the reactor. The high inorganic content accumulated in the digested sludge did not, however, contribute to the observed increase in the sludge viscosity at high solid concentration. The sludge viscosity was largely found to depend on the organic solid concentration rather than the total solid content. Moreover higher inorganic content in the digested sludge resulted in better sludge dewaterability.

Yasui et al., 2005 operated an anaerobic digestion process combined with ozonation and conventional anaerobic digestion process, simultaneously at a full scale for two years. Municipal wastewater treatment plant sludge was used in the study. New digestion process combined with ozonation for enhancing the biological degradability of sludge organics and solid liquid separation unit (centrifuge) in the digester for extension of SRT. At the end of the study, new anaerobic digestion process resulted in high VSS degradation, as much as 1.3 times of methane production and owing to accumulation of inorganic solids in the digested sludge, water content of the dewatered sludge cake reduced from 80 % to 68 %.

Alkaline Treatment: Alkaline treatment is a harsh method. At extremely high pH values of medium, the cell loses its viability, it cannot maintain an appropriate turgor pressure and disrupts. Alkali added to the cell suspension reacts with the cell walls in several ways, including the saponification of lipids in the cell walls, which leads to solubilization of membrane. The high alkali concentrations cause much degradation. Disruption of sludge cells leads to leakage of intracellular material out of the cell (Neyens et al., 2003). Alleman et al., 1994 also demonstrated that alkaline treatment is effective in solubilizing munitions-grade nitrocellulose into soluble organic carbon forms. Woodard and Wukasch (1994) conducted a laboratory-scale study in the development of a hydrolysis/thickening/filtration technology to improve the efficiency of solid digestion of waste activated sludge generated by the biological treatment of a pharmaceutical wastewater. Substantial solubilization (50-60 %) of activated sludge suspended solids was achieved at room temperature, with a relatively short hydrolysis time. Rajan et al. (1989) showed that low-level alkaline pretreatment of waste activated sludge with NaOH can increase levels of solubilization up to 46%. Furthermore, Ray et al. (1990) examined the ability of the single-stage high-rate anaerobic digester to stabilize the alkaline treated WAS with digesters operated at 35°C and five different hydraulic retention times, 20, 13, 10, 7.5 and 5 days. Pretreatment with sodium hydroxide improved the volatile solid reduction by 25-35 % and increased gas production by 29-112 % over the control sludge samples undergoing no alkaline treatment. In the other study, the performance of an anaerobic digestion fed with waste activated sludge (WAS) pretreated with NaOH was examined. Four reactors were employed to evaluate the ability of a

single-stage high-rate digester to treat waste activated sludge at retention tomes of 20, 13, 10 and 7.5 days at 35°C. Reactor A was fed with untreated WAS. The other three reactors B, C and D were respectively fed with WAS pretreated with NaOH (20 meq/l), WAS pretreated with NaOH (40 meq/1), and WAS pretreated with NaOH (20 meq/l). The performances of reactors B, C and D, for and VS removal, and gas production were superior to that of reactor A. The dewaterability of digested sludge was improved in reactors B, C and D. The gas productions of reactors B, C and D were, respectively, increased by 33, 30 and 163 % over that of reactor A.

Neyens et al. (2003) investigated the alkaline hydrolysis of thickened sludge (6 % DS content). As a result of the experimental investigations, it can be concluded that alkaline thermal hydrolysis using $Ca(OH)_2$ is efficient in reducing the residual sludge amounts and in improving the dewaterability. The percentage DS of the sludge cake is 46 %, compared to the traditional 28%, resulting in a significantly reduced energy for subsequent drying as compared with the traditional treatment (135 kJ/IE per day compared to 388 kJ/IE per day).

Ultrasonic treatment: Ultrasonic energy can be applied as pre-treatment to disintegrate sludge flocs and disrupt bacterial cells' walls, and the hydrolysis can be improved, so that the rate of sludge digestion and methane production is improved (Wang et al., 2005). Ultrasound treatment as sludge disintegration results in increase of chemical oxygen demand in the sludge supernatant and size reduction of sludge solids (Tiehm et al., 1997).

There are four paths, which are shown as following, responsible for the ultrasonic activated sludge disintegration:

- hydro-mechanical shear forces,
- oxidizing effect of •OH, •H, •N and •O produced under the ultrasonic radiation,
- thermal decomposition of volatile hydrophobic substances in the sludge, and

- increase in temperature during ultrasonic activated sludge disintegration (Wang et al., 2005).

Ultrasonic process leads to cavitations bubble formation in the liquid phase. These bubbles grow and then violently collapse when they reach a critical size. Cavitational collapse produces intense local heating and high pressure on liquid–gas interface, turbulence and high shearing phenomena in the liquid phase. Because of the extreme local conditions, OH•, HO_2•, H• radicals and hydrogen peroxide can be formed. Thus, sonication is a combination of different phenomena: chemical reactions using radicals, pyrolysis, and combustion and shearing. 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. High frequencies promote oxidation by radicals, whereas low frequencies promote mechanical and physical phenomena like pressure waves. With complex influents, radical performance decreases. It has been shown that degradation of excess sludge is more efficient using low frequencies (Bougrier et al., 2005).

Ultrasound frequencies range from 20 kHz to 10 MHz. Particularly at low frequencies from 20 kHz to 40 kHz cavitations occur when the local pressure in the aqueous phase falls below the evaporating pressure resulting in the explosive formation of small bubbles. These bubbles oscillate in the sound field over several oscillation periods, grow by a process termed rectified diffusion, and collapse in a nonlinear manner. Cavitation is accomplished by high-pressure gradients, an extreme increase of the temperature inside the bubbles, and in he region around the bubble. Therefore, cavitations lead to strong mechanical forces (Atchley et al., 1988).

Bougrier et al. (2005) was studied solubilization of waste activated sludge by ultrasonic treatment. Different ultrasonic energy supplies (ranged from 0 to 15,000

kJ/kg TS) were applied to the activated sludge in their study with a constant operating frequency of 20 kHz and a constant supplied power of about 225 W. As conclusions of that study, COD, matter, and nitrogen solubilization increased with supplied energy. Biogas production increased too. The ultrasonic process led to floc size reduction and cells lyses. For specific supplied energy lower than 1000 kJ/kg TS, energy was used in order to reduce floc size. Then, supplementary energy was used to break flocs or cells. That permitted the release of organic substances into the liquid phase. Organic substances were more available, so biodegradability was improved. In term of biogas production, it did not seem interesting to have a supplied energy higher than 7000 kJ/kg TS. Indeed, when the supplied energy was higher than 7000 kJ/kg TS, biogas generation was constant and solubilization was less marked.

Tiehm et al. (1997) showed that applying ultrasound (3.6 kW, 31 kHz, 64 s) to sludge disintegration can release the organic substances into the sludge, so that the soluble chemical oxygen demand (SCOD) in the supernatant increases from 630 to 2270 mg/L. Moreover, the digestion time reduces from 22 days to 8 days.

Xie et al. (2009) was investigated the effect of low intensity ultrasound on anaerobic sludge activity. Dehydrogenate activity (DHA) and the content of coenzyme F_{420} were detected to indicate the change of activity of anaerobic sludge induced by ultrasound at 35 kHz. Single-factor and multiple-factor optimization experiments showed that the optimal ultrasonic intensity and irradiation period were 0.2 W/cm^2 and 10 min, respectively, and the biological activity was enhanced dramatically under the optimal condition. The chemical oxygen demand (COD) removal efficiency was increased by ultrasonic treatment and the COD in the effluent was 30 % lower than that of the control.

40 ml of anaerobic sludge samples were put into six serum bottles and were irradiated with different ultrasonic intensity from 0 to 1.0 W/cm^2 with the same irradiation period of 10 min, and then these sludge samples were incubated at 35 °C with shaking. Then, other sludge samples were stimulated at the optimal ultrasonic intensity with different irradiation periods, and the same operation was repeated to determine the optimal irradiation period. The result of exposure with different ultrasonic intensities on DHA showed that at the ultrasonic intensity of 0.2 W/cm^2,

DHA increased to the maximum, and above that value DHA decreased drastically. When ultrasonic intensity exceeded 0.6 W/cm^2, the activity of anaerobic sludge was inhibited by sonication, resulting in lower DHA than that of the control. The changes of F_{420} showed the same trend with the DHA. The content of F_{420} increased to the maximum at the same ultrasonic intensity of 0.2 W/cm^2 and it was lower than the control when the intensity exceeded 0.4 W/cm^2. At the irradiation period of 10 min, both the DHA and the content of coenzyme F_{420} increased to their peak value. As the irradiation time was prolonged, the DHA decreased gradually, and at all exposure time tested in the experiment, ultrasound with intensities of 0.2 W/cm^2 produced positive effects on the activity. With relatively short irradiation time, cell damage and membrane permeability induced by ultrasound which could accelerate substance exchange and biological activity appears to be temporary and reversible, but with the prolonged exposure time, the flaw may expand and the structure of cell wall will be destroyed, which leads to the decrease of activity.

Pham et al. (2009) studied on pre-treatment of wastewater sludge by ultrasonic waves at frequency of 20 kHz using fully automated lab-scale ultrasonication equipment. Different wastewater sludge solids concentrations, ultrasonication intensities, and exposure times of pre-treatment were investigated for the optimization of ultrasonication treatment process. The parameters of pre-treatment process were optimized by using response surface methodology. A 2^3 central composite design was performed for optimization. It was observed that the ultrasonication intensity and pre-treatment exposure time significantly affected the efficiency of the ultrasonication process followed by the solids concentration. The optimal conditions of ultrasonic pre-treatment were 0.75W/cm^2 ultrasonication intensity, 60 min, and 23 g/L total solids concentration. The increases in soluble chemical oxygen demand and biodegradability, by aerobic sludge digestion process, in terms of total solids consumption increased by 45.5 % and 56 %, respectively.

Show et al. (2007) was examined on the correlation of sonication operating condition, sludge property, formation and behavior of cavitations bubbles in sludge disruption under low-frequency ultrasound sonication. The role of sonication time, sonication density, type of sludge and solids content in ultrasound sonication was

examined. Sonication was conducted with an ultrasound reactor equipped with a probe transducer (Autotune Series, Sigma Chemical Co., USA). The frequency was 20 kHz and the maximum power output was 200 W. Fifty milliliters of sludge sample was placed in a beaker with the probe placed at the middle of the sample, which was at a level of about 2 cm above the beaker bottom. Sludge samples were sonicated at different sonication times ranging from 0.5 to 15 min and at sonication densities between 0.18 and 0.52 W/mL. It can be concluded from the experimental results and theoretical considerations that the most superior effects of ultrasound disruption were associated with the secondary sludge at higher sonication density (0.52 W/mL) and shorter sonication time (1 min), within an optimum total solids (TS) content ranging between 2.3 % and 3.2 %. Particle disruption was most profound in the initial period of sonication due to the explosive cavitational effect caused by transient bubbles. Sonication density plays a critical role in cavitation bubble.

CHAPTER THREE
MATERIALS & METHODS

3.1 Sludge Types

Waste activated sludge was taken periodically from Cigli Wastewater Treatment Plant located in Izmir City, Turkey, which is extended aeration activated sludge plant treating domestic wastewaters. Sludge's codes are given in Table 3.1. At the start-up of the reactors, granular anaerobic sludge taken from a full-scale UASB reactor treating beer industry wastewater, Efes Pilsen Inc., was used as inoculum for anaerobic reactors. The properties of inoculum sludge and activated sludge are given in Table 3.2 and Table 3.3, respectively. All analysis was done according to procedures given in Standard Methods (APHA, 2005).

Table 3.1 Codes of Activated sludge sample used in the experimental study

Sludge's code	
I	Sample used in Fenton Process optimization study
II	Sample used in ultrasonic treatment optimization study
III	Sample used in ozone oxidation optimization study
IV	Sample used in anaerobic digestion study with Fenton Process
V	Sample used in anaerobic digestion study with ultrasonic treatment
VI	Sample used in anaerobic digestion study with ultrasonic treatment

Table 3.2 Properties of anaerobic inoculum sludge

Parameters	Anaerobic inoculum sludge
pH	8.04 ± 0.1
EC (Electrical conductivity), μS / cm	3.4 ± 0.3
ORP (Redox potential), Mv	-195 ± 3
TS (Total solids), %	7.5 ± 0.3
VS (Volatile solids),%	84.2 ± 1.7
SS (Suspended solids), mg/L	72775 ± 4480
VSS (Volatile suspended solids), mg/L	64738 ± 4315
SCOD (Soluble chemical oxygen demand), mg/L	1893 ± 46
TN (Total nitrogen in sludge'supernatant), mg/L	95.5 ± 5.7
TP (Total phosphorus in sludge'supernatant), mg/L	125 ± 5.2
CST (Capillary Suction Time), s	248.5 ± 1.9

Table 3.3 Properties of activated sludge used in the experimental study

Parameters/ Sludge's code	I	II	III	IV	V	VI
pH	6.97	7.30	6.92	7	7	7.12
EC (Electrical conductivity), µS / cm	6.96	7.23	7.05	7.22	7.35	7.14
TS (Total solids), %	1.44	2.14	1.42	1.82	1.4	1.57
VS (Volatile solids),%	46.2	47.99	52.15	56.72	51.77	54.95
SS (Suspended solids), mg/L	11800	22960	10100	14650	9250	9950
VSS (Volatile suspended solids), mg/L	7250	11520	7300	9367	7100	7240
SCOD (Soluble chemical oxygen demand), mg/L	1120	1200	240	420	420	480
DOC (Dissolved organic carbon), mg/L	216.5	252.6	102.2	-	-	-
TN (Total nitrogen in sludge's supernatant), mg/L	47	25	8	47.2	46.6	49.1
TP (Total phosphorus in sludge's supernatant), mg/L	50	41.3	25.8	40.6	63.5	64.2
CST (Capillary suction time), s	58.4	13.8	17.4	120.6	124.5	102.5
SRF (Specific resistance to filtration), m/ kg	$2.65x10^{14}$	-	-	-	-	-

3.2 Biological Sludge Disintegration Methods

3.2.1 Fenton Process

Fenton Process was applied to 1.5 L sludge sample. This method was carried out by firstly adjusting the pH of the sludge to 3 using H_2SO_4. Second step was addition of Fe(II) (in casu $FeSO_4.7H_2O$) at certain concentrations ranged between 1.0 to 5.0 g Fe(II)/kg DS. After this period, different H_2O_2 concentrations ranged between 5 to 100 g/kg TS was added to the sample. The mixed sample was stirred at 100 rpm for 60 min. After reaction, the sample was neutralized with $Ca(OH)_2$.

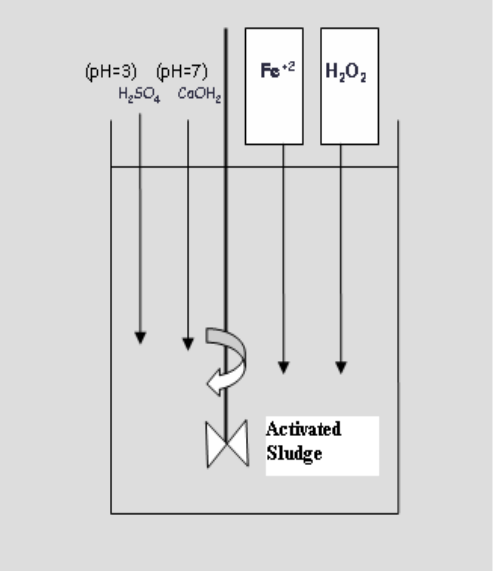


Figure 3.1 Scheme of Fenton's reagent contact reactor

Ferrous ($FeSO4{\cdot}7H_2O$) used as source of Fe(II), was analytical grade and purchased from Merck. Hydrogen peroxide solution (37% (w/w)) in stable form, H_2SO_4 (98–99%) and NaOH were all provided from Merck. An amount of 1000 mg /L Fe(II) stock solution was prepared for further dilution to obtain a solution of desired concentrations. Fe(II) stock solution was stored at dark place to prevent oxidation of Fe(II). The pH of aqueous solutions was adjusted using either sodium hydroxide or sulfuric acid where needed.

3.2.2 Ozone Treatment

Ozone was produced by a corona discharge of OZO 1VTT model ozone generator with a maximum ozone production capacity of 5 g/h (Figure 3.2). The ozone produced from pure oxygen with a purity of 99.5% was bubbled through the reactor using a diffuser with the diameter of 15 mm and with the height of 25 mm.

Figure 3.2 View of ozone treatment system

The reactor was made of pyrex-glass with a total reactor volume of 2 L, sample volume was 1 L (Figure 3.2). Initial ozone concentration (4.7 g/h) and residual ozone concentrations after reaction were measured by the standard potassium iodide absorption method (APHA, 2005). Different ozone dose ranged between 0.005 gO_3/g TS and 0.25 gO_3/g TS were used in the experiments. Ozone dose was calculated as follows:

$$\text{Ozone dose}=[(\text{ozone}_i-\text{ozone}_r)*t)]/(TS*V) \quad \text{(Eq.4)}$$

Where;

ozone_i is initial ozon concentration,

$ozone_r$ is residual ozone concentration after reaction,

t is ozonation time,

TS is total solids of biological sludge, and

V is sludge volume.

3.2.3 Ultrasonic Treatment

The ultrasonic apparatus was an ultrasonic homogenizer (Bandelin Sonopuls HD 2200). This apparatus was equipped with a VS 70 T probe with an operating frequency of 20 kHz and a supplied power of 200 W (Figure 3.3).

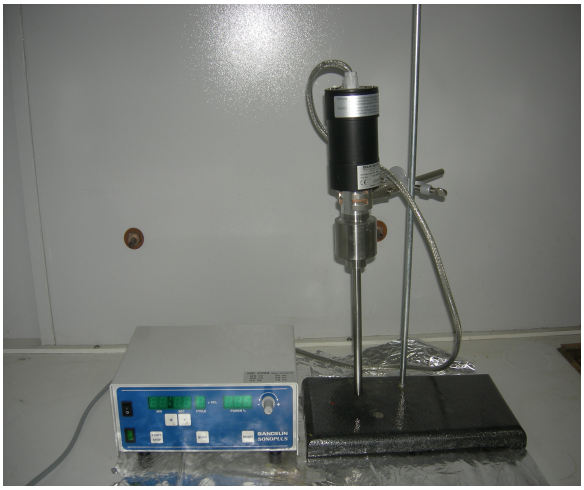


Figure 3.3 View of ozone treatment system

For each experiment, 500 mL of sludge were filled in a glass beaker without temperature adjustment (no cooling) and ultrasonic probe was submerged into the sludge containing beaker to the depth of 2 cm above the bottom of the beaker. Specific energy was considered as a main variable parameter. The range of the specific energy varied from 0 to 15880 kJ/kg TS. SE was determined according to the following equation (Bougrier et al., 2006):

$$SE = P \times t / V \times TS_0 \qquad \text{(Eq. 5)}$$

Where;

SE is specific energy (kJ/kg TS),

P is ultrasonic power (W),

T is ultrasonic time (s),

V is sample volume (L), and

TS_0 is initial total solids concentration (g/L).

In the experiments, ultrasonic power fixed at maximum and power efficiencies of ultrasonic homogenizer were recorded during the ultrasonic pre-treatment for each experiment. The average values were considered as the ultrasonic power.

3.3 Box–Wilson Experimental Design

The Box–Wilson design is a response surface methodology, which is an empirical modeling technique, devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results. Basically this optimization process involves three major steps (Mantha et al., 1998): - performing the statistically designed experiments, - estimating the coefficients in a mathematical model, and - predicting the response and checking the adequacy of the model.

Experimental points for Box–Wilson statistical design are shown in Table 3.4.

Table 3.4 Experimental data points used in Box–Wilson statistical design

Experimental No	X_1	X_2
Axial Points		
A_1	+1	0
A_2	-1	0
A_3	0	+1
A_4	0	-1
Factorial Points		
F_1	+k	-k
F_2	-k	-k
F_3	+k	+k
F_4	-k	+k
Central Point		
C	0	0

The experiments consist of four axial (A), four factorial (F), and central points (C). In the Table 2, "+1" and "-1" represent the maximum and minimum point, "0" represents the central point, and "+k" and "-k" represent the intermediate points. Experimental data was used for determination of the response function coefficients for each independent variable by iteration.

The performance of the system was described by the following response function:

$$E = b_0 + b_1X_1 + b_2X_2 + b_{12}X_1X_2 + + b_{11}X_1^2 + b_{22}X_2^2 \quad \text{(Eq. 6)}$$

Where;

E is the predicted response function,

X_1 and X_2 are independent variables,

b_o is the constant,

b_1–b_2 are the linear coefficients,

b_{12} is the cross product coefficient, and

b_{11} and b_{22} are the quadratic coefficients.

The coefficients of the response functions were determined by using the experimental data. The Statistica 5.0 Computer Program was used for regression analysis.

3.4 Anaerobic Digestion Study

Anaerobic digestion studies were carried out using two pilot scale anaerobic reactors with 8.5-L volume each. The reactors were operated at 37 ± 3 °C under mesophilic conditions. Reactors operated for 30 days of operation period after they reached steady state conditions. The reactors were heated by thermostats and the temperature was kept constantly by heat transfer oil jacket.

The reactors were constructed from stainless-steel and operated with PLC. The reactors were mixed by mechanical mixers. Figure 3.4 illustrates the reactors used in the anaerobic digestion studies.

In start-up phase, inoculum sludge was fed to the anaerobic reactor which was provided from a full scale UASB reactor treating beer industry wastewaters of Efes Pilsen Inc., Izmir. Two anaerobic reactors with 8.5 L of working volume were operated. At start-up phase, 8.5 L of inoculum sludge was first fed to the reactors and the sludge was withdrawn each day till 1/2 volume of the reactor. The same amount of waste activated sludge was step by step fed to the reactors.

Figure 3.4 View of the reactors used in anaerobic digestion study

In order to see the effect of disintegration on anaerobic sludge digestion, control reactor fed with raw sludge was operated parallel with the reactor fed with disintegrated sludge in optimum conditions.

Optimum disintegration conditions were determined for each disintegration process before anaerobic digestion study. In order to determine the optimum operation condition, reactors were operated as batch system and semi-batch system.

Different sludge retention times as 5 and 10 days were applied during the operation in order to determine optimum retention time. For batch system, no fed to the reactors and no withdrawn from the reactors during the operation period, only small volume of sludge was taken from the reactors for analyses. 1.7 L and 0.85 L of sludge were withdrawn from the reactors and the same volume of sludge content were fed to the reactors for 5 days and 10 days of sludge retention time, respectively for everyday during the operation period.

3.5 Analytical Methods

After disintegration process, for determination of disintegration performance of sludge "disintegration degree, DD" parameter, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids, particle size distribution, and protein content were also analyzed for evaluation of disintegration performance.

To see the effect of disintegration processes on supernatant characteristics of sludge, soluble chemical oxygen demand (SCOD), dissolved organic carbon (DOC), total nitrogen (TN), ammonium nitrogen (NH_4-N) and total phosphorus (TP) in sludge's supernatant were analyzed.

For system evaluations of anaerobic digester, pH, and temperature were monitored daily while alkalinity, VFA and redox potential (ORP) values were measured regularly during the operation.

For performance evaluations of anaerobic digesters, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), protein content, particle size distribution, daily total gas and methane productions, and gas composition in the biogas (CH_4, CO, CO_2, H_2S) were analyzed during the operation period.

For evaluating dewatering characteristics of disintegrated sludge and anaerobically digested sludge, capillary suction time (CST) test and specific resistance to filtration (SRF) test was carried out. The belt press simulator of crown press was also used for evaluation of dewatering properties of sludge.

All analyses were regularly done according to Standard Methods (APHA, 2005). Lacking any standard methodology, analyses were performed according to the most accepted methods in research studies. Most of the measurements in this study were done in triplicate. Confidence intervals are at the 95% significance level.

3.5.1 Disintegration Degree

After disintegration process, for determination of disintegration performance "disintegration degree, DD" parameter which is developed by Muller (2000) may be considered as the main parameter. The high DD values mean high disintegration degree. This parameter is calculated as following equation.

$$DD = [(COD_1 - COD_2) / (COD_3 - COD_2)]. 100 \quad \text{(Eq. 7)}$$

Where;

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

COD_2 is COD concentration of sludge's supernatant before disintegration,

COD_3 is COD concentration of sludge's supernatant after chemical disintegration

Chemical disintegration is processed the sludge at 90 °C for 10 min after the addition of NaOH. Sludge's supernatant was obtained with centrifugation and centrifugation is carried out at 15 000 rpm, and 4°C for 20 min.

3.5.2 Particle Size Analysis

Particle size distributions were monitored using a Malvern Mastersizer 2000QM analyzer shown in Figure 3.5.

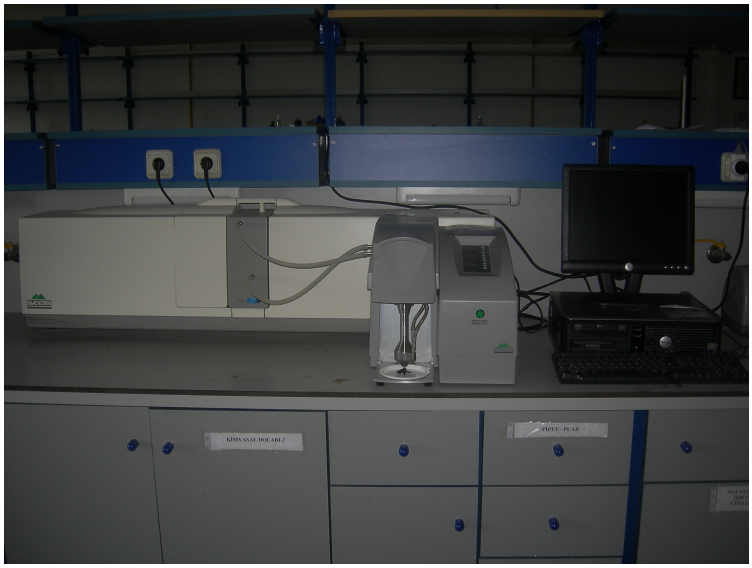


Figure 3.5 View of Malvern Mastersizer 2000QM particle size analyzer.

3.5.3 Protein Analysis

Extracellular polymeric substances (EPS) were extracted from the samples using the heat extraction technique originated by Goodwin & Forster (1985) and Frolund et al., 1996. Protein contents of EPS samples were analyzed using protein assay kits (Procedure No. TP0300 Micro Lowry, Sigma).

3.5.4 SCOD Analysis

COD parameter was analyzed using Open Reflux Method. In SCOD measurements, soluble part of sludge was obtained by centrifuging of sludge samples at 15000 rpm for 20 minute. Samples were diluted to 1/20 with pure water before analysis.

3.5.5 DOC Analysis

DOC concentrations were measured using a Shimadzu, ASI-V model TOC analyzer for disintegration evaluation. In DOC measurements, dissolved part of sludge was obtained by centrifuging of sludge samples at 15000 rpm for 20 minute. Samples were diluted to 1/20 with pure water before analysis.

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

Total nitrogen (TN) (Merck cell kit numbered 14537) and total phosphorus (PO_4 – P) (Merck cell kit numbered 00616) were analyzed by using spectroquant cell test obtained from Merck. Photometric measurements were done using a NOVA 60 photometer. Sludge's supernatant was obtained by centrifuging of sludge samples at 15000 rpm for 20 minute for TN and TP analysis.

3.5.7 Solubilization Degree of Sludge's Solids

Solubilization degree of sludge's solids in terms of SS and VSS was calculated as following equation (Bougrier et al., 2006):

$$S_X = [(X_0 - X_d) / X_0] \times 100\ \% \qquad \text{(Eq. 8)}$$

Where:

S_X is solubilization degree of sludge's solids (%),

X_0 is initial solid concentration of sludge, and

X_d is solid concentration of disintegrated sludge.

3.5.8 pH and Redox Potential (ORP) Measurements

pH and ORP values were measured by WTW model 340i multi analyzer.

3.5.9 Volatile Fatty Acid (VFA) Analysis

High Pressure Liquid Chromatography was used in VFA analyses. A HPLC, Agilent 1100 model equipped with C18 column was used in the experimental studies.

3.5.10 Analysis of Gas Components in the Total Gas Produced

Gas components in the total gas produced (CO, CO_2, CH_4, and H_2S) were analyzed regularly using a Dräger model X-am 7000 multigas analyzer. Figure 3.6 shows the multi gas analyzer used in the experimental studies.

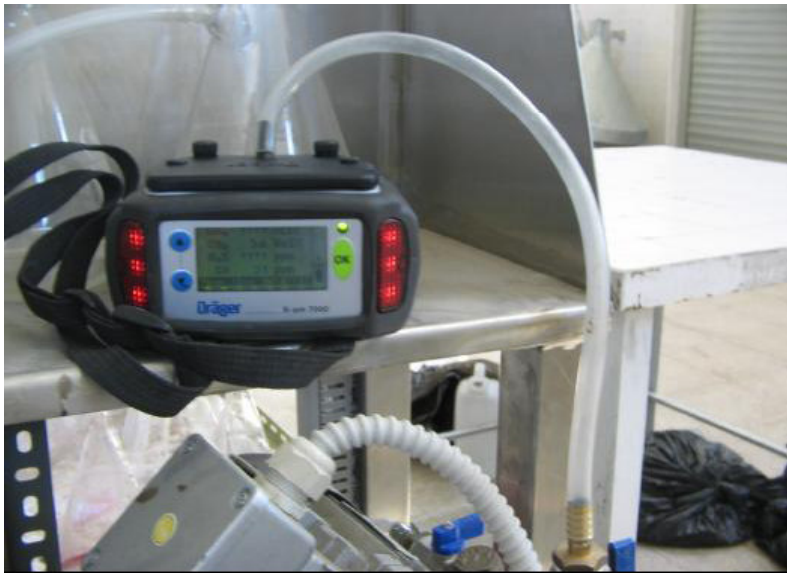


Figure 3.6 View of Dräger model X-am 7000 multigas analyzer

3.5.11 Capillary Suction Time Test

The time the filtrate requires to travel a fixed distance in the filter paper is referred to as capillary suction time (CST). The whole purpose of Capillary Suction Time Test is to determine dewatering characteristics of a given sludge rapidly and easily. The advantages of this test are to be simple, inexpensive, and easy. A large CST is usually indicator of poor sludge dewaterability (EPA, 1987).

In this thesis, Capillary Suction Time Test (CST) was used for the evaluation of the dewatering performances of both disintegrated sludge samples and sludge samples taken from anaerobic digesters. CST values were analyzed using a Triton 304 M CST-meter. A standard CST sample cylinder of 1.8 cm diameter was used during experiments with Whatman # 17 filter paper. The apparatus (Figure 3.7) consist of a timing device, an upper plate containing probes that activate and deactivate the timing device, and a lower plate that holds the filter paper and a metal sample container.

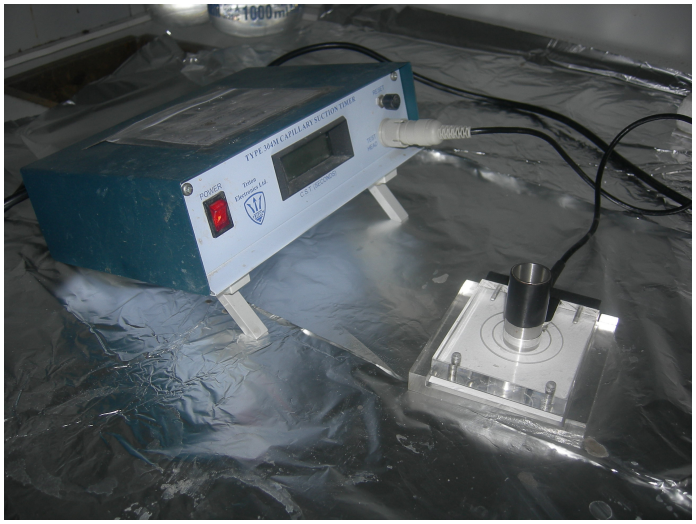


Figure 3.7 View of capillary suction time analyzer

A sample of sludge is placed in the sample container. As water migrates through the paper and reaches the first probe, it activates the timer. When the water reaches the second probe, the timer deactivates. The time interval between timer activation and deactivation is the capillary suction time and is a measure of the dewaterability of sludge. All CST measurements were conducted in triplicates and average of three values was taken into consideration for standard deviation to be less than 1 s.

3.5.12 Specific Resistance to Filtration (Buchner Funnel) Test

Specific resistance is used to compare filtration characteristics of different types of sludge and to determine the optimum conditioning chemical requirements for a specific sludge. The better dewatering characteristic of sludge is that which produces the lower specific resistance. Specific resistance value of sludge is determined by applying the Buchner Funnel Test to the sludge. The Buchner Funnel Test equipment consists of a graduated cylinder, Buchner Funnel and a vacuum pump as shown in Figure 3.8.

A series of conditioned sludge samples are prepared in large beakers. First about 200 ml of sludge is placed into the beakers. The sludge tested should be representative of the sludge to be used on the dewatering units. This sludge can be sampled from a pilot-plant or a similar full- scale treatment plant.

A Buchner funnel is mounted on top of the graduated cylinder and the funnel is fitted with a Whatman #2 filter paper, and then 100 ml of conditioned sludge is poured into the funnel. After 2 minutes gravity drainage, the vacuum pump is turned on (2 bar). At about 10-second intervals, the filtrate volume is measured and recorded until additional water can not be removed. After this period, the sludge cake is removed from the filter and placed in a weighed dish. The wet weight of the cake is measured and then after drying at 180 °C, the dry weight is measured and dry solids content of the sludge cake (%) is determined. In addition, total suspended solids as the units of mg/L and % is also determined on the filtrate.

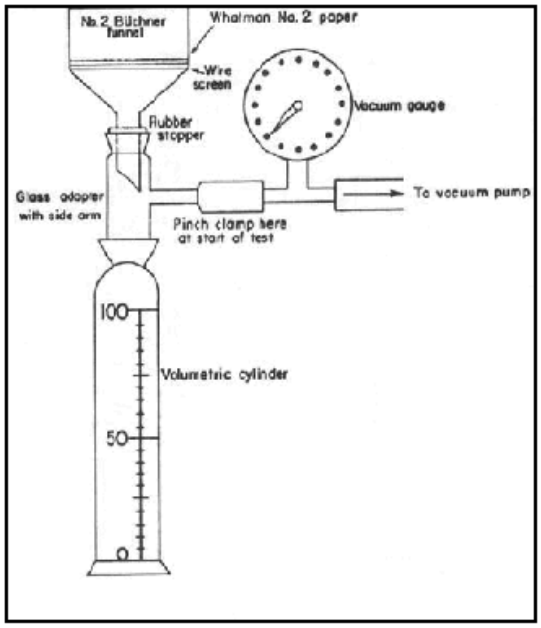


Figure 3.8 Buchner Funnel Apparatus (EPA, 1987)

After this experimental procedure, a plot was made of time/filtrate volume. The slope of the straight line portion of the graph is ‘b’ and is used to calculate the specific resistance (r) from following equation.

$$r = (2PA2b) / \mu w \qquad (Eq.6)$$

Where,

r is specific resistance (m/kg),

P is pressure of filtration (N/m^2),

A is area of filter (m^2),

b is slope of time/volume vs. volume curve (sec/m^2),

μ is viscosity of filtrate ($N (sec)/m^2$), and

w is weight of dry solids / volume of filtrate (kg/m^3).

In this thesis, Specific Resistance to Filtration (SRF) Test was applied to Fenton processed sludge samples for evaluation of dewatering characteristics. Viscosities of filtrate samples were also measured using Brookfield RVDV III Rheometer for calculation of SRF (r) value.

3.5.13 Crown Press Application

The full scale belt filter pres simulator of crown press (purchased from Phipps and Bird, USA) was used to investigate dewatering performance of the anaerobically digested samples. Figure 3.9 shows the drainage kit and the Crown press used in this work.

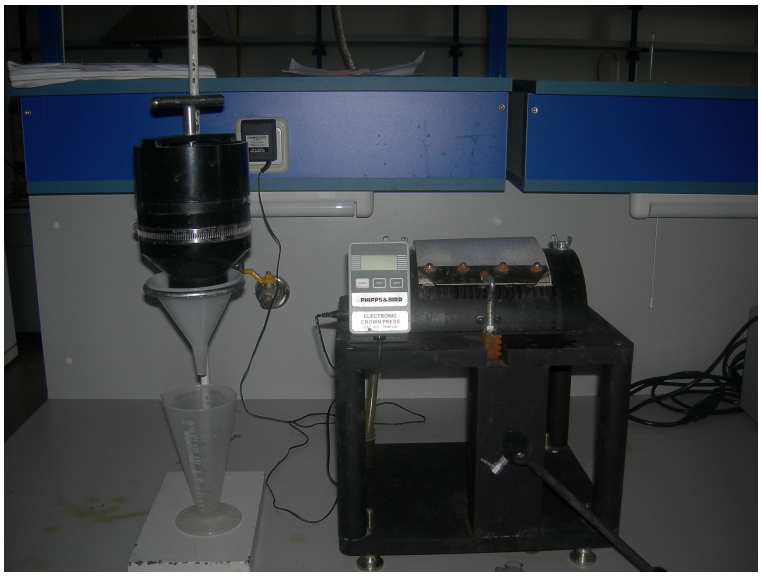


Figure 3.9 View of gravity drainage plow simulator kit and Crown press

Prior to press, water drainage rate of the samples were determined using a gravity drainage plow simulator kit. For this purpose sludge slurry (200 ml) was drained through a screen and the volume collected after 2 min was measured. After then, the solids remaining on the screen were pressed with crown press and the final cake solids determined. The belt press simulator of crown press supplied from Phipps and Bird, Richmond, VA was used for evaluation of dewatering properties of sludge. Sludge slurry (200 ml) was drained through a screen and the volume collected after 2 min was measured. The solids remaining on the screen were then pressed and the final cake solids determined.

CHAPTER FOUR
RESULTS & DISCUSSION

4.1 Optimization Study of Fenton Process Conditions

Box-Wilson experimental design was applied to optimize Fenton Process conditions for both floc disintegration and dewatering. For Fenton Process, the significant variables like H_2O_2 and Fe(II) concentration were chosen as the independent variables and designated as X_1 and X_2, respectively. H_2O_2 concentration (X_1) varied between 10 and 100 g/kg dry solids (DS), while Fe(II) concentration (X_2) was ranged from 1 to 5 g/kg DS.

Parameters (responses) used for determination of effect of Fenton Process on sludge disintegration are;

- Disintegration Degree (DD), %
- Increase in TOC of sludge's supernatant after Fenton Process (E_{TOC}), %
- Increase in total nitrogen of sludge's supernatant after Fenton Process (E_{TN}) , %

Parameters (responses) used for determination of effect of Fenton Process on sludge filterability are;

- Decrease in SRF (Specific Resistance to Filtration) in sludge after Fenton Process (E_{SRF}), %
- Decrease in CST (Capillary Suction Time) in sludge after Fenton Process (E_{CST}), %

The experimental conditions determined by the Box– Wilson Experimental Design are presented in Table 4.1. The experiments consist of four axial (A), four factorial (F), and central points (C). The central point was repeated three times resulting in 11 experiments in total.

Table 4.1 Experimental conditions according to a Box–Wilson Experimental Design for Fenton Process

Experimental No	X_1 (g H_2O_2/kg TS)	X_2 (g Fe(II)/kg TS)
Axial points		
A_1	100	3
A_2	10	3
A_3	55	5
A_4	55	1
Factorial points		
F_1	86.8	1.6
F_2	23.2	1.6
F_3	86.8	4.4
F_4	23.2	4.4
Center point		
C_1	55	3
C_2	55	3
C_3	55	3

4.1.1 Optimization of Fenton Process Conditions in terms of Biological Sludge Disintegration

Increase in DD of sludge and TOC of sludge's supernatant are determined as the substance that can be readily used to produce methane in the anaerobic digestion (Wang et al., 2005). Increase in DD of sludge and TOC of sludge's supernatant with Fenton Process is a good indicator of floc disintegration.

Experimental results were evaluated using the regression analysis by working Statistica 5.0 Computer Program to determine the coefficients of the response function (Eq. 6). Determined coefficients given in Table 4.2 were used for the calculating of predicted values of disintegration degrees.

Table 4.2 Coefficients of the DD response function

Coeffi-cients	b_0	b_1	b_2	b_{12}	b_{11}	b_{22}
Values	-37.078726	0.855438	19.283546	0.006685	-0.00701	-2.65642

Observed disintegration degrees obtained from the experiment were compared with the predicted ones obtained from the response function. The results are represented in Table 4.3. The correlation coefficient (R^2) between the observed and predicted values of DD was %99.95 for Fenton Process. These results indicated excellent agreement between the observed and predicted values of disintegration degrees.

Table 4.3 Observed and predicted values of DD

Experimental No	Predicted DD, %	Observed DD, %
Axial points		
A_1	14.31	14.29
A_2	4.92	4.76
A_3	20.61	19.05
A_4	5.76	7.14
Factorial points		
F_1	9.34	8.33
F_2	3.30	2.38
F_3	20.33	21.43
F_4	13.10	14.29
Center point		
C_1	23.81	23.81
C_2	23.81	23.81
C_3	23.81	23.81

In order to optimize Fenton Process conditions in terms of Fe(II) and H_2O_2 concentrations, Fe(II) was fixed at some concentrations in the dose range determined based on Box-Wilson Experimental Design, and disintegration degrees were observed at increasing H_2O_2 concentrations. Results are summarized in Figure 4.1. Results given in Figure 4.1 demonstrate that increasing the ferrous ion concentration enhanced the disintegration degree at a certain point (4 g/kg TS), after that point ferrous ion started to inhibit disintegration of sludge. Same as, increasing H_2O_2 concentration positively affected sludge disintegration up to 60 g/kg TS, at higher concentrations, the decreasing trend of disintegration degree was observed. Maximum DD of 25.2 % was achieved at 60 g H_2O_2 / kg TS and 4 g Fe(II)/ kg TS, and optimum Fe(II)/ H_2O_2 ratio was found as 0.067. This ratio is in agreement with Neyens et al., 2003.

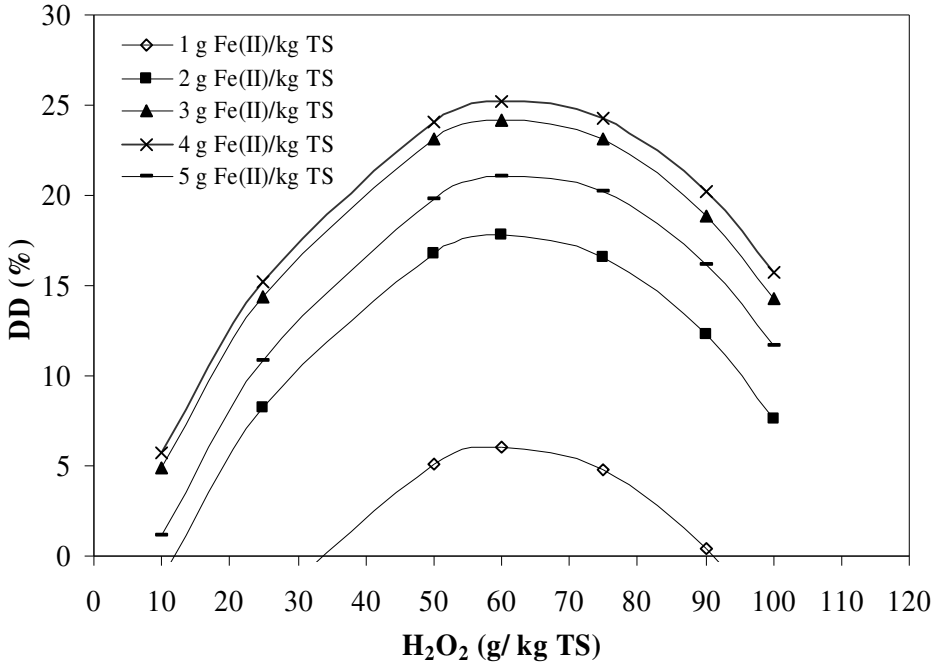


Figure 4.1 Variations of DD with the H_2O_2 concentration at different Fe(II) concentrations

Increase in TOC of sludge supernatant with Fenton Process demonstrate that Fenton processed sludge stabilize higher degree and produce higher methane gas in anaerobic digestion than raw sludge. The other response function for evaluating the effect of Fenton process conditions on biological sludge disintegration was chosen as the percent increase in total nitrogen of sludge supernatant of Fenton processed sludge according to the raw sludge (E_{TOC}). The estimated coefficients of the response function of E_{TOC} are presented in Table 4.4.

Table 4.4 Coefficients of the E_{TOC} response function

Coeffi-cients	b_0	b_1	b_2	b_{12}	b_{11}	b_{22}
Values	-111.2399	2.566239495	57.8549126	0.02004717	-0.02103	-7.96983

Predicted values of E_{TOC} using the estimated coefficients are compared with the experimental results in Table 4.5. Response function predictions were in good agreement with the experimental data. The correlation coefficient (R^2) between the

observed and predicted values of E_{TOC} was 99.95 % for Fenton Process. This value shows excellent agreement between predicted and observed values.

Table 4.5 Observed and predicted values of E_{TOC}

Experimental No	Predicted E_{TOC}, %	Observed E_{TOC}, %
Axial points		
A_1	42.94	42.86
A_2	14.76	14.29
A_3	61.83	57.14
A_4	17.28	21.43
Factorial points		
F_1	28.02	25
F_2	9.89	7.14
F_3	60.99	64.29
F_4	39.29	42.86
Center point		
C_1	71.43	71.43
C_2	71.43	71.43
C_3	71.43	71.43

Variations of E_{TOC} with H_2O_2 concentration at different the Fe(II) concentrations are depicted in Figure 4.2. E_{TOC} increased with increasing Fe(II) concentrations up to 4 g Fe(II)/ kg TS, but at higher concentrations E_{TOC} decreased. Similarly, increasing H_2O_2 concentration increased E_{TOC} at 60 g/kg TS, after that point E_{TOC} decreased. Maximum E_{TOC} of 75.74 % was achieved at 60 g H_2O_2 / kg TS and 4 g Fe(II)/ kg TS. Up to 60 g H_2O_2 / kg TS concentration, hydroxyl radicals preferentially attack the organic substances and destruct the activated sludge microorganisms cell walls in biomass and oxidized them to dissolved organic substances and these substances released to the liquid phase and increased the DD of sludge and TOC of sludge's supernatant, at higher H_2O_2 concentrations, decreases in DD and E_{TOC} may be explained with two phenomena that a competition between the organic substances and H_2O_2 and H_2O_2 acts as a scavenger of the highly potent hydroxyl radicals, and inhibit the disintegration or high H_2O_2 concentrations may caused the mineralization of organic substances to the final step of water and carbon dioxide. This phenomenon was observed in other studies for waste activated sludge (Bougrier et al., 2006) and wastewater (Catalkaya et al., 2007).

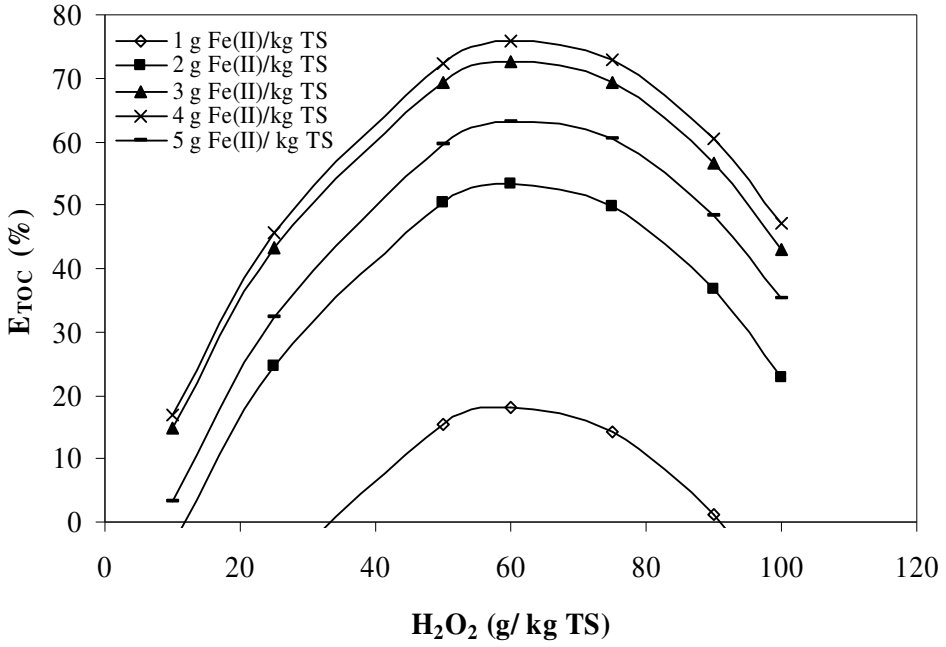


Figure 4.2 Variations of E_{TOC} with the H_2O_2 concentration at different Fe(II) concentrations

Disintegration breaks up the microbial cells and leads to release of intracellular compounds into the liquid phase. So, concentrations of nitrogen form on sludge's supernatant increase after Fenton application. For observation this increase, Fenton Process was applied to sludge samples at experimental points determined by Box-Wilson Experimental Design and total nitrogen concentrations of sludge's supernatant were measured and then increase in total nitrogen concentrations of sludge's supernatant according to the raw sludge (E_{TN}) were calculated. The determined coefficients given in Table 4.6 were used for the calculating of predicted values of E_{TN}. Observed and predicted values of E_{TN} are given in Table 4.7.

Table 4.6 Coefficients of the E_{TN} Response Function

Coeffi-cients	b_0	b_1	b_2	b_{12}	b_{11}	b_{22}
Values	-18.70577424	1.028527623	30.71962712	-0.02863881	-0.00811	-4.46874

Good agreement between the observed and predicted values of E_{TN} was determined. Correlation coefficient between them was calculated as 94.93 %.

Table 4.7 Observed and predicted values of E_{TN}

Experimental No	Predicted E_{TN}, %	Observed E_{TN}, %
Axial points		
A_1	46.36	45.30
A_2	41.85	38.20
A_3	47.325	47.80
A_4	37.995	32.90
Factorial points		
F_1	43.175	46.60
F_2	37.44	42.70
F_3	47.154	46.60
F_4	46.52	47.80
Center point		
C_1	60.53	60.80
C_2	60.53	60.20
C_3	60.53	60.50

Variations of E_{TN} with H_2O_2 concentration at different the Fe(II) concentrations are given in Figure 4.3.

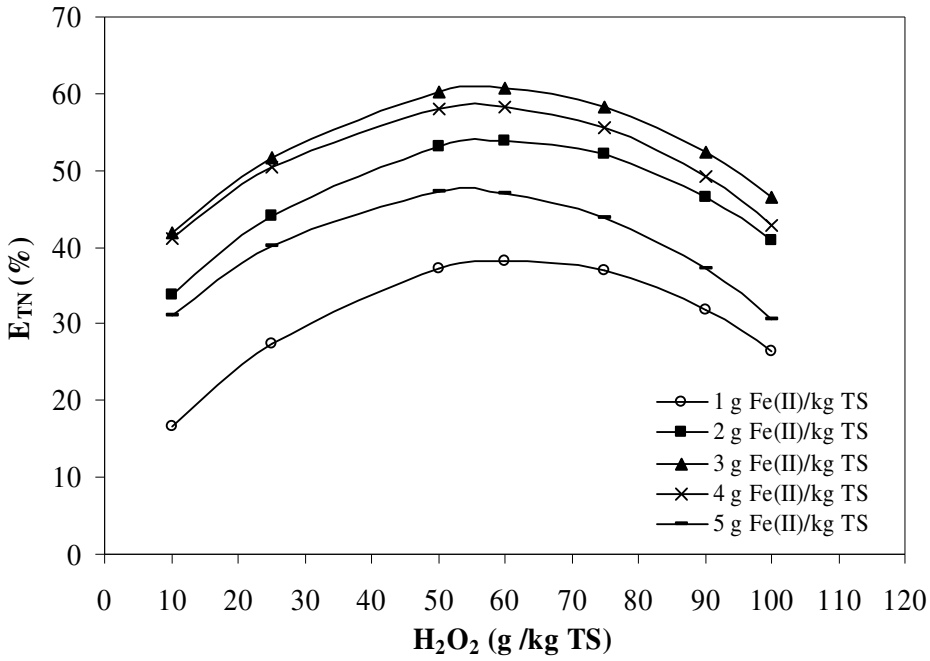


Figure 4.3 Variations of E_{TN} with the H_2O_2 concentration at different Fe(II) concentrations

E_{TN} increased with increasing H_2O_2 concentration and maximum E_{TN} was achieved at 60 g H_2O_2/ kg TS for all Fe(II) concentrations. At higher concentrations

than 60 g H_2O_2/ kg TS, E_{TN} decreased. When comparing the results based on Fe(II) concentrations, 1 and 5 g Fe(II)/ kg TS applications gave lower E_{TN} values than other applications for all H_2O_2 concentrations. 3 and 4 g Fe(II)/ kg TS applications gave very closed results. Maximum E_{TN} was achieved as 60.60 % at 3 g Fe(II)/ kg TS and 60 g H_2O_2/ kg TS application.

4.1.2 The Effect of Fenton Process on Dewaterability of Biological Sludge

For determination of the filterability characteristics of Fenton processed sludge, Capillary suction time (CST) parameter was examined. CST test was applied to Fenton Processed sludge samples at different conditions determined by Box-Wilson Experimental Design.

CST parameter is a primarily useful to compare the filtration characteristics of different sludge it is a rapid, easy, inexpensive, and reproducible method of characterizing the dewaterability of a given sludge (Eckenfelder et al., 1981). Lower CST values of sludge show that sludge has good filtration characteristics.

The percent decrease in CST value of Fenton processed sludge according to the raw sludge (E_{CST}) was considered as the response function in Box-Wilson Experimental Design for determining filtration characteristics of sludge. The calculated coefficients given in Table 4.8 were used for the calculating of predicted values of response function. Observed E_{CST} values and predicted ones are given in Table 4.9.

Table 4.8 Coefficients of the E_{CST} response function

Coeffi-cients	b_0	b_1	b_2	b_{12}	b_{11}	b_{22}
Values	36.46484	0.151324	-0.660796	-0.004492	-0.000245	0.541043

Correlation coefficient between predicted and observed values was calculated as a high value of 97 %.

Table 4.9 Observed and predicted values of E_{CST}

Experimental No	Predicted E_{CST}, %	Observed E_{CST}, %
Axial points		
A_1	50.7	50.5
A_2	40.7	42.0
A_3	53.0	54.8
A_4	43.7	43.0
Factorial points		
F_1	47.5	48.3
F_2	40.0	39.8
F_3	53.6	52.7
F_4	47.0	45.0
Center point		
C_1	46.2	46.2
C_2	46.2	46.2
C_3	46.2	46.2

Variations of E_{CST} with H_2O_2 concentration at different the Fe(II) concentrations are given in Figure 4.4.

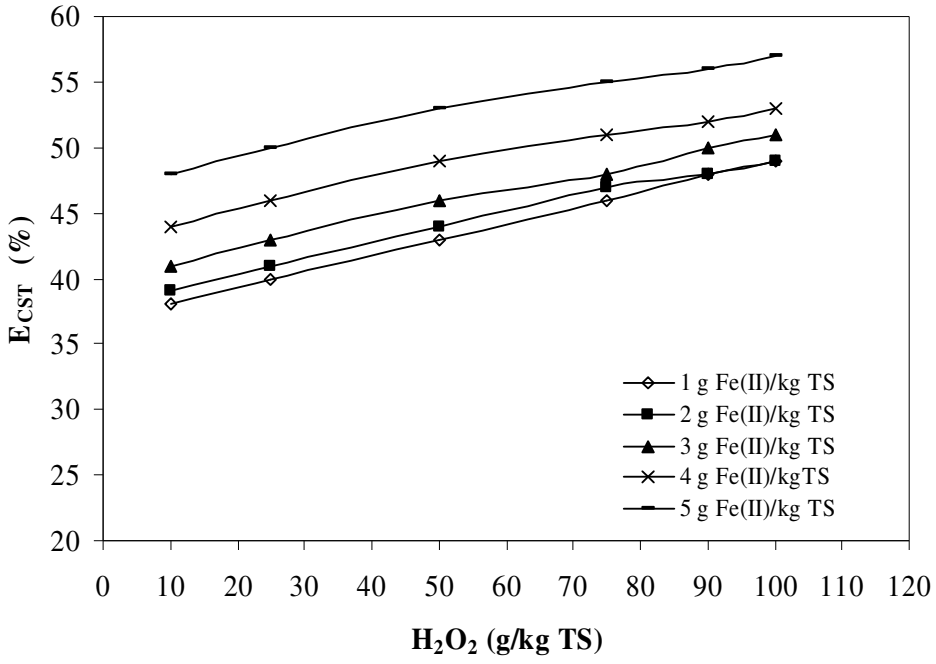


Figure 4.4 Variations of E_{CST} with the H_2O_2 concentration at different Fe(II) concentrations

In all cases, higher Fe(II) and H_2O_2 concentrations cause higher decreases in CST. Maximum E_{CST} was achieved at the highest H_2O_2 application of 100 g H_2O_2/ kg TS for all Fe(II) concentrations. Fenton process improved the filtration characteristics of sludge. Maximum increase in E_{CST}, in other words minimum CST value was achieved at 5 g Fe(II)/ kg TS ve 100 g H_2O_2/ kg TS. E_{CST} was calculated as 57 % in this application.

SRF is relatively complicated method comparing to CST and gives information about sludge behavior on vacuum filtration units. Similar with the CST parameter, low values SRF indicate that good dewatering characteristic of sludge. The percent decrease in SRF value of Fenton processed sludge according to the raw sludge (E_{SRF}) was considered as another response function in Box-Wilson Experimental Design for evaluating dewatering characteristics of sludge. The estimated coefficients of the response function of E_{SRF} are presented in Table 4.10. Observed and predicted values of E_{SRF} are given in Table 4.11.

Table 4.10 Coefficients of the E_{SRF} response function

Coeffi-cients	b_0	b_1	b_2	b_{12}	b_{11}	b_{22}
Values	85.091111	0.107130	1.198562	-0.00786	-0.00045	-0.099918

Table 4.11 Observed and predicted values of E_{SRF}

Experimental No	Predicted E_{SRF}, %	Observed E_{SRF}, %
Axial points		
A_1	91.7	92.1
A_2	88.6	88.9
A_3	91.0	91.8
A_4	90.3	90.2
Factorial points		
F_1	91.6	91.5
F_2	88.7	88.7
F_3	91.4	90.6
F_4	89.9	89.2
Center point		
C_1	91.0	91.2
C_2	91.0	90.9
C_3	91.0	91.0

Correlation coefficient between predicted and observed values was calculated as a high value of 92 %. Variations of E_{SRF} with H_2O_2 concentration at different the Fe(II) concentrations are given in Figure 4.5.

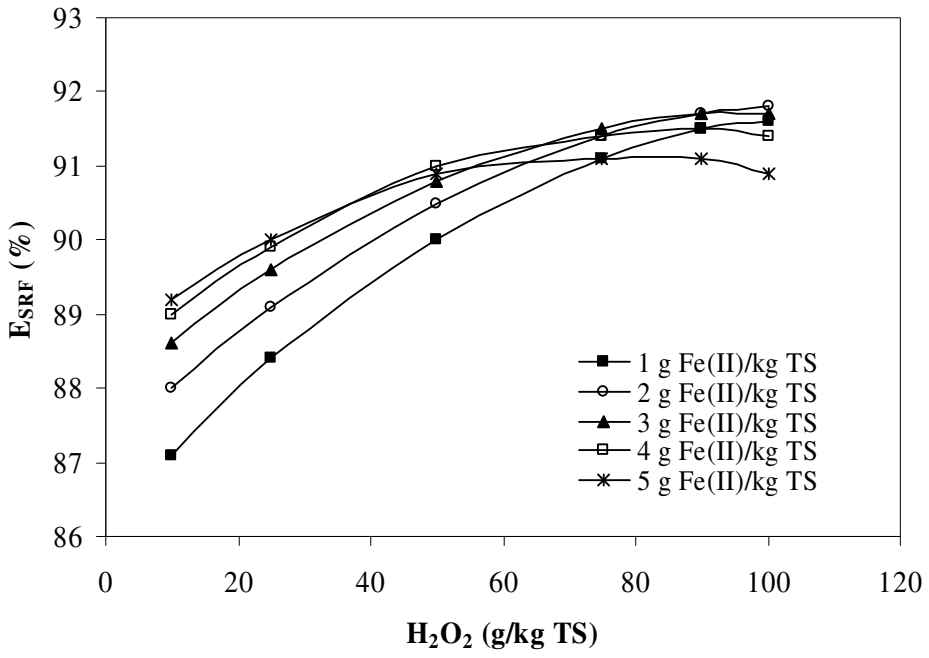


Figure 4.4 Variations of E_{SRF} with the H_2O_2 concentration at different Fe(II) concentrations

SRF of sludge decreased with increasing H_2O_2 concentrations up to 75 g/kg TS, and E_{SRF} remained almost fixed at approximately 92 % above these concentrations for all Fe(II) application. The high E_{SRF} values showed that Fenton Process improves the filterability characteristics of sludge, and it can be applied to biological sludge as a pre-treatment method for conditioning purpose before mechanical dewatering units.

4.2 Anaerobic Digestion Study with Fenton Process

After optimization study of Fenton Process conditions for biological sludge disintegration, sludge digestion studies were carried out for raw sludge and Fenton Processed sludge. A ratio of 0.067 g Fe(II) per gram H_2O_2, and 60 g H_2O_2 / kg TS were chosen as the optimum conditions for biological sludge disintegration as a

result of the optimization study using Box-Wilson experimental design. These conditions were applied to sludge before anaerobic digestion.

Sludge digestion studies were carried out using two 8.5 L anaerobic reactors. Reactors were operated at 37 ± 2 °C in mesophilic conditions for 30 days of operation period. Reactors operated as batch and semi-batch systems in order to determine optimum operation condition. Different sludge retention times as 5 and 10 days were applied during the operation in order to determine optimum retention time. Sludge digestion procedure was given in detail in Chapter 3.4.

Control reactors fed with raw sludge were coded as CR_B, CR_5, CR_{10}. Reactors fed with Fenton processed sludge were coded as FR_B, FR_5, $FR_{10.}$ Reactor's codes used anaerobic digestion studies with Fenton Process are given in Table 4.12.

Table 4.12 Reactor's codes used anaerobic digestion studies with Fenton Process

Reactor's code	Fenton Process	Sludge retention time
CR_B	No applied	Batch operation
FR_B	Applied	Batch operation
CR_5	No applied	5 days
FR_5	Applied	5 days
CR_{10}	No applied	10 days
FR_{10}	Applied	10 days

4.2.1 Control of Anaerobic Digesters Stability

In digestion study with Fenton Process, pH and temperature were monitored daily while alkalinity, volatile fatty acids (VFA), and redox potential (ORP) values were measured regularly during the operation period for control of anaerobic digester stability.

Anaerobic digestion study was carried out at mesophilic conditions; hence temperature was kept at 37 ± 2 °C for all reactors during the operation period (Fig.4.4). pH is another important parameter for digester stability. For anaerobic biological systems, optimum pH range is given as 6 to 9 (Filibeli et al., 2000). pH varied from 6.80 to 8.80 in reactor contents as seen in Figure 4.5.

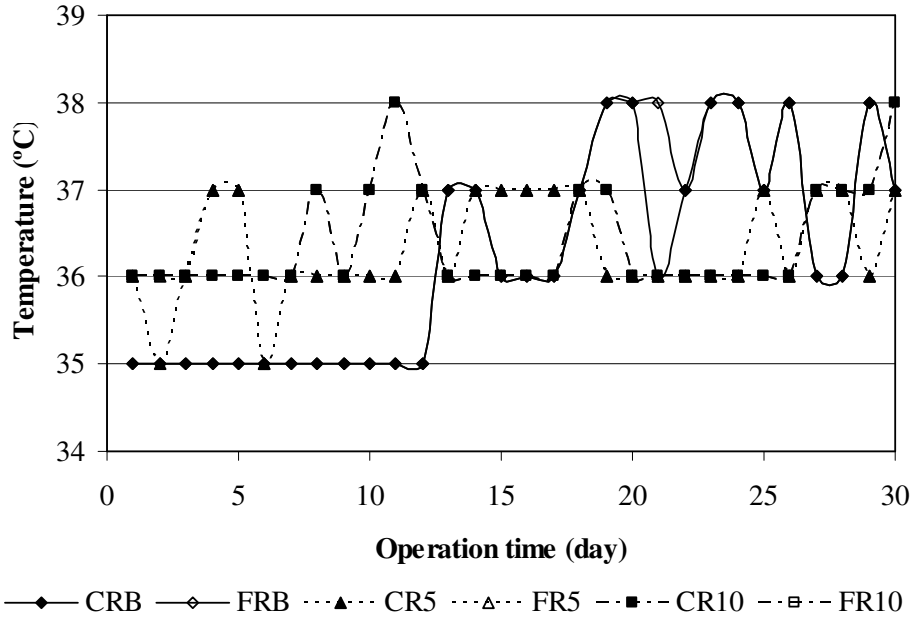


Figure 4.4 Temperature changes in reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10} during operation period

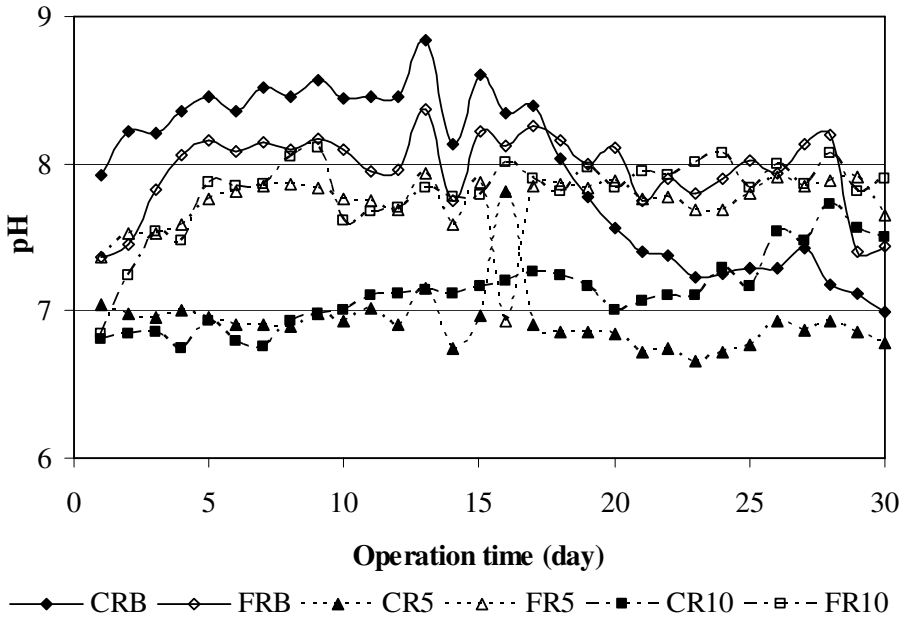


Figure 4.5 pH changes in reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10} during operation period

Redox potential (ORP) in reactor contents were in the very negative range of – 300 mV and – 500 mV were observed as seen in Figure 4.6.

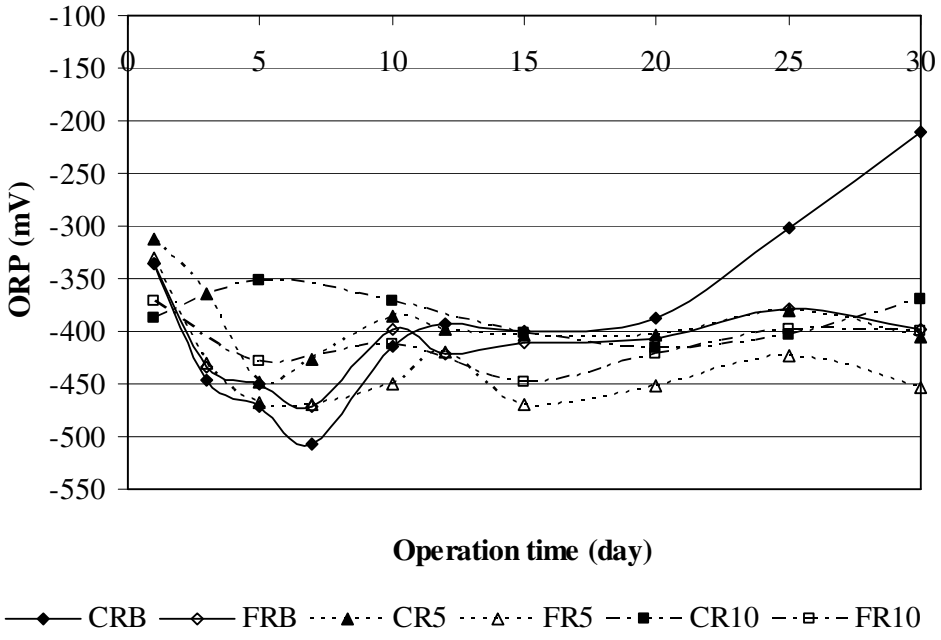


Figure 4.6 ORP changes in reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10} during the operation

Alkalinity is one of the most central concepts in aquatic chemistry because it controls the pH. Alkalinity is comprised of different species of the salts of weak acids, so it is convenient and conventional the express all alkalinity as its $CaCO_3$ equivalence. Since CO_2 often exceeds other weak acids in aqueous anaerobic systems with microbial activity, sufficient bicarbonate alkalinity must be present to neutralize it and is therefore of prime importance. In anaerobic systems the salts of volatile acids also contribute to alkalinity at neutral pH, but are not available for neutralization for additional volatile acids even though they may constitute a major fraction of the total alkalinity. Anaerobic systems operate in the neutral pH in which bicarbonate is the dominant species; thus bicarbonate alkalinity is the major interest (Speece, 1996). Total alkalinity values were measured regularly as a measure of the stability of the digestion unit. Results of alkalinity measurements are represented in

Figure 4.7. Alkalinity range of 1580 – 5917 mg $CaCO_3$/ L were measured during the operation period.

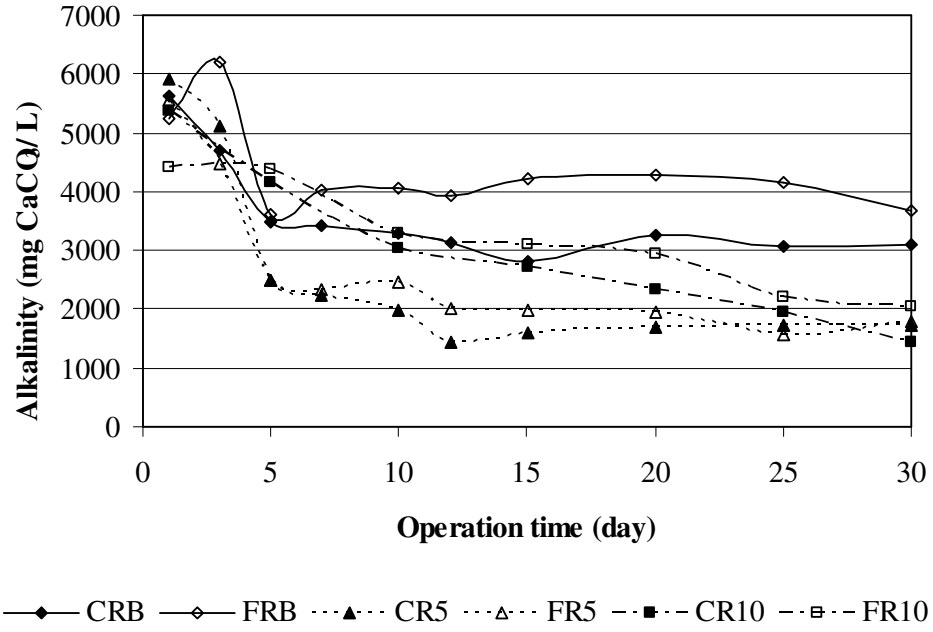


Figure 4.7 Total alkalinity changes in reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10} during operation period

VFA content was also checked for reactor stability and VFA results are gien in Table 4.13. VFA values did not exceed 1000- 1500 mg/L which is not recommended for anaerobic methanogens (Malina and Pohland, 1992). VFA values did not exceed this recommended range even first operation days.

Table 4.13 VFA (Lactic acid, Lc/ Acetic acid, Ac/ Propionic acid, Prc) changes in reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10}

Days	1			3			5			10			15		
Reactor's code	Lc	Ac	Prc	Lc	Ac	Prc	Lc	Ac	Prc	Lc	Ac	Prc	Lc	Ac	Prc
CR_B	0	0	0	0	182	0	207	0	101	339	0	0	305	0	0
FR_B	0	19	0	0	0	0	0	0	0	234	65	0	316	0	0
CR_5	403	150	128	461	0	146	460	0	125	205	0	0	91	0	107
FR_5	500	534	128	370	168	0	439	0	0	276	0	0	203	0	0
CR_{10}	380	120	95	395	0	125	390	0	90	180	0	0	80	0	0
FR_{10}	450	480	110	300	130	0	400	0	0	220	0	0	180	0	0

4.2.2 Evaluation of Anaerobic Digestion Performance of Sludge

For performance evaluations of anaerobic digesters, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), protein content, particle size distribution, and gas composition in the biogas (CH_4, CO, CO_2, H_2S) were analyzed during the operation period.

Total solids changes in reactor contents as a function of operation time are given in Figure 4.8. Total solids varied between 3% and 5% for reactors operated as batch system (CR_B and FR_B) while those ranged from 1% and 5% for reactors operated with 5 and 10 days sludge retention times (CR_5, FR_5, CR_{10}, and FR_{10}). Total solids in reactors fed with Fenton processed sludge were lower than those in control reactors for all sludge retention times. Lower TS values for reactors operated with 5 and 10 days sludge retention times than those in batch reactors were obtained and TS values decreased drastically especially during the first ten days for these reactors.

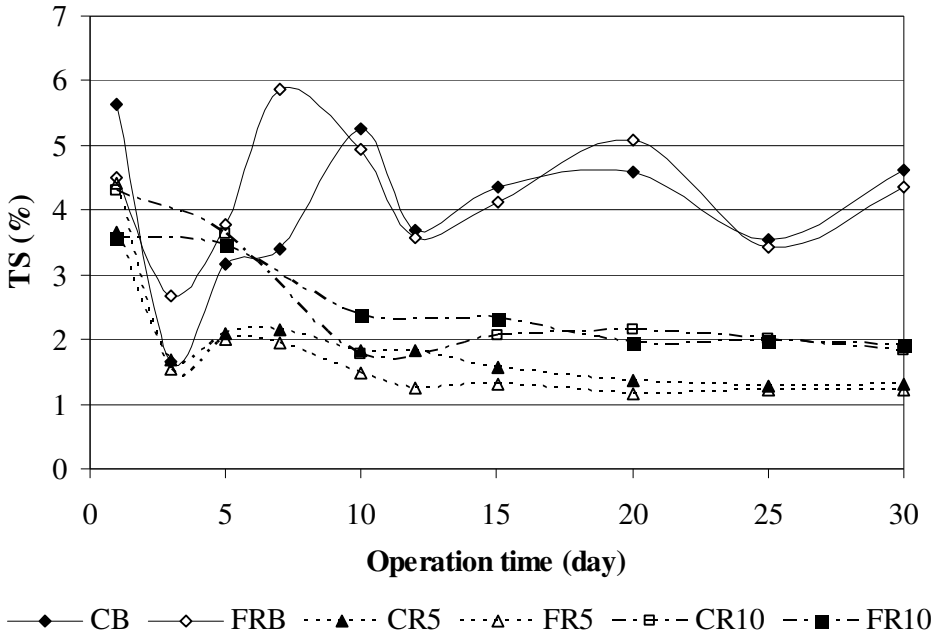


Figure 4.8. Total solids changes in the reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10} as a function of operation time

At the end of the operation, the highest decrease in TS was observed as 72 % in FR_5 according to the first operation day. For CR_5, this ratio was calculated as 65 %.

VS measurement results are shown in Figure 4.9. Better volatile solids reductions were observed for reactors operated with 5 and 10 days SRT comparing to reactors operated as batch system. VS concentrations in reactors fed with Fenton reagents were lower than those in control reactors for all sludge retention times. Similar with TS results, the highest reductions in VS were obtained in reactor coded as FR_5 while the lowest reductions in VS were observed in reactor coded as CR_B. Very close DS and VS reductions were observed among the reactors fed with Fenton processed sludge and control ones. At the end of operation, decrease in VS was recorded as 49 % according to the first operation day in FR_5. This ratio was determined as 42 % for CR_5

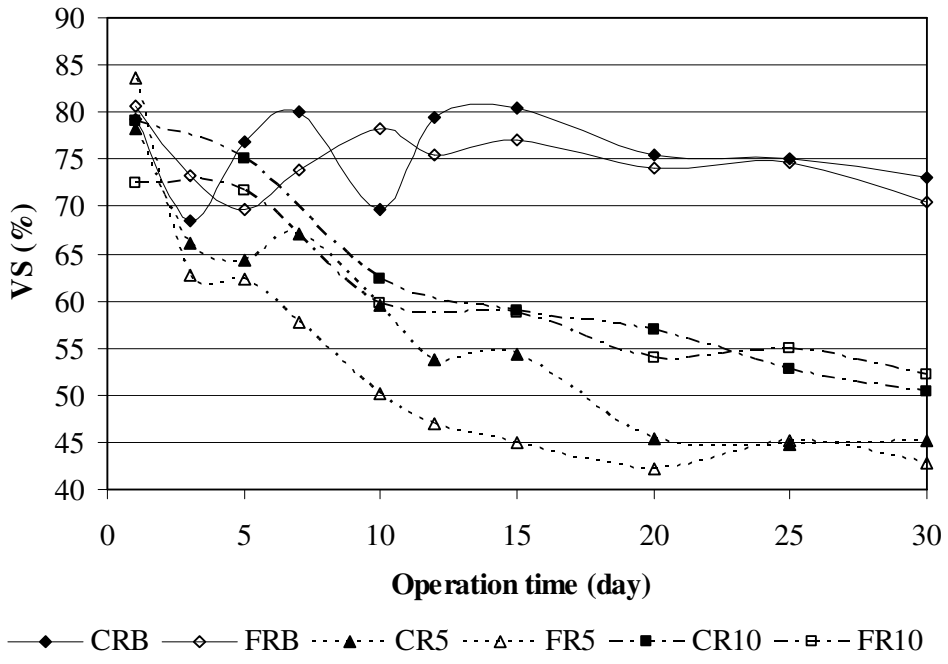


Figure 4.9 Volatile solids changes in reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10} as a function of operation time

Figure 4.10 and Figure 4.11 demonstrate the changes of SS and VSS as a function of operation time, respectively.

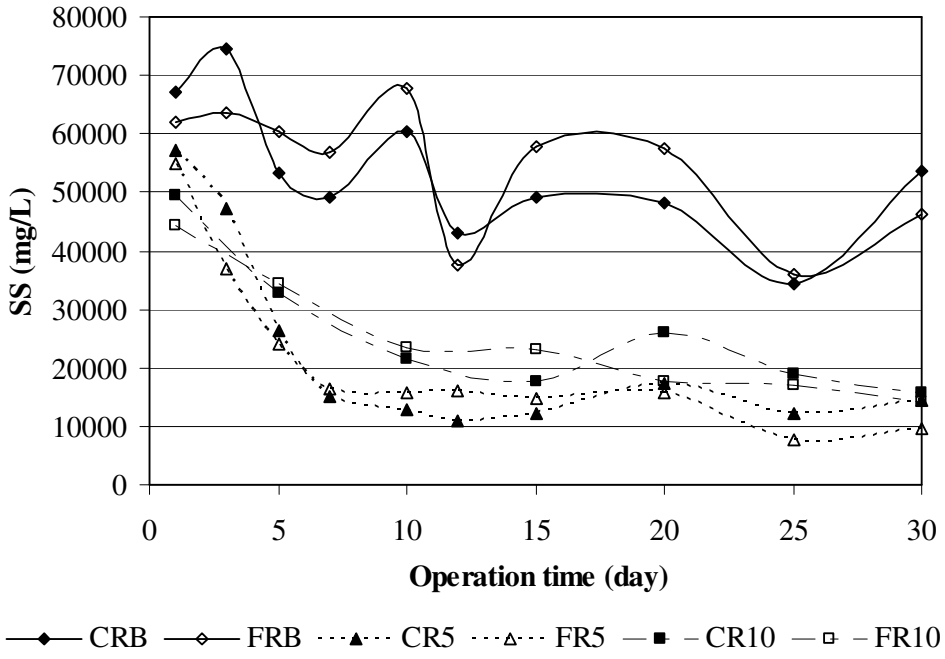


Figure 4.10 Suspended solids changes in reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10} as a function of operation time

The disintegration of the sludge cells was also reflected in decreasing SS contents of the sludge. Better SS reductions were observed for reactors operated with 5 and 10 days SRT comparing to reactors operated as batch system. SS in reactors fed with Fenton processed sludge were lower than those in control reactors for all sludge retention times. SS and VSS decreased quickly especially in first week of operation period in reactors operated with 5 and 10 days of sludge retention times. After ten days of operation SS and VSS had no change significantly and much closed values of SS and VSS were observed for 5 and 10 days of SRT.

Maximum decrease in SS was observed in the reactor fed with Fenton processed sludge and operated with 5 days sludge retention time (FR_5) and minimum decrease in SS was observed in the reactor fed with raw sludge and operated as batch system (CR_B). Minimum SS value of 7700 mg/L was achieved at 25^{th} day of operation period, while the value was 55100 at the end of first operation day. At the end of the operation, decreases in SS were observed as 20 %, 25 %, 74 %, 83 %, 68 %, and 68 % for CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10}, respectively, according to the first

operation day. Here, the efficiency of the Fenton process in sludge solubilization has been confirmed by the laboratory data.

Similar VSS results were obtained with SS results and the highest decrease in VSS was observed in the reactor coded as FR_5. Minimum VSS value of 5100 mg/L was obtained at the end of 25th day of operation and the value was 47700 mg/L at the end of first operation day. At the end of the operation, decreases in VSS were observed as 20 %, 32 %, 82 %, 87 %, 78 %, and 77 % for CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10}, respectively, at the end of first operation day. Based on these results it was suggested that the Fenton process was effective in improving sludge solubilization.

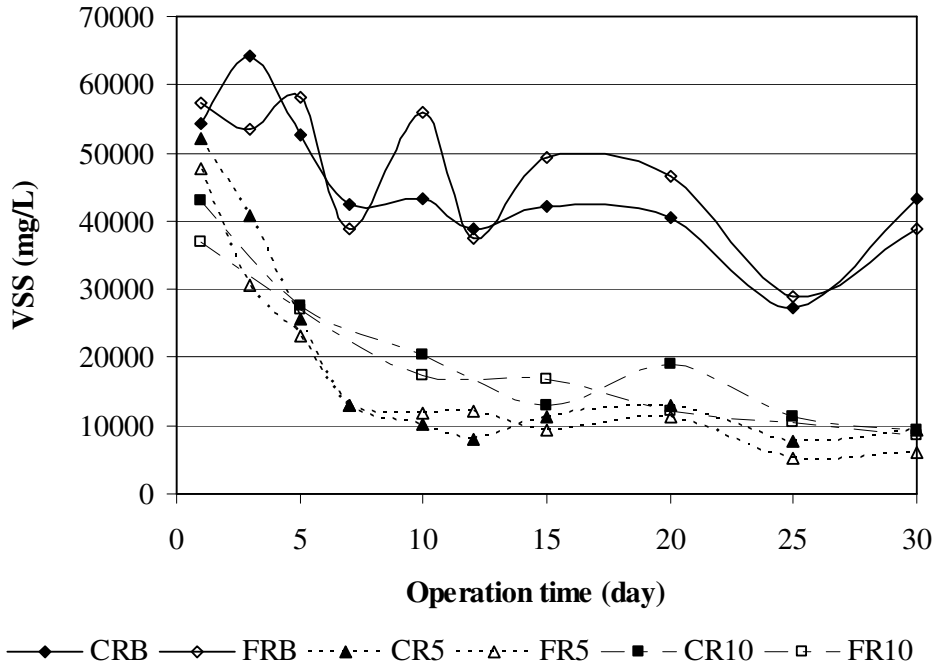


Figure 4.10 Volatile suspended solids changes in reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10} as a function of operation time

Table 4.14 and Table 4.15 show the CH_4/ CO_2/ H_2S / CO gas composition in CR_B and FR_B, respectively during operation period. For batch systems methane gas was decreasing during the operation period. Reactor fed with Fenton processed sludge (FR_B) gave higher methane gas production comparing to the control one (CR_B). H_2S

concentrations in FR_B were higher than in CR_B but H_2S values were lower than toxic level (100 ppm) for methanogens during the operation period for both CR_B and FR_B.

Table 4.14 CH_4/ CO_2/ H_2S / CO gas composition in CR_B during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	18	3.6	92	28
2	21	5.1	26	8
3	29	4.9	7	5
4	22	4.8	3	0
5	24	4.4	2	6
6	18	2.8	0	0
7	16	3.2	0	0
10	20	4.4	5	2
12	18	3.2	2	0
15	15	3.0	0	0
18	12	0.6	1	0
20	9	0.4	2	2
22	9	0	2	3
25	6	0	0	0
30	5	0.4	1	0

Table 4.15 CH_4/ CO_2/ H_2S / CO gas composition in FR_B during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	18	8.6	96	3
2	21	8.6	36	3
3	29	9	15	14
4	22	7.4	4	4
5	24	5.2	5	0
6	18	6.8	4	2
7	16	5.4	2	0
10	20	7.2	0	0
12	18	7.2	1	2
15	15	7.6	18	6
18	12	4.4	16	5
20	9	4.6	14	4
22	9	5.2	17	6
25	6	3.8	6	5
30	5	5.6	13	7

Table 4.16 and Table 4.17 show the CH_4/ CO_2/ H_2S / CO gas composition in CR_5 and FR_5, respectively during operation period. Reactor fed with Fenton processed sludge and operated with 5 days of SRT (FR_5) gave higher methane gas production

comparing to the control one (CR_5). In addition, Fenton process led to increase H_2S and CO levels in the reactors.

Table 4.16 CH_4/ CO_2/ H_2S / CO gas composition in CR_5 during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	25	3.6	>100	28
2	16	5.1	26	8
3	15	4.9	7	5
4	13	4.8	3	0
5	27	4.4	2	6
6	18	2.8	0	0
7	46	3.2	0	0
10	38	2.4	0	0
12	43	3.0	0	0
15	35	4.4	5	2
18	22	3.2	2	0
20	20	3.0	0	0
22	27	2.8	1	0
25	41	3.6	4	0
30	28	3.0	0	0

Table 4.17 CH_4/ CO_2/ H_2S / CO gas composition in FR_5 during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	32	4.2	>100	36
2	38	3.6	>100	5
3	45	3.2	>100	7
4	33	3.5	>100	21
5	48	3.2	>100	315
6	54	2.2	>100	157
7	62	2.0	>100	118
10	46	1.8	>100	126
12	42	1.8	>100	145
15	27	2.6	>100	243
18	42	2.2	>100	65
20	36	1.4	>100	116
22	27	2.0	>100	90
25	34	2.6	>100	80
30	32	0.6	>100	17

Table 4.18 and Table 4.19 represent the CH_4/ CO_2/ H_2S / CO gas composition in CR_{10} and FR_{10}, respectively during operation period. Reactor fed with Fenton Processed sludge and operated with 10 days of SRT (FR_{10}) gave higher methane gas

production comparing to the control one (CR_{10}). In addition, Fenton process led to increase H_2S and CO levels in the reactors for 10 days of SRT application.

Table 4.18 CH_4/ CO_2/ H_2S / CO gas composition in CR_{10} during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	28	3.6	>100	28
2	14	5.1	26	8
3	25	4.9	7	5
4	16	4.8	3	0
5	21	4.4	2	6
6	18	2.8	0	0
7	11	3.2	0	0
10	44	4.4	5	2
12	32	3.2	2	0
15	28	3.0	0	0
18	22	2.8	1	0
20	16	3.6	4	0
22	14	3.0	0	0
25	21	3.2	4	3
30	26	3	2	3

Table 4.19 CH_4/ CO_2/ H_2S / CO gas composition in FR_{10} during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	33	4.2	>100	36
2	24	3.6	>100	5
3	36	3.2	>100	7
4	27	3.5	>100	21
5	31	3.2	>100	315
6	35	2.2	>100	157
7	36	2.0	>100	118
10	41	2.6	>100	243
12	34	2.2	>100	65
15	22	1.4	>100	116
18	32	2.0	>100	90
20	26	2.6	>100	80
22	24	0.6	>100	17
25	26	2.0	65	0
30	28	2.4	5	0

Minimum methane productions were obtained in control reactor operated as batch system (CR_B). Reactors operated with 5 and 10 days of SRT gave nearly same oscillation during the operation period for methane. Especially for 5 days of SRT, very narrow oscillation was observed and the highest methane productions were also

obtained. For batch system methane gas was decreasing during the operation period. Reactors fed with Fenton processed sludge gave higher gas production comparing to the control reactors.

Cell lyses transforming cell content into the medium is the first, and breakdown of EPS fraction in the sludge is the second stage of floc disintegration. The protein results as depicted in Figure 4.11 showed that Fenton process enhanced the degradation of extracellular polymeric substances. Protein concentrations of reactor contents decreased with operation time in all reactors and the higher reductions were observed Fenton processed reactors comparing the control ones. The highest reduction according to the first operation day was observed as 79.5 % in FR_5 at the end of operation. The lowest protein value of 133 mg/L was obtained at the end of operation period, while this concentration was 648 mg/L in the first operation day.

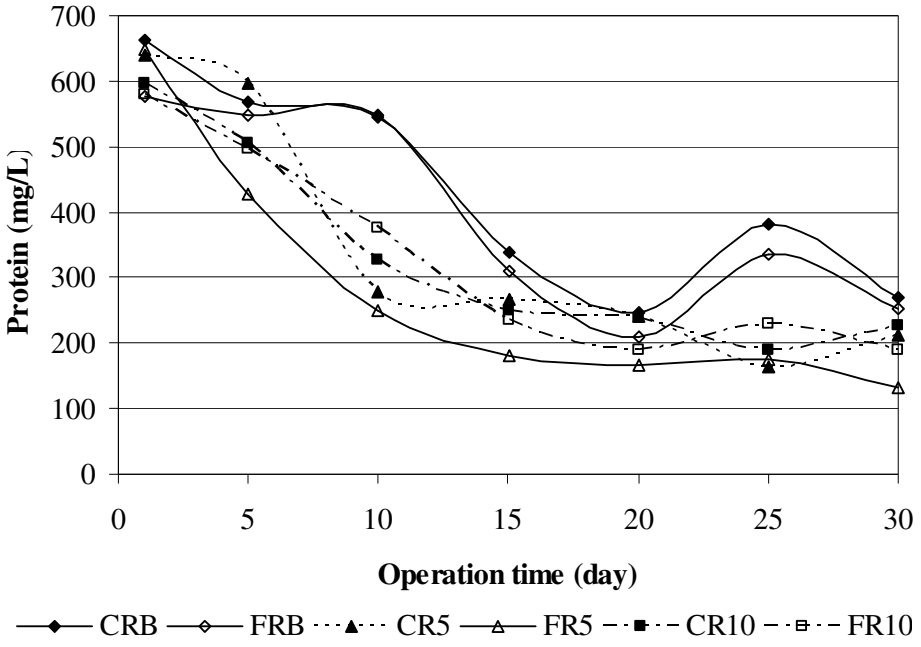


Figure 4.11 Protein changes in the reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10} as a function of operation time

The reduction in particle size generally allows an easier hydrolysis of solids within the sludge due to larger surface areas in relation to the particle volumes. The

result is an accelerated and enhanced degradation of the organic fraction of the solid phase (Xie et al., 2009). Although Particle size distribution shows the sludge disintegration, this parameter is not efficient for process optimization (Vranitzky et al., 2005). Table 4.20 and Figure 4.12 shows the particle size results in control reactor operated as batch system during the operation period. In Table 4.20, d (0.1), d (0.5), and d (0.9) demonstrate 10 %, 50 %, and 90 % of particles (in volume) having a diameter lower or equal to d (0.1), d (0.5), and d (0.9), respectively. Particle size had no change significantly during the operation time in reactor coded as CR_B.

Table 4.20 Particle size changes in CR_B during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	D (0.9)
1	85.888	468.516	34.948	341.848	1120.774
5	94.607	475.050	37.840	361.945	1110.285
10	115.478	549.900	47.200	472.240	1213.391
15	97.020	453.577	38.423	353.483	1038.316
20	97.245	386.103	38.406	333.040	828.023
25	101.613	433.290	39.438	343.269	981.981
30	95.215	426.854	36.527	328.609	985.094

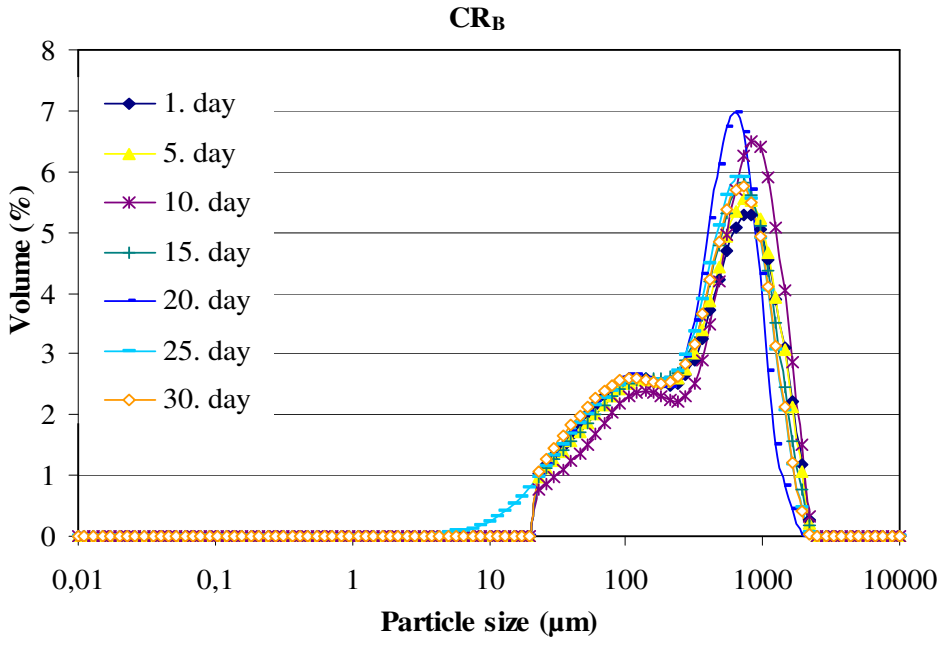


Figure 4.12 Particle size changes in CR_B during operation period

Table 4.21 and Figure 4.13 represent the particle size results of reactor coded as FR_B.

Table 4.21 Particle size changes in FR_B during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	D (0.5)	d (0.9)
1	81.868	536.41	31.394	429.916	1259.09
5	90.193	536.048	34.907	449.270	1221.00
10	99.88	557.441	38.618	485.506	1235.69
15	92.111	513.64	35.545	427.875	1165.602
20	107.019	517.23	41.3	424.834	1168.77
25	25.721	289.732	19.902	222.984	654.397
30	94.188	387.303	37.394	274.974	910.391

As seen in Table 4.22 and Figure 4.13 particle size had no significantly change during first 20 days for reactor coded as FR_B, after that values decreased, and the highest decrease in particle size were obtained at 30th day of operation period.

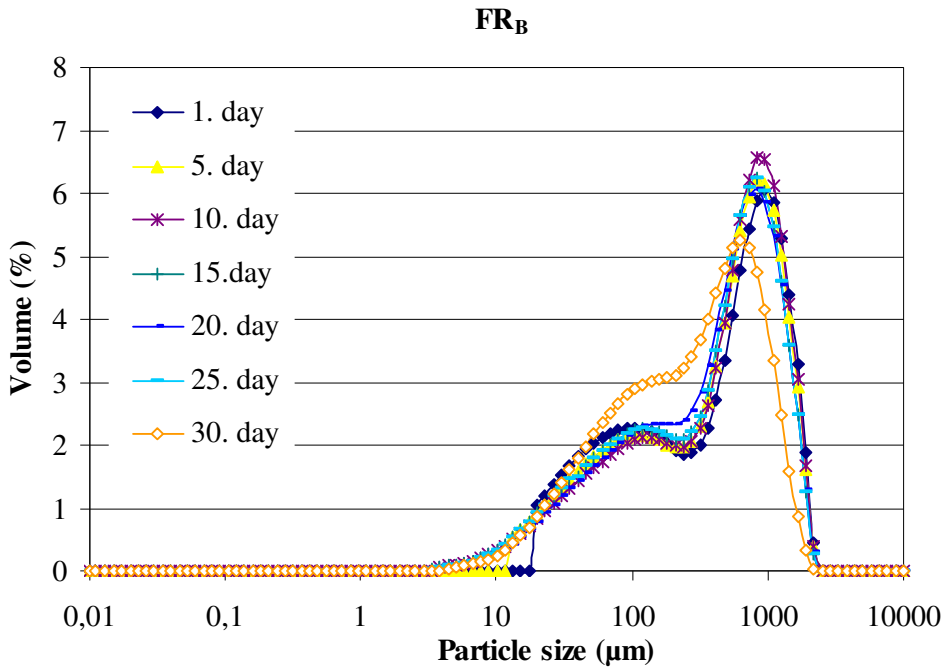


Figure 4.13 Particle size changes in FR_B during operation period

Particle size changes in reactor coded as CR_5 with operation time are given in Table 4.23 and Figure 4.14. In CR_5, particle size was nearly same value and

significant decrease was not observed in first ten days of operation. After ten days of operation, values decreased with operation time. As seen in Figure 4.14, two peaks were observed for first days but after ten days operation second peak were decreased due to particle size reduction. At the end of operation period, particle size reduced the ratio of 81.7 % comparing to first operation day based on volume weighted mean D (4.3).

Table 4.23 Particle size changes in CR_5 during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	D (0.5)	d (0.9)
1	98.801	524.602	39.406	427.091	1201.333
5	66.611	454.257	27.752	254.515	1161.518
10	64.241	436.457	26.988	224.752	1133.717
15	24.32	122.067	16.499	59.02	283.737
20	28.465	243.383	18.877	67.697	881.009
25	26.57	193.285	17.634	61.003	675.351
30	22.542	96.052	15.777	50.061	161.351

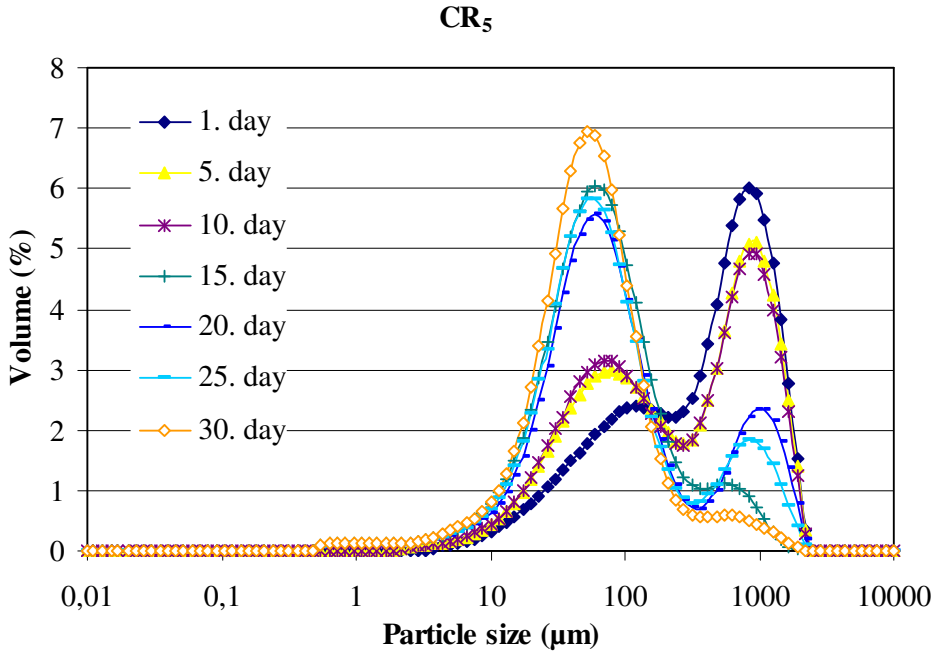


Figure 4.14 Particle size changes in CR_5 during operation period

Table 4.24 and Figure 4.15 gives particle size results of FR_5. Particle size decreased with operation time, and 86.9 % of particle size reduction was recorded at the end of 30 days operation. This ratio was calculated as at the end of the operation period 81.7 % for CR_5. According to this result, Fenton process led to a little improvement in particle size reduction for reactors operated with 5 days of sludge retention time.

Table 4.24 Particle size changes in FR_5 during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	78.184	501.129	30.382	365.969	1211.55
5	34.799	359.454	20.015	109.42	1065.186
10	31.87	260.014	18.174	76.636	851.393
15	24.657	172.428	14.785	58.735	566.965
20	22.431	124.067	14.179	50.278	199.482
25	22.93	141.738	14.398	50.56	392.45
30	20.152	65.626	12.347	42.494	118.371

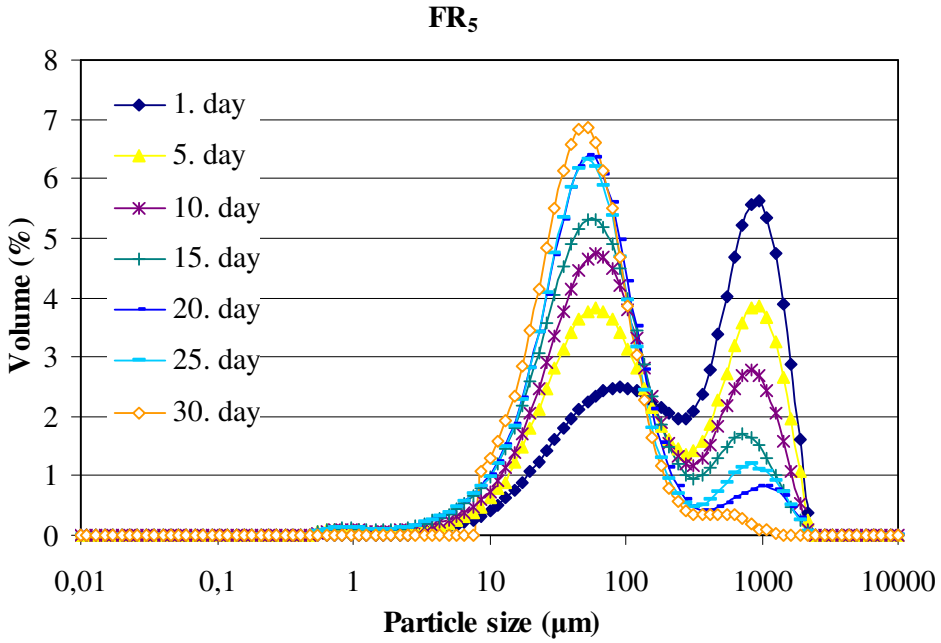


Figure 4.15 Particle size changes in FR_5 during operation period

Table 4.25 and Figure 4.16 shows the particle size results in control reactor operated with ten days of sludge retention time (CR_{10}). In CR_{10}, particle size was nearly same value and no reduction was observed in first ten days of operation. After ten days of operation, values decreased with operation time. As seen in Figure 4.16, two peaks were observed in first operation days. After that, second peak were decreased due to particle size reduction.

Table 4.25 Particle size changes in CR_{10} during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	94.083	501.811	36.528	410.931	1149.713
5	78.396	411.081	31.64	281.142	994.511
10	48.902	343.094	27.805	195.422	883.334
15	29.693	151.094	19.222	62.547	246.663
20	29.458	151.094	19.482	67.396	671.908
25	24.293	109.219	16.986	17.495	52.94
30	24.116	74.125	17.495	52.94	129.292

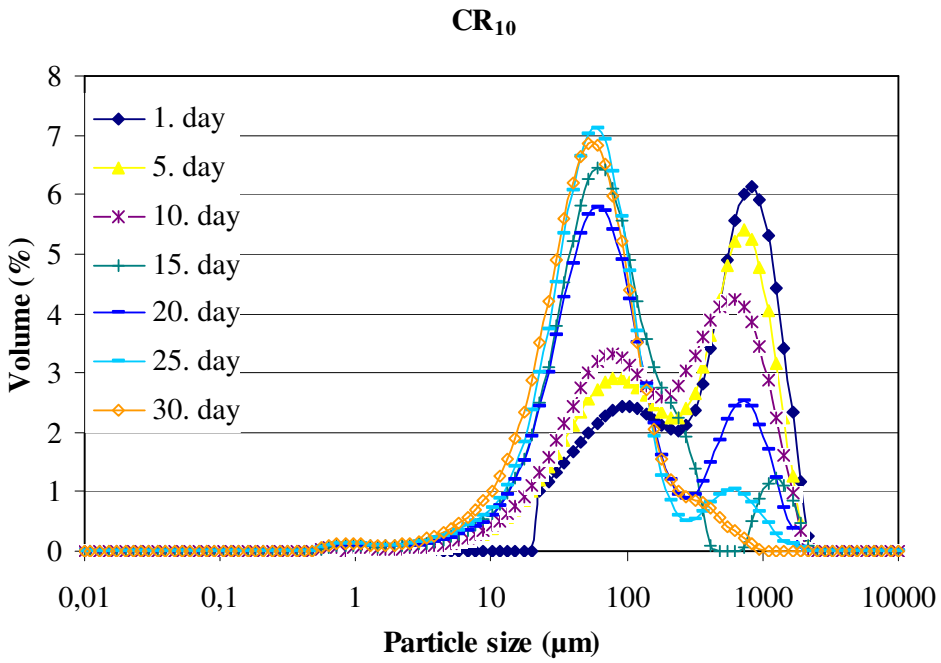


Figure 4.16 Particle size changes in CR_{10} during operation period

The highest reduction in particle size according to the first operation day was observed as 85 % at the end of operation period (based on D (4.3)).

Particle size changes in reactor coded as FR_{10} are given in Table 4.26 and Figure 4.17 during operation period. Particle size in the first operation day was recorded as 288.394 µm and the value was 73.849 µm at the end of the operation period, particle size reduced 74.4 % in FR_{10} (reduction ratios were calculated based on D (4.3)). Reduction ratio was calculated as 85 % for CR_{10}. For reactors operated with ten days of sludge retention time, control reactor and reactor fed with Fenton processed sludge gave similar results in terms of particle size; hence Fenton process had no significant effect on particle size reduction of sludge in this application.

Table 4.26 Particle size changes in FR_{10} during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	58.671	288.394	24.772	141.017	750.275
5	42.86	393.964	24.409	175.618	1041.083
10	44.937	186.188	21.818	69.52	614.147
15	34.818	165.682	19.204	65.793	544.865
20	28.475	200.804	16.489	62.166	688.539
25	25.609	188.97	15.119	57.179	656.507
30	22.397	73.849	14.199	48.344	144.662

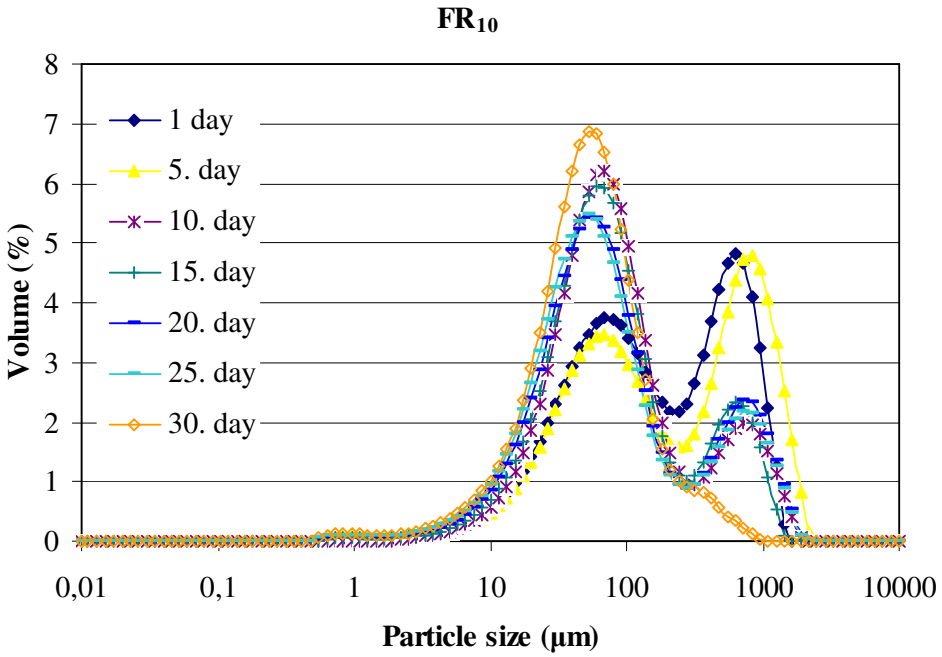


Figure 4.17 Particle size changes in FR_{10} during operation period

4.2.3 Evaluation of Dewatering Performance of Digested Sludge

CST is a quick and simple method to evaluate the filterability of sludge. This method neglects the shear effect on sludge, and it can not determine differences between dewatering processes but gives an approach dewatering capacity of sludge (Meeten et al., 1995).

In anaerobic digestion studies, CST parameter was used for evaluation of filtration characteristics of digested sludge and to see the effect of Fenton Process on dewatering characteristics of sludge in anaerobic digestion units.

CST variations in reactor contents during the operation period are given in Figure 4.18. For semi-batch system, CST values were decreased with increasing operation time. Anaerobic digestion increased the filterability characteristics of sludge for these reactors.

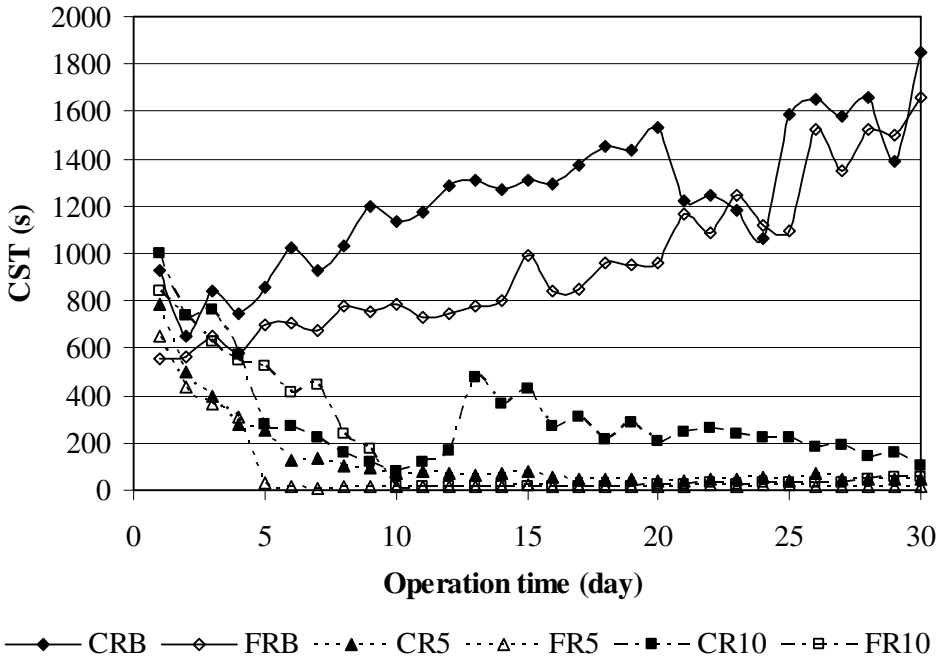


Figure 4.18 CST changes in reactor contents of CR_B, FR_B, CR_5, FR_5, CR_{10}, and FR_{10} during the operation period

Higher CST values were obtained in batch systems comparing to the semi batch systems. It was not observed the positive effect of Fenton Process on sludge filterability in batch systems. Especially, in FR_5 CST values increased strongly in a first 5 days of operation period. CST value of 647.9 was measured in the first operation day while the value was measured 28.4 at 5^{th} operation day. 95.6 % decrease in CST was calculated at 5^{th} operation day according to the first day of operation. The reduction ratios were calculated as 93.7 %, 98.1 %, 89.6, and 93.6 for CR_5, FR_5, CR_{10}, and FR_{10}, respectively, at the end of the operation period. CST results also showed that reactors operated with 5 days of sludge retention time more effective in increasing filterability characteristics of biological sludge than reactors operated with 10 days of sludge retention time.

In anaerobic digestion studies, a crown press was used as a simulator of belt filter press for evaluation of dewatering characteristics of digested sludge. The reactor contents were regularly processed through a crown press during the 30 days of operation period.

Table 4.27 shows the final cake solids obtained from crown press application during the operation period in anaerobic digestion studies with Fenton Process. A small improvement in cake solids of FR_5 and FR_{10} contents for 10 days of operation was observed. On the other hand, final cake solids did not improve with operation time for control reactors.

Table 4.27 Final cake solids obtained from crown press application during operation period in Fenton Process studies

Reactor's code/	Final cake solids, %					
Days	1	10	15	20	25	30
CR_5	13.05	11.44	13.15	11.51	13.94	9.63
FR_5	10.59	12.88	9.61	10.77	9.98	11.45
CR_{10}	11.7	11.50	11.88	12.37	10.50	10.17
FR_{10}	13.6	14.01	13.52	12.09	11.84	11.79

Table 4.28 summarized final drainage volume of sludge after 120 sec of filtration in gravity drainage plow simulator kit. Fenton process preceding anaerobic digestion did not significantly affect of drainage rate during 120 sec of filtration.

Table 4.28 Drainage volume after 120 sec of filtration in gravity drainage plow simulator kit during operation period in Fenton Process studies

Reactor's code /	Drainage volume, mL					
Days	1	10	15	20	25	30
CR_5	170	170	180	190	170	170
FR_5	140	135	170	140	125	145
CR_{10}	150	160	175	185	195	175
FR_{10}	115	120	110	120	185	175

4.3 Optimization Study of Ozone Oxidation Conditions

Ozone dose was considered as a main variable parameter for evaluation of disintegration performance of sludge. The range of ozone dose varied from 0 to 0.25 gO_3/g TS. Ozone dose was determined by using initial ozone concentration, residual ozone concentration after reaction, reaction time, and initial total solids concentration according to the Eq. 7 given in Chapter 3.3.2. Table 4.29 shows the ozone oxidation conditions used in the experiments.

Disintegration degree (Muller, 2000) parameter based on soluble COD calculations (procedure given in Chapter 3.5.1) was considered as the main response for evaluation of biological sludge disintegration.

Table 4.29 Ozone oxidation conditions

Experiment no	Reaction time (min)	Ozone dose (gO_3/g TS)
1	0	0
2	1	0.005
3	5	0.02
4	10	0.05
5	15	0.07
6	20	0.09
7	25	0.1
8	30	0.13
9	45	0.18
10	60	0.25

COD, total nitrogen, and total phosphorus concentrations in sludge's supernatant, DOC and protein concentrations were also measured for each experiment to determine the effects of ozone oxidation on floc disintegration of biological sludge. A particle size distribution in sludge after ozone oxidation was used as another response to see the floc disintegration effect of ozone oxidation. In addition, the effect of ozone oxidation on solubilization sludge' solids was evaluated with suspended solids and volatile suspended solids measurements. CST parameter was also monitored for determination of sludge filterability characteristics of ozonated sludge.

4.3.1 Optimization of Ozone Oxidation Conditions in terms of Biological Sludge Disintegration

The disintegration degree permits to evaluate the maximum level of sludge solubilization. Increase of DD is determined as the substance that can be readily used to produce methane in the anaerobic digestion (Wang et al., 2005). Variation of disintegration degree with ozone dose is given in Figure 4.19. The disintegration degree of biological sludge increased significantly with increasing ozone in each experiment. The maximum disintegration degree of 51.1 % was obtained for 0.1 gO_3/gDS for 25 min reaction time. At higher ozone dose than 0.1 gO_3/g TS, DD

trend was decreased. Up to 0.1 gO_3/g TS ozone dose, hydroxyl radicals preferentially attack the organic substances and destruct the activated sludge microorganisms cell walls in biomass and oxidized them to dissolved organic substances and these substances released to the liquid phase and increased the DD, for higher ozone dose, decreases in DD may be explained by oxidation: high ozone dose above 0.1 gO_3/ g TS promote oxidation by radicals and ozone oxidation led to a mineralization phenomenon preceding a solubilization phenomenon. This result was observed in other study for waste activated sludge (Bougrier et al., 2006).

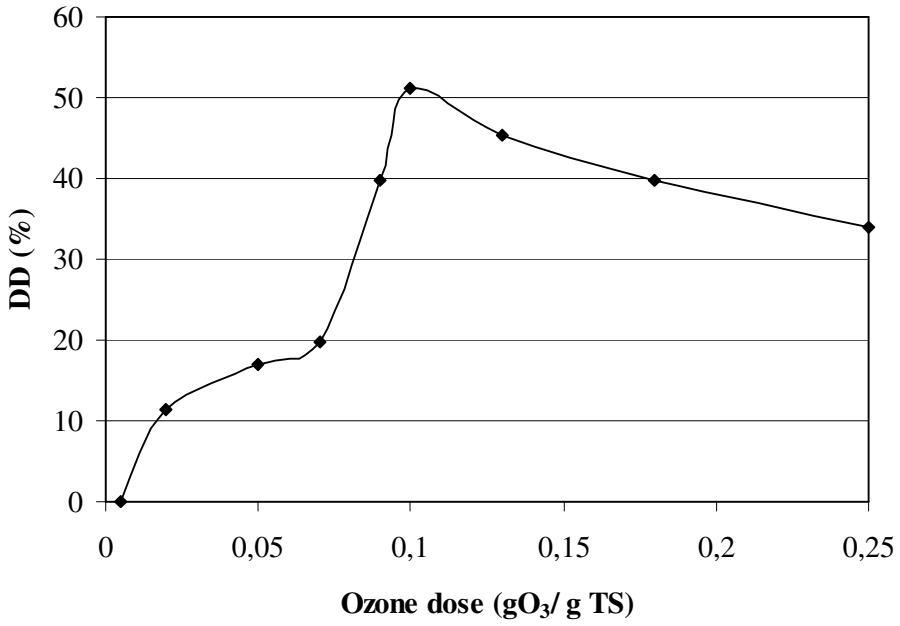


Figure 4.29 Variation of disintegration degree with ozone dose

Figure 4.30 demonstrates the variation of DOC with ozone dose.

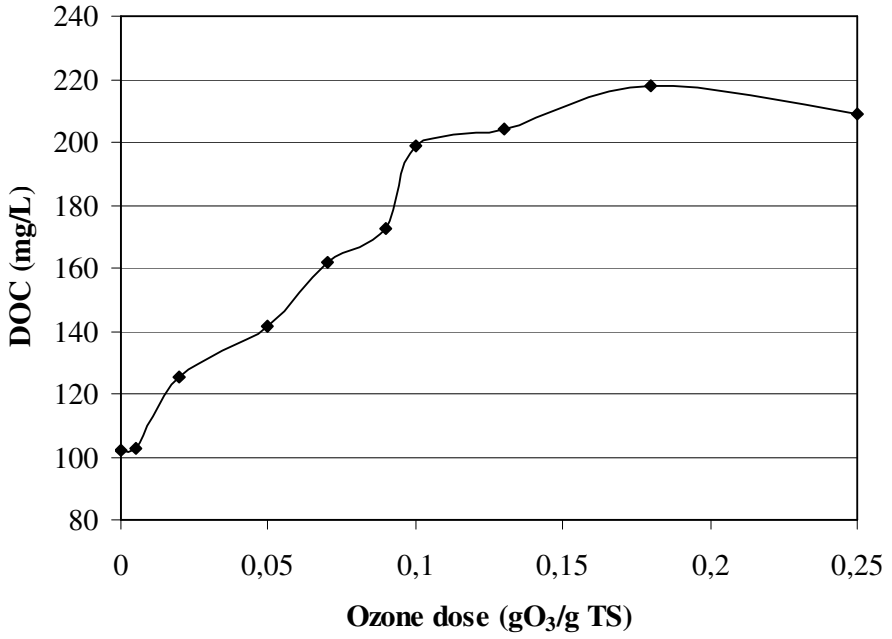


Figure 4.30 Variation of DOC with ozone dose

Increase in DOC with ozone oxidation demonstrate that ozonated sludge stabilize higher degree in biological digestion processes than non-ozonated sludge. SCOD results obtained from ozone oxidation experiments are given in Figure 4.31. The variation of SCOD with ozone dose showed very close trend with the variation of DD. SCOD increased quickly with increasing ozone dose, then peaked in 0.1 gO_3/ g TS ozone dose and 25 min reaction time and then decreasing trend was observed. When ozone dose was 0.1 gO_3/ g TS and the reaction time was 25 min, SCOD increased to 960 mg/L from the 240 mg/L. Ozone oxidation is a process of sludge disintegration, which increases SCOD, and ozone oxidation of soluble substances, which decreases SCOD. As ozone dose increases, more soluble organics were mineralized. Similar evaluation was reported before in the other study (Zhang et. al., 2009). Considering sludge lyses and ozone cost, the optimal ozone dose was found as 0.1 gO_3/gDS and extra ozone dose is unnecessary for sludge disintegration.

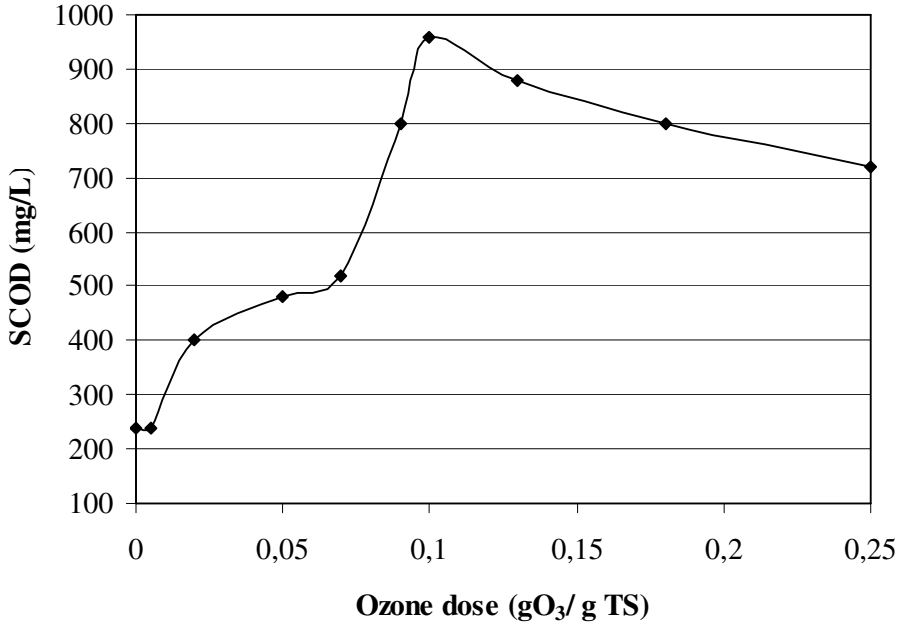


Figure 4.31 Variation of SCOD with ozone dose

Figure 4.32 shows the SS and VSS variation with ozone dose. The disintegration of the sludge cells was also reflected in the decreasing SS and VSS content of sludge. SS and VSS results showed that ozone oxidation played an important role in sludge destruction and solubilization during the ozone oxidation. In Figure 4.32, it can be seen that SS and VSS content of sludge decreased with increasing ozone dose. 34 % of the SS and 12.3 % of the VSS was solubilized for 0.25 gO_3/g TS. Solubilization degrees in here were calculated by Eq. 8 given in Chapter 3.5.7. These solubilization degrees were comparable to the results of Chu et al., 2008 but lower than the results of Weemaes et al., 2000. Lower values obtained in our study could be attributed to the nature and composition of sludge: higher TS concentration led to higher disintegration degree (Khanal et al., 2007).

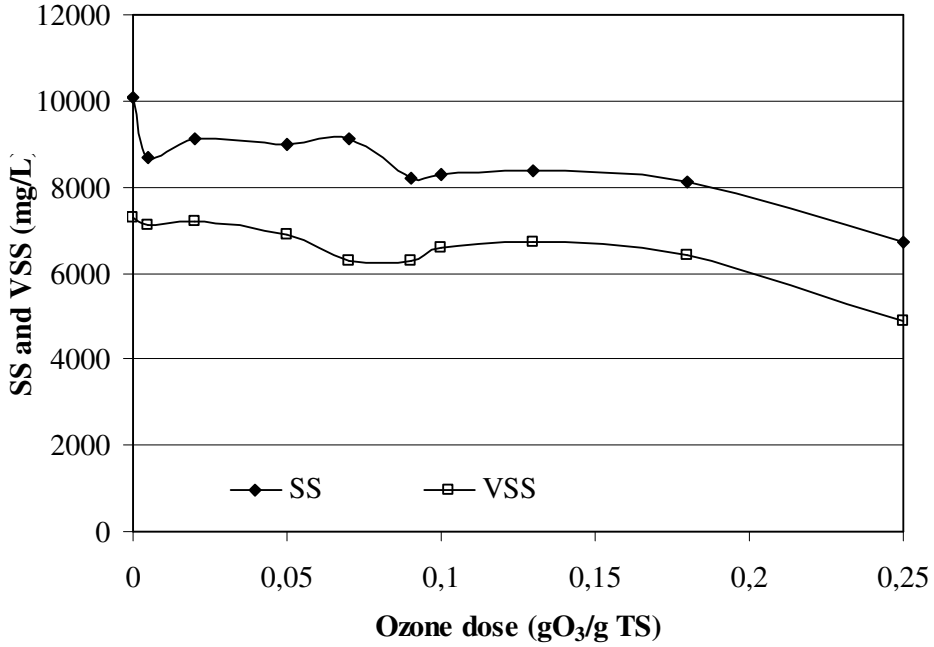


Figure 4.32 Variation of SS and VSS with ozone dose

Ozone penetrates into the microorganisms, increases the osmosis of cell membranes, damages the uniformity of the cell walls, and releases the intracellular substances into water. This process is very effective and contributes to the rapid initial increase of total nitrogen and total phosphorus.

Figure 4.33 presents the variation of total phosphorus in sludge's supernatant (TP) with ozone dose. Phosphorus released to the sludge supernatant in a few minutes in other words very low ozone doses due to ozone oxidation, after that only slight improve was observed in TP with increasing ozone dose. Clearly, during the ozone oxidation of sludge, most of the phosphorus in the supernatant existed in the form of organic products. When ozone dose was 0.005 gO_3/g TS and the reaction time was 1 min, TP increased to 109.3 mg/L from the 40.2 mg/L and maximum TP concentration was achieved as 120.6 for 0.1 gO_3/g TS at 25 minutes of reaction time.

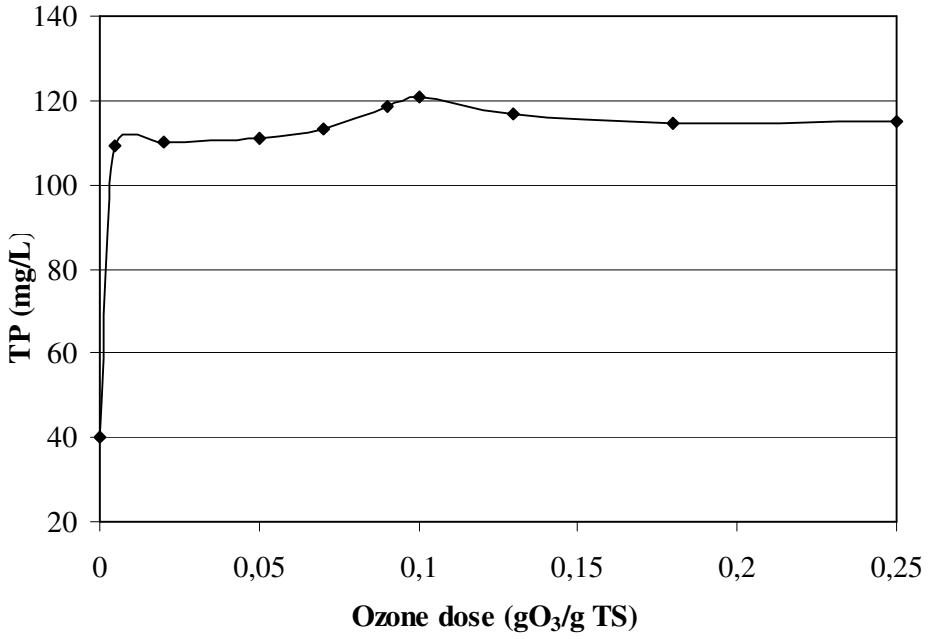


Figure 4.33 Variation of total phosphorus in sludge's supernatant with ozone dose

Figure 4.34 shows the variation of total nitrogen in sludge's supernatant (TN) with ozone dose. The total nitrogen increased with ozone oxidation especially at ozone dose of 0.005 – 0.05 gO_3/g TS, and then TN was became stable and re-increases in total N in supernatant at dose of 0.1 – 0.18 gO_3/g TS. Re-increases in TN may be explained by protein degradation above 0.1gO_3/g TS ozone dose as represented in Figure 5. But nitrogen fractions have to be analyzed for detailed explanation. Maximum increase of TN was achieved as 512.5 % for 0.1gO_3/g TS at 45 min reaction time.

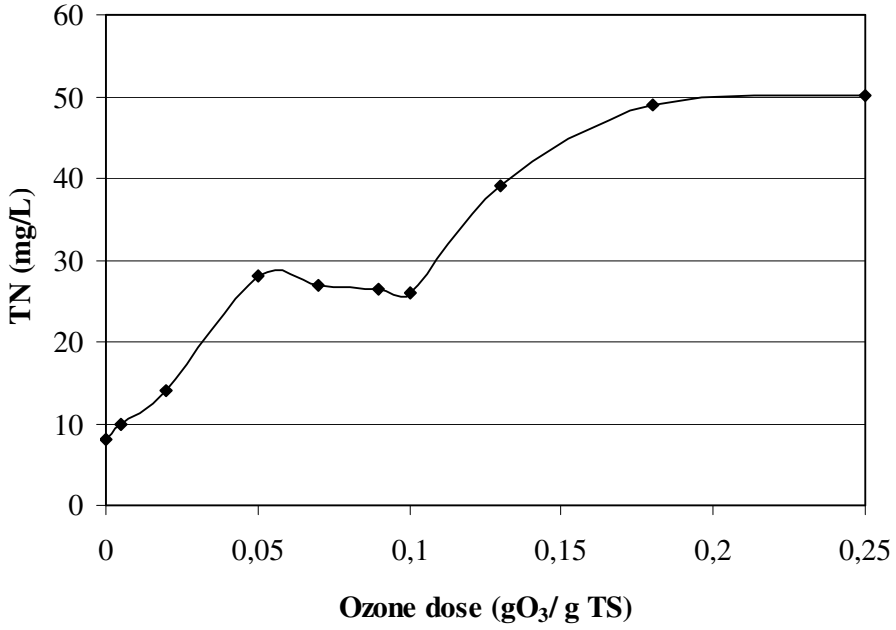


Figure 4.34 Variation of total nitrogen in sludge's supernatant with ozone dose

The total nitrogen in sludge's supernatant increased with ozone oxidation especially at ozone dose of 0.005 – 0.05 gO_3/g TS, and then the values became stable and re-increases in total N in supernatant at dose of 0.1 – 0.18 gO_3/gDS may be explained by protein degradation above 0.1gO_3/gDS ozone dose as represented in Figure 4.35. Nitrogen fractions have to be analyzed for detailed explanation.

Cell lyses transforming cell content into the medium is the first, and breakdown of extracellular polymeric substance (EPS) fraction in the sludge is the second stage of floc disintegration. Cell lyses in the first stage cause to release of protein content into the liquid phase of sludge. In the second stage, disintegration enhances the degradation of extracellular polymeric substances (EPS).

Protein results obtained from ozone oxidation experiments are depicted in Figure 4.35. A little increase in protein concentration was observed up to 0.1 gO_3/g TS and then protein concentration decreased strongly with increasing ozone dose.

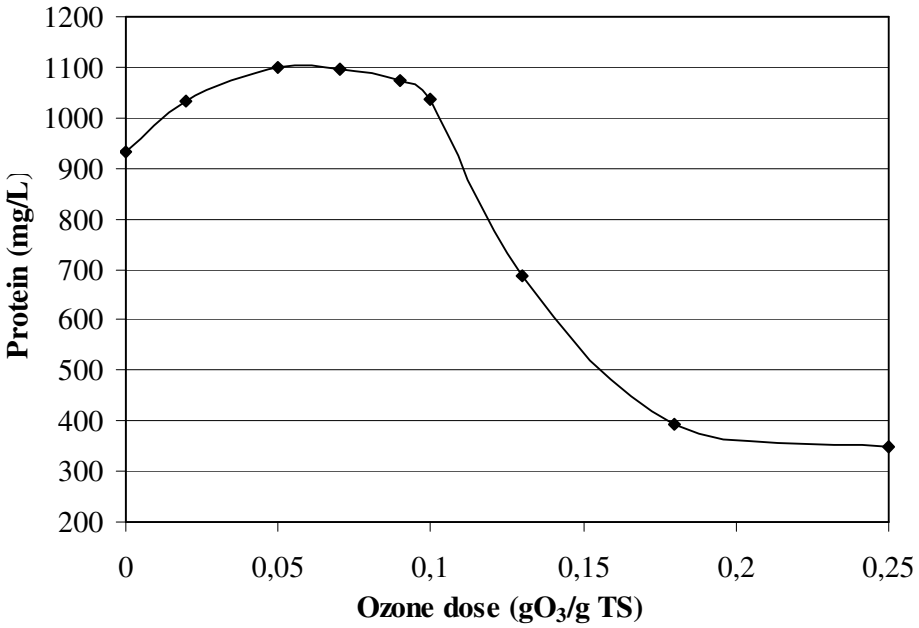


Figure 4.35 Variation of protein with ozone dose

For raw sludge, protein concentration was measured as 932.8 mg/L while the value was 347.3 mg/L for 0.25 gO_3/g TS. Decrease in protein concentration was calculated as 62.8 % for this experiment. Ozone oxidation enhanced the degradation of EPS and protein concentration decreased with increasing ozone dose.

Table 4.30 and Figure 4.36 summarize the particle size results in ozone oxidation experiments. Reductions in particle size were obtained in ozonated sludge comparing to that in raw sludge. Particle size of sludge was found to be relatively stable up to 0.1 gO_3/g TS and then particle size decreased with increasing ozone dose. Particle size reductions can be clearly seen in Table 4.30. For 0.1 gO_3/g TS, surface weighted mean was decreased from 40.7 µm for raw sludge to 29.4 µm: that is to say a decrease of 17.4%. Bougrier et al. (2006) was reported a similar observation before and their reported 8.5% of particle size decrease for same ozone dose. Based on volume-weighted mean, particle size decrease in sludge was obtained as 30 % for 0.1 gO_3/g TS in our experiments.

Table 4.30 Particle size changes for different ozone dose

Ozon dose (gO_3/g TS)	Particle size (µm)				
	Surface weighted mean D(3.2)	Volume weighted mean D(4,3)	d (0.1)	d (0.5)	D (0.9)
0	40.713	101.514	24.750	84.485	191.367
0.005	40.983	101.196	24.821	84.393	188.293
0.02	40.270	101.196	24.263	83.357	186.715
0.05	40.421	94.581	24.447	83.150	179.935
0.07	38.720	101.652	23.393	82.118	187.009
0.09	35.824	99.408	21.395	78.115	179.259
0.1	33.601	90.449	20.088	75.051	171.135
0.13	32.720	88.547	19.520	73.818	169.287
0.18	31.557	86.723	18.834	72.937	164.904
0.25	29.445	80.221	17.765	70.673	155.494

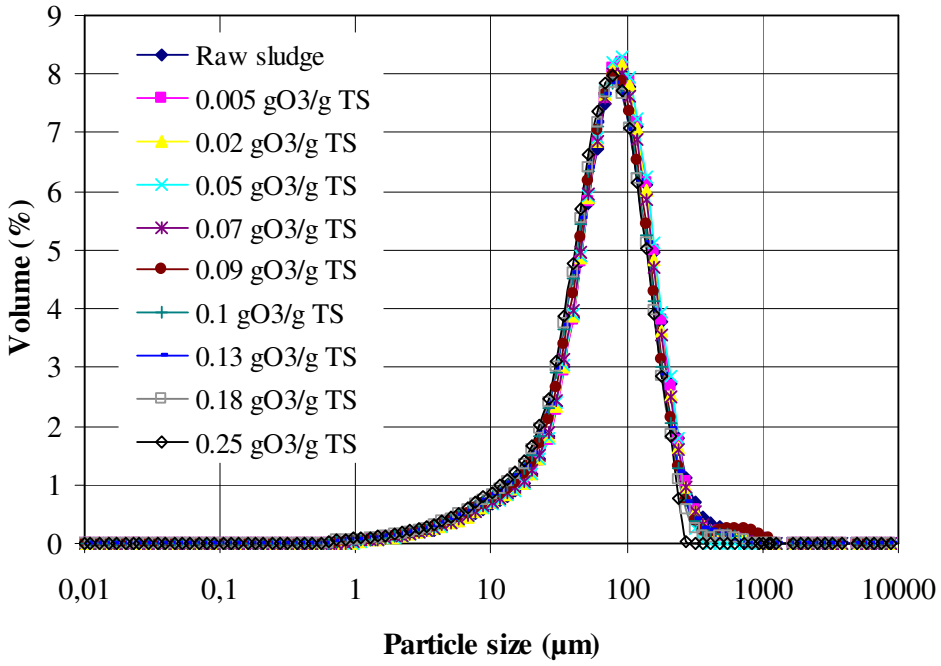


Figure 4.36 Variation of particle size distribution for different ozone dose

4.3.2 The Effect of Ozone Oxidation on Dewaterability of Biological Sludge

In order to determine the filterability characteristics of sludge after ozone oxidation, CST test was carried out for each experiment. CST variations with ozone dose are given in Figure 4.37. A little decrease in CST was observed up to 0.1 gO_3/g DS, after than CST increased drastically increasing ozone dose. Above 0.1 gO_3/g DS, ozone oxidation deteriorated the filtration characteristics of sludge.

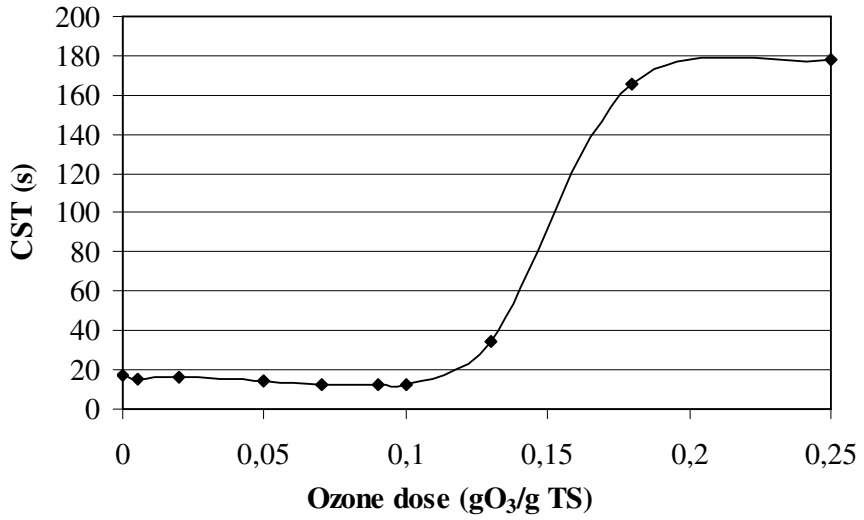


Figure 4.37 Variation of CST with ozone dose

4.4 Anaerobic Digestion Study with Ozone Oxidation

After optimization study of ozone oxidation conditions for biological sludge disintegration, sludge digestion studies were carried out for raw sludge and ozonated sludge. 0.1 gO_3/g TS ozone dose achieved at the highest DD was chosen as the optimum dose for biological sludge disintegration. Optimum dose was applied to sludge before anaerobic digestion.

Sludge digestion studies were carried out using two 8.5 L anaerobic reactors. Reactors were operated at 37 ± 2 °C in mesophilic conditions for 30 days of operation period. Reactors operated as batch and semi-batch systems in order to

determine optimum operation condition. Different sludge retention times as 5 and 10 days were applied during the operation in order to determine optimum retention time. Sludge digestion procedure was given in detail in Chapter 3.4.

Control reactors fed with raw sludge were coded as CR_B, CR_5, CR_{10}. Reactors fed with ozonated sludge were coded as OR_B, OR_5, OR_{10} and subscripts in here represents the sludge retention times. Reactor's codes used anaerobic digestion studies with ozone oxidation are given in Table 4.12.

Table 4.31 Reactor's codes used anaerobic digestion studies with ozone oxidation

Reactor's code	Ozone oxidation	Sludge retention time
CR_B	No applied	Batch operation
OR_B	Applied	Batch operation
CR_5	No applied	5 days
OR_5	Applied	5 days
CR_{10}	No applied	10 days
OR_{10}	Applied	10 days

4.4.1 Control of Anaerobic Digesters Stability

In anaerobic digestion studies with ozone oxidation, pH and temperature parameters were measured daily for control of anaerobic digester stability. Alkalinity and volatile fatty acids (VFA) parameters were monitored regularly for evaluation of anaerobic digester performance.

The Temperature was kept at 37 ± 2 °C for all reactors and temperature changes in reactors were given in Figure 4.38. pH values given in Figure 4.39 varied from 6.90 to 8.80 in reactors.

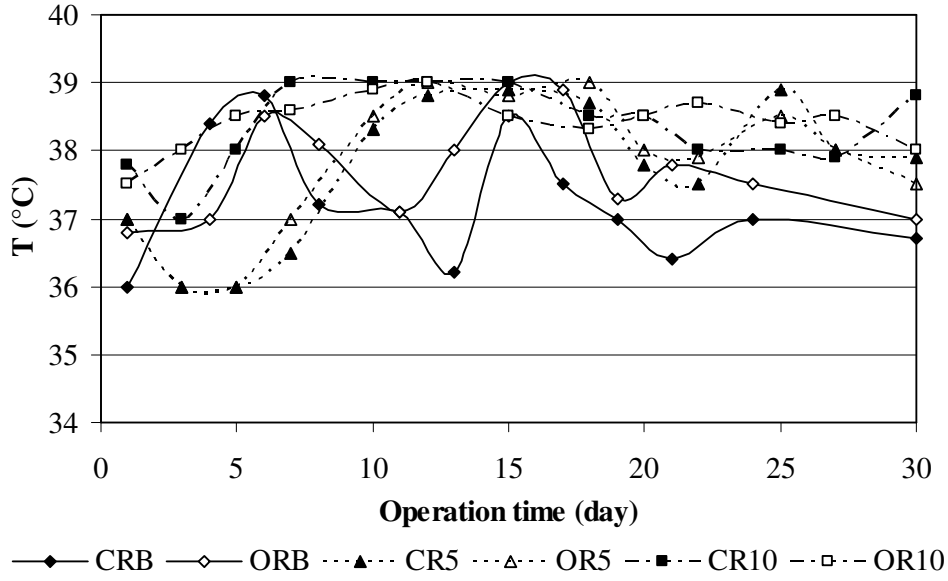


Figure 4.38 Temperature changes in reactor contents of CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} during operation period

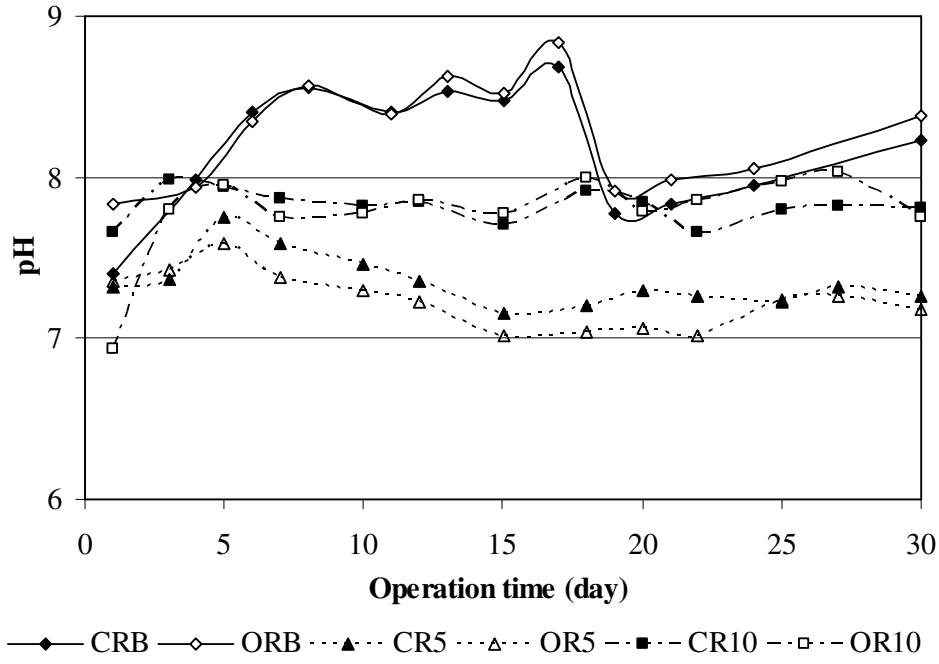


Figure 4.39 pH changes in reactor contents of CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} during operation period

In anerobic digestion studies with ozone oxidation, total alkalinity values were measured regularly as a measure of the stability of the digestion unit. An alkalinity range of 1400 – 3700 mg $CaCO_3$/ L were measured during the operation period (Figure 4.40).

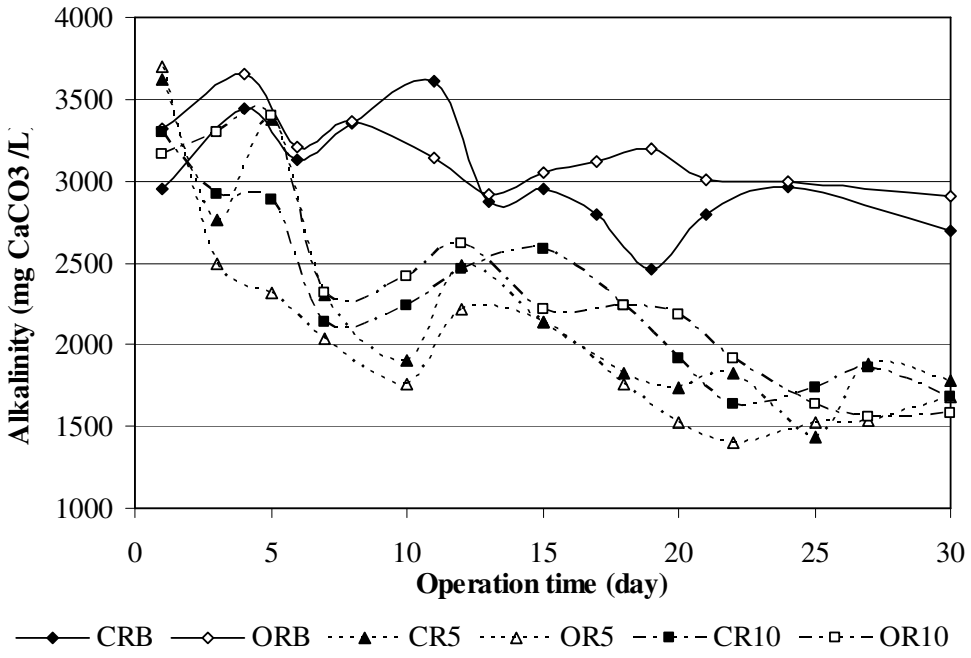


Figure 4.40 Total alkalinity changes in reactor contents of CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} during operation period

VFA content was also checked for reactor stability and results are given in Table 4.32. In batch reactors, lower VFA values were recorded comparing the semi batch systems in first operation days, then values increased during operation period.

Table 4.32 VFA (Lactic acid, Lc/ Acetic acid, Ac/ Propionic acid, Prc) changes in reactor contents of CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} during operation period

Days	1			4			8			15			24		
Reactor's code	Lc	Ac	Prc	Lc	Ac	Prc	Lc	Ac	Prc	Lc	Ac	Prc	Lc	Ac	Prc
CR_B	0	0	0	0	1131	373	0	107	90	0	1320	215	0	830	237
OR_B	0	699	0	0	3896	0	0	2576	638	0	3015	402	0	3022	0
CR_5	350	1520	236	356	1125	152	160	0	96	0	805	0	0	242	0
OR_5	0	1630	292	0	1286	0	0	239	0	0	405	0	0	121	0
CR_{10}	0	1522	520	0	1575	200	0	948	0	0	330	0	0	0	0
OR_{10}	0	549	0	0	1507	0	0	1650	0	0	862	0	0	148	0

4.4.2 Evaluation of Anaerobic Digestion Performance of Sludge

For evaluations of anaerobic digestion performance of sludge, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), protein content, particle size distribution, and gas composition in the biogas (CH_4, CO, CO_2, H_2S) were analyzed during the operation period.

In anaerobic digestion studies with ozone oxidation, total solids changes during the operation period are given in Figure 4. 41.

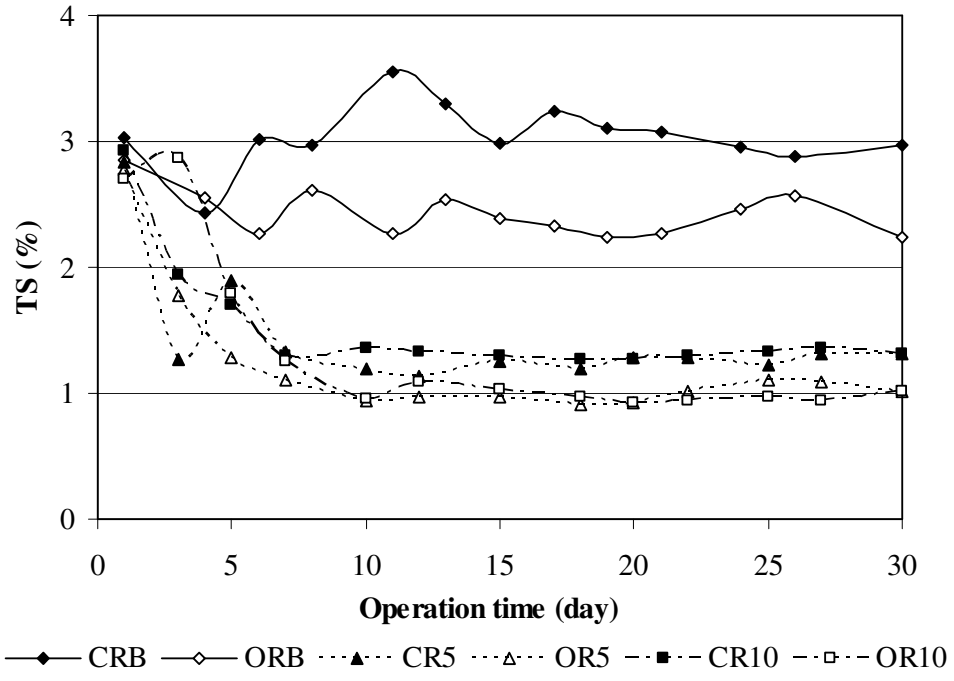


Figure 4.41 Total solids changes in reactor contents of CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} during operation period

Total solids concentrations varied between 2 % and 3 % for reactors operated as batch system while those ranged from 0.9 % and 2.9 % for reactors operated with 5 and 10 days of sludge retention times. At the end of the operation period percent decreases in TS in reactor contents according to the first operation day was calculated as 1.7 %, 22 %, 54 %, 63.7 %, 54.9 %, and 62.7 % for CR_B, OR_B, CR_5,

OR_5, CR_{10}, and OR_{10}, respectively. TS concentrations in reactors fed with ozonated sludge were lower than those in control reactors for all sludge retention times.

Lower TS values for reactors operated with 5 and 10 days sludge retention times than those in batch reactors were obtained. TS values decreased drastically especially during the first ten days for these reactors for these reactors.

VS measurement results obtained from anaerobic digestion studies with ozone oxidation are shown in Figure 4.42. Better volatile solids reductions were observed for reactors operated with 5 and 10 days of sludge retention time comparing to reactors operated as batch system. VS concentrations in reactors fed with ozonated sludge were lower than those in control reactors for all sludge retention times. Reactors operated with 5 and 10 days of sludge retention time gave much closed results in terms of VS.

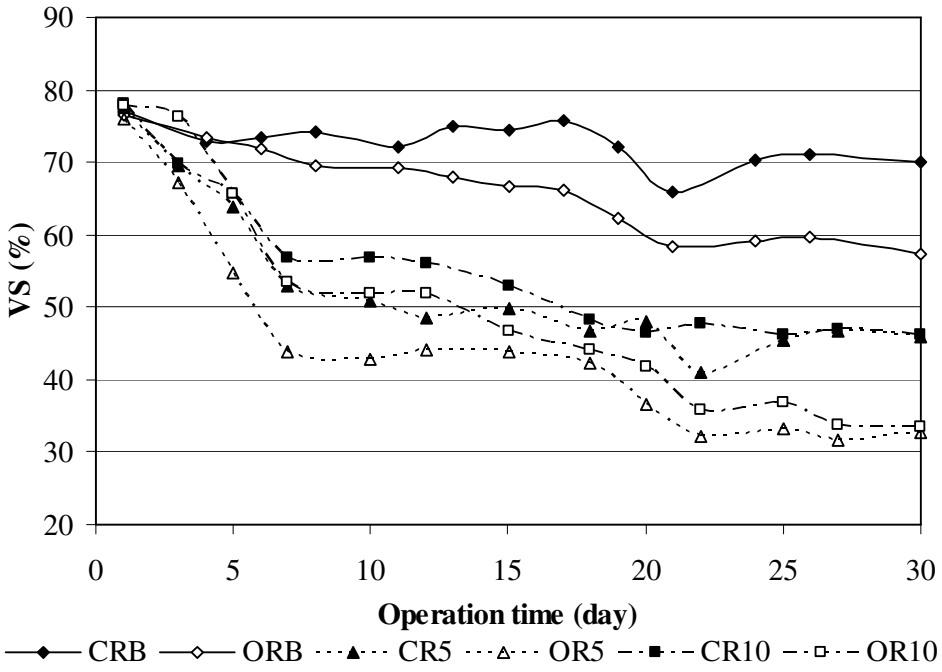


Figure 4.42 Total solids changes in reactor contents of CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} during operation period

At the end of the operation, the highest decrease in VS was observed as 57 % in OR_5 according to the first operation day. For CR_5, this ratio was calculated as 40.9 %. Ozone oxidation preceding anaerobic digestion led to reduce sludge's solids.

Figure 4.43 and Figure 4.44 demonstrates the changes of SS and VSS as a function of operation time, respectively. SS and VSS decreased quickly especially in first week of operation period in reactors operated as semi batch system. After ten days of operation SS and VSS had no change significantly and nearly same values of SS and VSS were observed for 5 and 10 days of SRT. At the end of the first operation day, SS value for CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} was determined as 45800 mg/L, 44650 mg/L, 42800 mg/L, 41940 mg/L, 43710 mg/L, and 43470 mg/L, respectively. The value was 31750 mg/L, 31400 mg/L, 9480 mg/L, 6930 mg/L, 9800 mg/L, and 6600 mg/L at the end of the operation period for CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10}, respectively. At the end of the first operation day, VSS value for CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} was determined as 44900 mg/L, 35125 mg/L, 37080 mg/L, 25900 mg/L, 35650 mg/L, and 33050 mg/L, respectively.

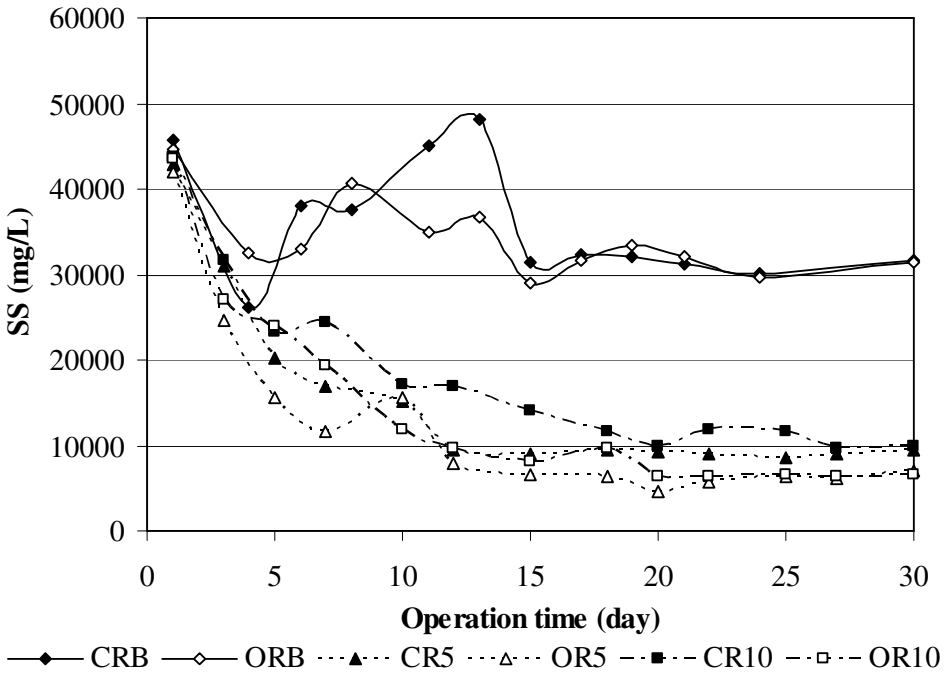


Figure 4.43 Suspended solids changes in reactor contents of CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} during operation period

The value was 29150 mg/L, 25200 mg/L, 5250 mg/L, 3390 mg/L, 5500 mg/L, and 3960 mg/L at the end of the operation period for CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10}, respectively. Higher reductions in SS and VSS were observed in reactors fed with ozonated sludge than in control reactors. The lowest SS and VSS were achieved in reactor coded as OR_5. The minimum SS value of 4550 mg/L was achieved at 20th day of operation period, while the value was 41940 at the end of first operation day. SS reduction was recorded as 89 % in 20th day of operation.

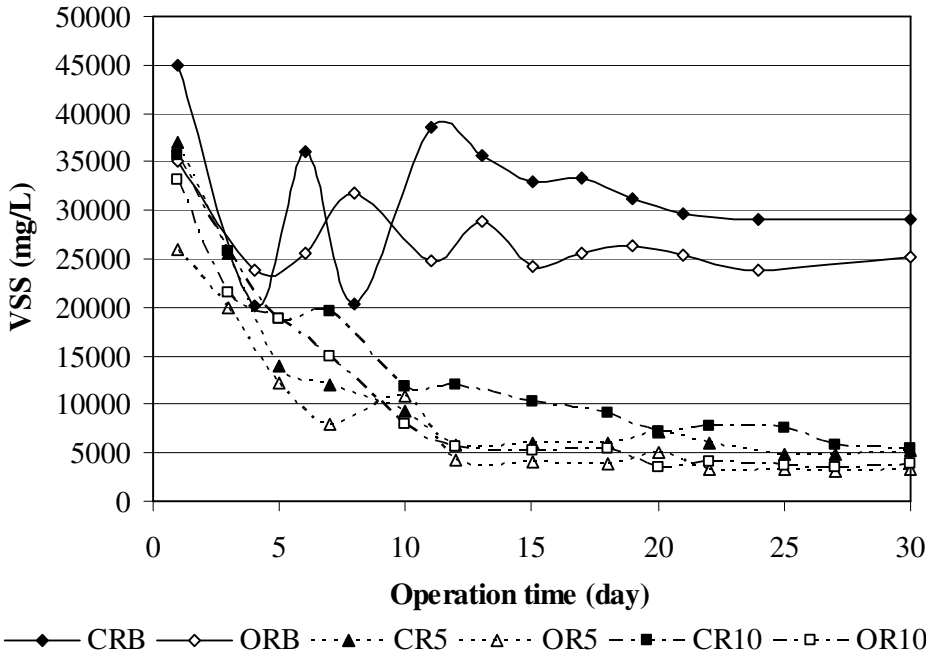


Figure 4.44 Volatile suspended solids changes in reactor contents of CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} during operation period

In same operation day, VSS reduced to 3800 mg/L from 31160 mg/L and VSS reduction was calculated as 88 %. Based on these results it was suggested that the ozone oxidation was effective in improving sludge solubilization.

Table 4.33 and Table 4.33 show the CH_4/ CO_2/ H_2S / CO gas composition in CR_B and OR_B, respectively during operation period. For batch systems methane gas was decreasing during the operation period.

Table 4.33 CH_4/ CO_2/ H_2S / CO gas composition in CR_B during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	27	2	29	2
4	13	1.4	1	0
6	38	1.4	0	0
11	25	1.2	5	11
13	24	0.6	1	0
15	10	1.4	5	0
17	8	0.8	3	0
19	2	0.6	4	3
21	0	0.6	7	5
25	0	0	0	0
30	0	0.4	1	0

Reactor fed with ozonated sludge (OR_B) gave higher methane gas production comparing to the control one (CR_B). Although H_2S concentrations in OR_B were higher than in CR_B, H_2S values did not exceed toxic levels (100 ppm) for methanogens during the operation period for both CR_B and OR_B.

Table 4.34 CH_4/ CO_2/ H_2S / CO gas composition in OR_B during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	>100	4.4	31	0
4	82	2.6	13	4
6	46	1.8	6	0
11	32	3.0	31	9
13	20	1.6	7	5
15	15	2.8	12	5
17	9	1	2	0
19	5	1.6	2	0
21	3	1.4	1	0
25	0	3	2	0
30	1	1.2	1	0

Table 4.35 and Table 4.36 show the CH_4/ CO_2/ H_2S / CO gas composition in CR_5 and OR_5, respectively during operation period. Reactor fed with ozonated sludge (OR_5) gave higher methane gas and carbon dioxide production comparing to the control one (CR_5).

Table 4.35 CH_4/ CO_2/ H_2S / CO gas composition in CR_5 during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	35	0	24	22
3	32	2.6	15	0
5	44	7.4	8	0
7	43	6.2	0	0
10	34	6.8	1	0
12	32	0.6	0	0
15	35	2.2	0	0
18	32	6.4	0	0
20	29	5	0	0
22	31	4.4	4	0
25	27	6	3	0
27	32	4.4	9	4
30	30	5.4	8	3

In the first six days of operation, CH_4 concentrations was recorded above 100 ppm, then values decreased and the values was stable approximately 33 % Lel after 10 days operation for OR_5. In addition, ozone oxidation led to increase H_2S levels in the reactors.

Table 4.36 CH_4/ CO_2/ H_2S / CO gas composition in OR_5 during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	>100	15.5	32	28
3	>100	13	3	0
5	>100	11	2	0
7	86	10.6	0	0
10	57	10.2	0	0
12	42	0.8	0	0
15	30	8.8	1	2
18	36	12	0	0
20	27	9	2	0
22	29	8	5	4
25	43	7.2	2	5
27	26	7	5	4
30	31	8	16	9

Table 4.37 and Table 4.38 show the CH_4/ CO_2/ H_2S / CO gas composition in CR_{10} and OR_{10}, respectively during operation period. Reactor fed with ozonated sludge (OR_{10}) gave higher methane gas and carbon dioxide production comparing to the control one (CR_{10}).

Table 4.37 CH_4/ CO_2/ H_2S / CO gas composition in CR_{10} during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	32	4	13	7
3	18	2.6	8	0
5	29	2.2	0	2
7	25	2.4	0	0
10	30	5.6	0	0
12	32	4.6	3	0
15	28	4.4	3	0
18	25	5.0	2	0
20	31	2.4	0	3
22	26	2	0	0
25	30	5.2	2	0
27	29	6.1	7	2
30	31	1.6	0	0

In the first operation day, CH_4 concentrations was recorded above 100 ppm, then values decreased and very closed values (approximately 32 % Lel) were observed after 10 days operation for OR_{10}.

Table 4.38 CH_4/ CO_2/ H_2S / CO gas composition in OR_{10} during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	>100	7.2	100	27
3	96	8.4	24	0
5	84	6.2	8	8
7	52	6.6	12	0
10	43	7.4	0	0
12	29	2.6	3	0
15	30	5.8	3	0
18	32	1.4	2	4
20	29	1.8	0	0
22	39	4.4	0	0
25	42	6.7	2	2
27	28	2.3	4	0
30	30	1.4	0	0

The protein results obtained in anaerobic digestion study with ozone oxidation are depicted in Figure 4.39. Ozone oxidation enhanced the degradation of extracellular polymeric substances. Protein concentrations of reactor contents decreased with operation time in all reactors and the higher reductions were observed reactors fed with ozonated sludge comparing to control ones. Reduction in protein content according to the first operation day was 82 %, 85 %, 90.4 %, 91.1 %, 88.8 %, and

93.5 % for CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10}, respectively. The highest decrease in protein content according to the first operation day was observed in OR_{10} at the end of operation.

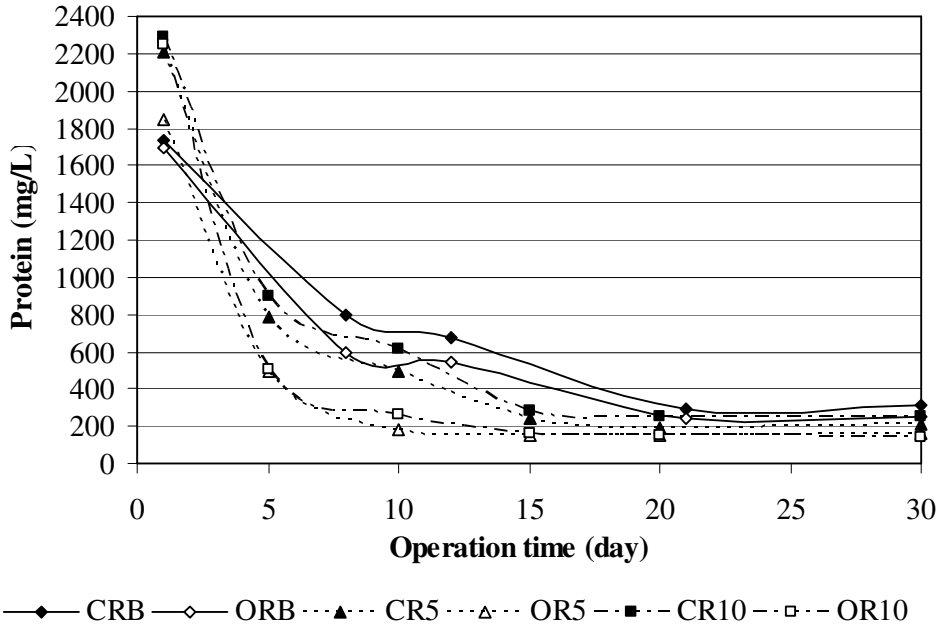


Figure 4.39 Protein changes in reactor contents of CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} during operation period

Table 4.39 and Figure 4.40 show the particle size results in control reactor operated as batch system during the operation period. In the first operation day, high values of particle size were observed. Then values decreased.

Table 4.39 Particle size changes in CR_B during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	D (0.5)	d (0.9)
1	95.891	504.503	39.456	417.726	1152.507
5	90.387	523.160	37.002	419.152	1224.172
10	86.668	517.926	37.018	422.070	1205.669
15	66.979	423.620	36.755	304.429	1002.544
30	51.765	424.737	30.255	296.407	1026.627

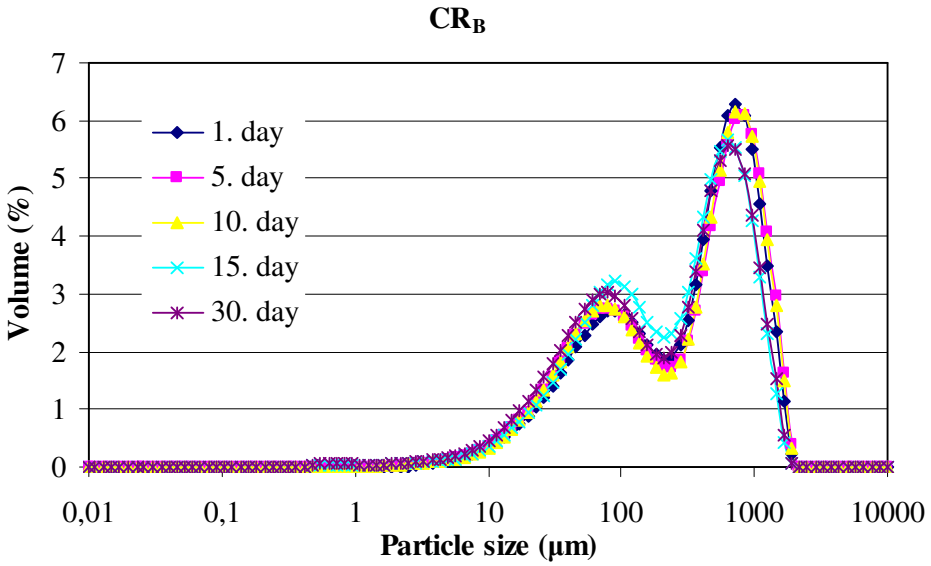


Figure 4.40 Particle size changes in CR_B during operation period

Table 4.40 and Figure 4.41 show the particle size results in reactor fed with ozonated sludge and operated as batch system during the operation period. As seen in Table 4.40 particle size had no significantly change during first 20 days for reactor coded as OR_B, after that values decreased, and highest reductions of particle size were obtained at the end of 30 day operation time. Ozone oxidation process before anaerobic digestion led to little improvement in particle size decrease.

Table 4.40 Particle size changes in OR_B during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	D (0.5)	d (0.9)
1	108.251	532.265	45.848	465.449	1168.885
5	94.226	477.391	40.319	398.338	1075.140
10	84.877	466.806	45.280	404.858	1006.731
15	78.487	526.438	40.828	439.203	1187.836
20	75.723	500.058	43.763	403.075	1137.528
30	51.944	404.955	31.010	237.901	1011.852

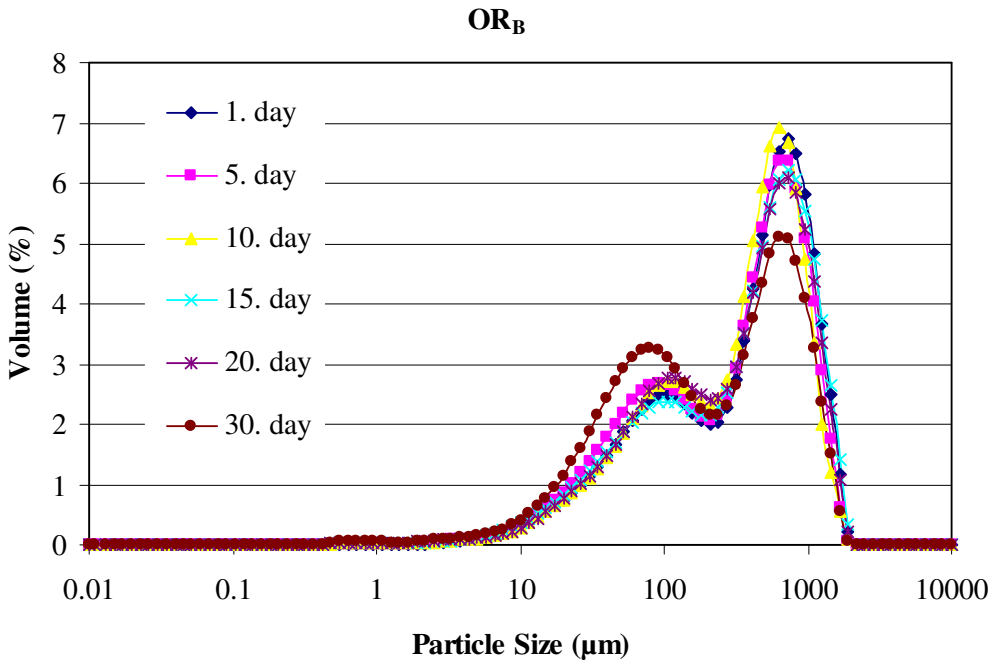


Figure 4.41 Particle size changes in OR_B during operation period

Particle size changes in reactor coded as CR_5 with operation time are given in Table 4.43 and Figure 4.42. In CR_5, particle size nearly was same value and no reduction was observed after first five days of operation. As seen in Figure 4.42, two peaks were observed for first days but after ten days operation second peak were decreased due to particle size reduction.

Table 4.43 Particle size changes in CR_5 during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	D (0.5)	d (0.9)
1	48.103	501.191	22.266	220.546	1342.496
5	21.643	77.289	14.126	53.782	180.529
10	21.497	94.864	14.536	60.237	230.322
15	20.684	101.791	14.081	60.562	240.615
25	18.157	49.570	12.020	42.698	98.056
30	22.193	66.632	14.674	48.549	127.596

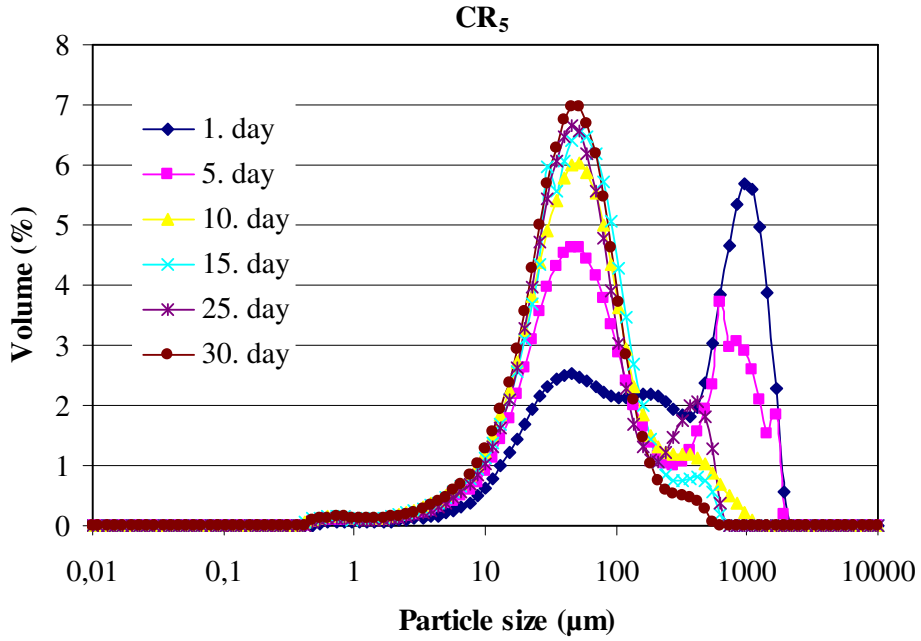


Figure 4.42 Particle size changes in CR_5 during operation period

Particle size changes in reactor coded as OR_5 with operation time are given in Table 4.44 and Figure 4.43. Particle size in the first operation day was recorded as 501.191 µm and the value was 66.632 µm at the end of the operation period, particle size reduced approximately 87 % in OR_5. The reduction ratio was calculated as 86.7 % for CR_5 (based on volume weighted mean). The reductions for CR_5 and OR_5 were calculated as 54 % and 77.2 %, respectively, based on D (3.2) Ozone oxidation preceding anaerobic digestion led to a little reduction in particle size comparing the classical anaerobic digestion.

Table 4.44 Particle size changes in OR_5 during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	D (0.5)	d (0.9)
1	98.801	524.602	39.406	427.091	1201.333
5	66.611	454.257	27.752	254.515	1161.518
10	64.241	436.457	26.988	224.752	1133.717
15	24.32	122.067	16.499	59.02	283.737
20	28.465	243.383	18.877	67.697	881.009
25	26.57	193.285	17.634	61.003	675.351
30	22.542	96.052	15.777	50.061	161.351

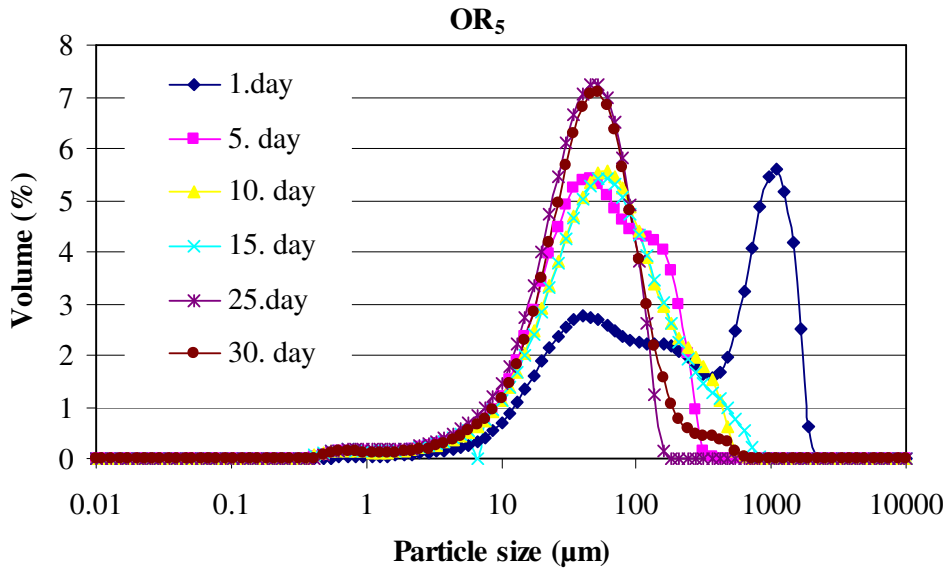


Figure 4.43 Particle size changes in OR_5 during operation period

Particle size changes CR_{10} are summarized in Table 4.45 and Figure 4.44. As seen in Figure 4.44, two peaks were observed in first operation days. After ten days operation, second peak were decreased due to particle size reduction.

Table 4.45 Particle size changes in CR_{10} during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	67.703	489.610	29.150	204.705	1287.086
5	58.671	287.301	28.151	222.887	621.439
15	24.293	109.219	16.986	17.495	24.293
25	24.116	74.125	17.495	52.94	129.29
30	18.814	60.004	14.293	48.099	111.930

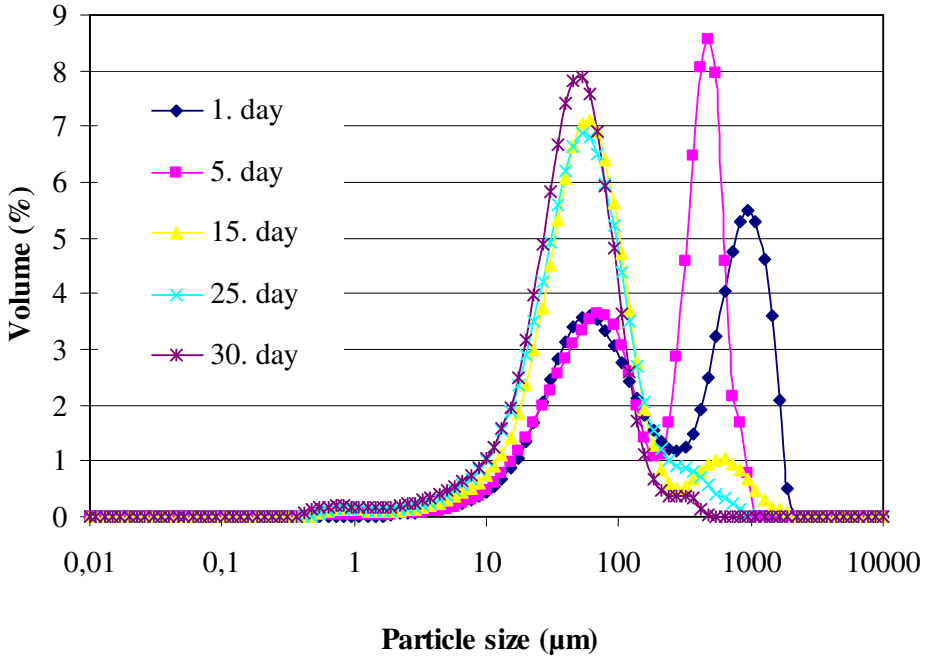


Figure 4.44 Particle size changes in CR_{10} during operation period

Particle size changes in reactor coded as OR_{10} with operation time are given in Table 4.46 and Figure 4.45. Particle size in the first operation day was recorded as 662.319 µm and the value was 67.948 µm at the end of the operation period, particle size reduced approximately 89% in OR_{10} (reduction ratios were calculated based on D (4.3)). The reduction ratio was calculated as 72.2 % for CR_{10}. Ozone oxidation preceding anaerobic digestion with 10 days of SRT led to higher reduction in particle size comparing the classical anaerobic digestion.

Table 4.46 Particle size changes in OR_{10} during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	132.946	662.319	53.815	661.909	1303.301
5	27.020	282.793	18.422	117.473	795.427
10	25.520	269.119	17.586	101.147	781.432
15	18.908	116.768	13.166	61.926	315.142
25	43.581	50.813	27668	48.478	77.275
30	20.916	67.948	14.073	48.615	129.772

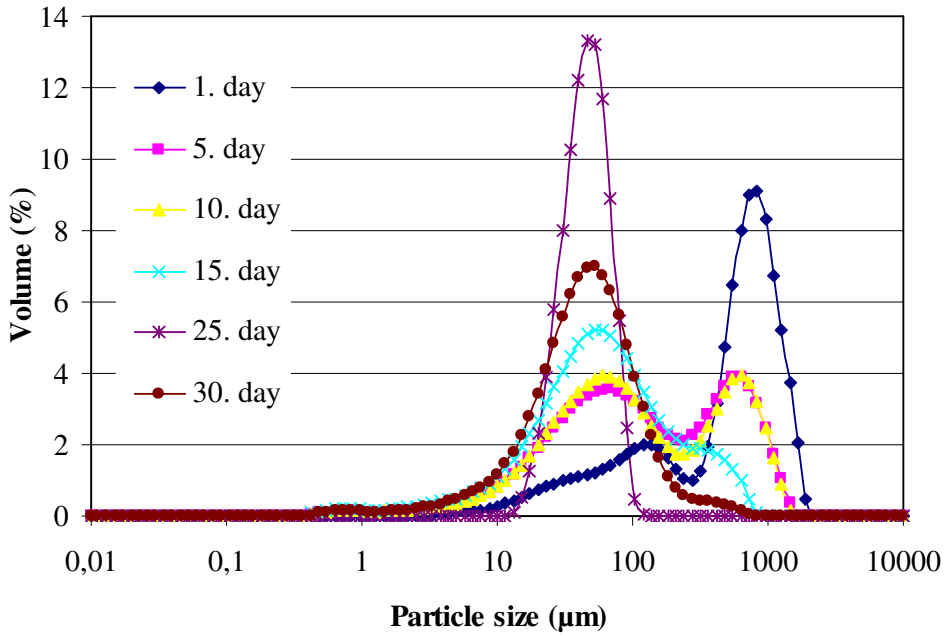


Figure 4.45 Particle size changes in OR_{10} during operation period

Semi batch systems led to higher reductions in particle size comparing batch system, and 5 days and 10 days of sludge retention times gave very similar particle size distributions during the operation period.

4.4.3 Evaluation of Dewatering Performance of Digested Sludge

In anaerobic digestion studies, CST parameter was used for evaluation of filtration characteristics of digested sludge and to see the effect of ozone oxidation on dewatering characteristics of sludge in anaerobic digestion units.

CST variations in reactor contents during the operation period are given in Figure 4.45. For reactors operated as semi batch system, anaerobic digestion improved the filtration characteristics of sludge and CST values decreased with increasing operation time. But ozone oxidation preceding anaerobic digestion had no a significant effect to increase filterability of sludge. Higher CST values were obtained in batch systems comparing to the semi batch systems. In batch system, ozone oxidation caused a little enhances the filterability of sludge.

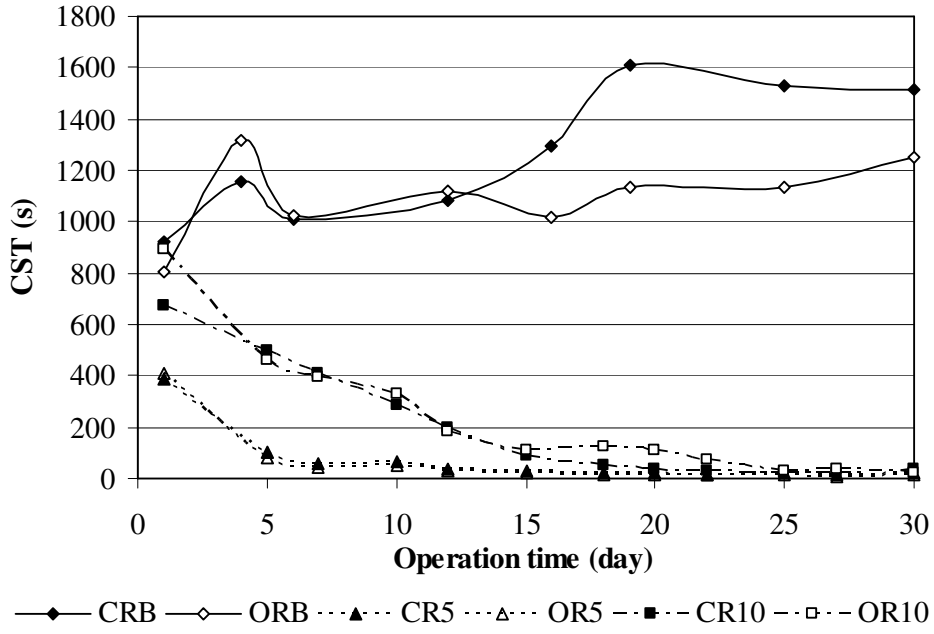


Figure 4.46 CST changes in reactor contents of CR_B, OR_B, CR_5, OR_5, CR_{10}, and OR_{10} during operation period

In anaerobic digestion studies with ozone oxidation, a crown press was used as a simulator of belt filter press for evaluation of dewatering characteristics of digested sludge. The reactor contents were processed regularly through a crown press during the 30 days of operation period.

Table 4.47 shows the final cake solids obtained from crown press application during the operation period in ozone oxidation studies.

Table 4.47 Final cake solids obtained from crown press application during the operation period in ozone oxidation studies

Reactor's code/	Final cake solids, %					
Days	1	5	10	15	20	25
CR_5	14.39	11.18	9.52	9.02	7.51	-
OR_5	13.03	11.36	9.24	-	-	-
CR_{10}	10.21	10.74	10.74	11.13	8.89	7.82
OR_{10}	11.43	11.11	8.92	7.96	-	-

Final cake solids did not improve with operation time for all reactors. In reactors fed with ozonated sludge, it not observed cake formation after 10 days of operation.

Table 4.48 summarized final drainage volume of sludge after 120 sec of filtration in gravity drainage plow simulator kit. Ozone oxidation preceding anaerobic digestion did not significantly affect of drainage rate during 120 sec of filtration. Ozone oxidation before anaerobic digestion led to little increase in drainage rate during 120 sec of filtration in gravity drainage plow simulator kit during the operation period

Table 4.48 Drainage volume after 120 sec of filtration in gravity drainage plow simulator kit during operation period

Reactor's code /	Drainage volume, mL					
Days	1	5	10	15	20	25
CR_5	100	120	160	170	180	180
OR_5	110	175	184	191	195	195
CR_{10}	130	130	140	178	182	180
OR_{10}	100	130	172	188	190	192

4.5 Optimization Study of Ultrasonic Treatment Conditions

Specific energy (SE) was considered as a main variable parameter for evaluation of disintegration performance of sludge. The range of the specific energy (SE) varied from 0 to 15880 kJ/ kg TS. SE was determined by using Eq. 5 given in Chapter 3.2.3. Table 4.49 shows the ultrasonic treatment conditions used in the experiments.

Disintegration degree (Muller, 2000) parameter based on soluble COD calculations (procedure given in Chapter 3.5.1) was considered as the main response for evaluation of biological sludge disintegration. COD, total nitrogen, and total phosphorus concentrations in sludge's supernatant, DOC and protein concentrations were also measured for each experiment to determine the effects of ultrasonic treatment on biological sludge disintegration. A particle size distribution in sludge after ultrasonic treatment was used as another response to evaluate the floc disintegration effect of ultrasonic treatment. In addition, the effect of ultrasonic treatment on solubilization sludge' solids was evaluated with suspended solids and

volatile suspended solids measurements. CST parameter was also monitored for determination of sludge filterability characteristics of sonicated sludge.

Table 4.49 Ultrasonic treatment conditions

Reaction Time (Min)	Ultrasonic Power (Watt)	Specific Energy (kJ kg/ TS)	Power Density (W/ mL)
1	20	112	0.040
5	26	729	0.052
10	32	1794	0.064
15	36.2	3045	0.072
20	39.4	4419	0.079
25	40	5607	0.080
30	40.4	6796	0.081
35	41.2	8086	0.082
40	43.2	9690	0.086
45	44.4	11204	0.089
50	46	12897	0.092
55	46.4	14310	0.093
60	47.2	15880	0.094

4.5.1 Optimization of Ultrasonic Treatment Conditions in terms of Biological Sludge Disintegration

The disintegration degree permits to evaluate the maximum level of sludge solubilization. Increase of DD is determined as the substance that can be readily used to produce methane in the anaerobic digestion (Wang et al., 2005). The disintegration degree of sonicated sludge increased with increasing specific energy in each experiment (Figure 4.47). For specific energy under 1000 kJ/kg TS, disintegration degree was low (14.8 % for 729 kJ/kg TS). This value is similar to those obtained by Bougrier et al., 2005. The maximum disintegration degree of 57.9 % was obtained for specific energy of 9690 kJ/kg TS and reaction time of 40 min. For specific energies above 9690 kJ/kg TS, DD decreased. Decreasing of DD may be explained by high oxidation effects of radicals. Up to 10000 kJ/kg TS, hydroxyl radicals preferentially attack the organic substances and destruct the activated sludge microorganism's cell walls in biomass and oxidized them to dissolved organic substances and these substances released to the liquid phase and increased the DD. For specific energies above 9690 kJ kg/ TS, as SE increases, more soluble organics were mineralized and DD decreased. High ultrasonic energies promote oxidation by

radicals and ultrasound led to mineralization preceding solubilization of sludge. Similar evaluations were reported before in the other studies for a different sludge disintegration method of ozone oxidation (Zhang et al., 2009; Bougrier et al ,2006).

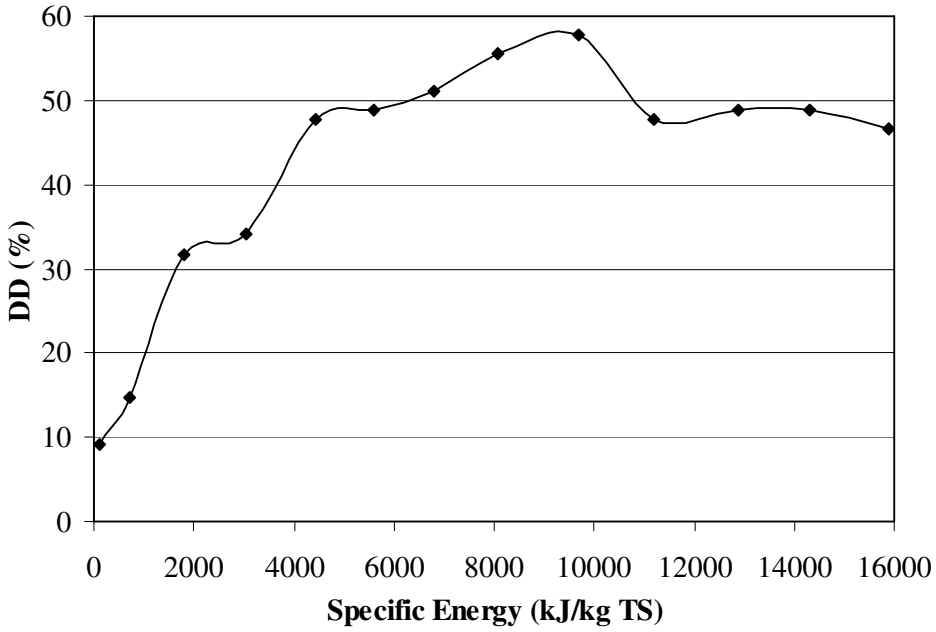


Figure 4.47 Variation of disintegration degree with specific energy

Ultrasonic treatment led to change of physico-chemical characteristics of sludge. For instance, temperature increased almost linearly with increasing specific energy Figure 4.48 presents the variation of pH and temperature with specific energy. Temperature increased from 22°C in raw sludge to 72°C for ultrasonic pre-treated sludge with maximum specific energy input of 15880 kJ kg/ TS. The rise of temperature helps to ultrasonic disintegration. On the other hand, the high increase in temperature leads to higher saturated vapor pressures, which makes it harder for vapor bubbles to collapse and thus decreases the intensity of cavitation[10]. The one of the reasons of decreasing DD above 9690 kJ kg/ TS may be high temperatures. In contrast, pH decreased during ultrasonic pre-treatment (Fig. 4.48). It decreased from 6.95 in raw sludge to 6.16 for ultrasonic pre-treated sludge at 15880 kJ kg/ TS application. Decreasing pH may be explained by acidic compound formation due to

the floc disintegration. Lipids were hydrolyzed to volatile fatty acids and these compounds led to decrease pH.

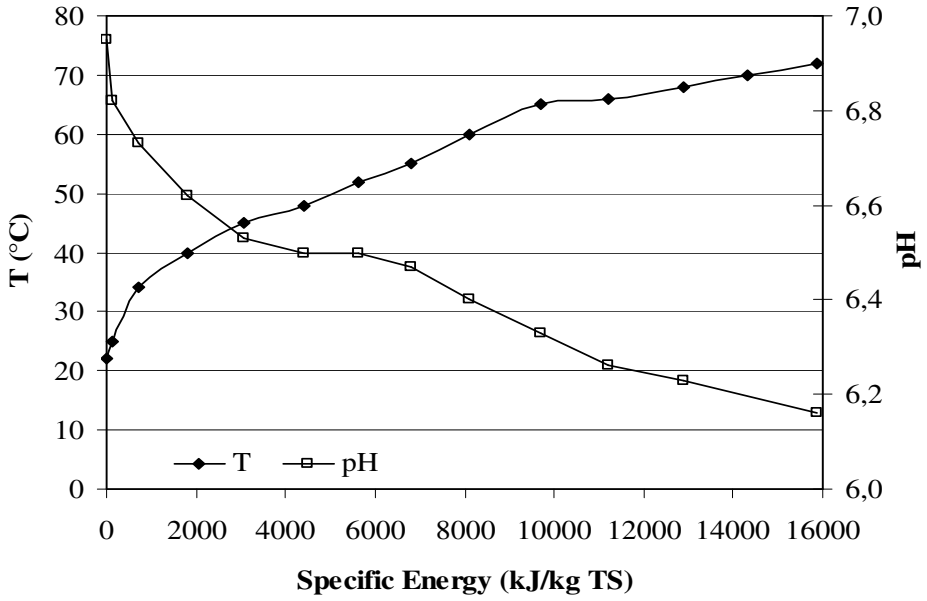


Figure 4.48 Variation of pH and temperature with specific energy

Results of DOC of sludge and SCOD analysis for each experiment are given in Figure 4.49 and 4.50, respectively.

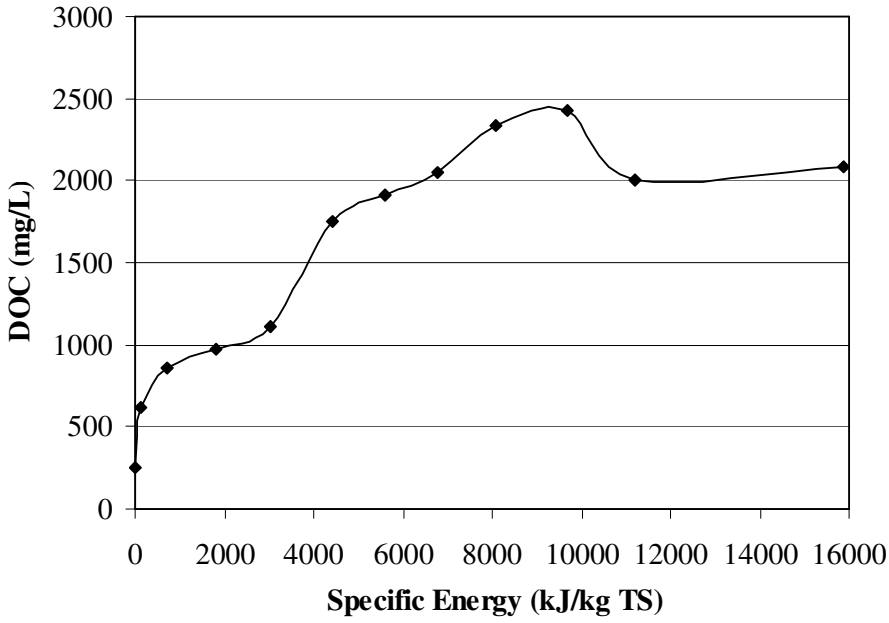


Figure 4.49 Variation of DOC with specific energy

DOC of sludge increased with increasing specific energy. The variation of DOC with specific energy showed very close trend with the variation of DD as shown in Figure 4.47. Very high DOC levels were monitored due to ultrasonic treatment and maximum DOC value of 2426 mg/ L was obtained for specific supplied energy of 9690 kJ/kg TS and reaction time of 40 min. SCOD increased significantly with increasing specific energy, also. Maximum SCOD was achieved for the same specific energy of 9690 kJ/ kg TS and SCOD increased from 1200 mg/ L to 5280 mg L^{-1}. For 9690 kJ/ kg TS, SCOD and DOC in sludge's supernatant increased by 340 % and 860 %, respectively.

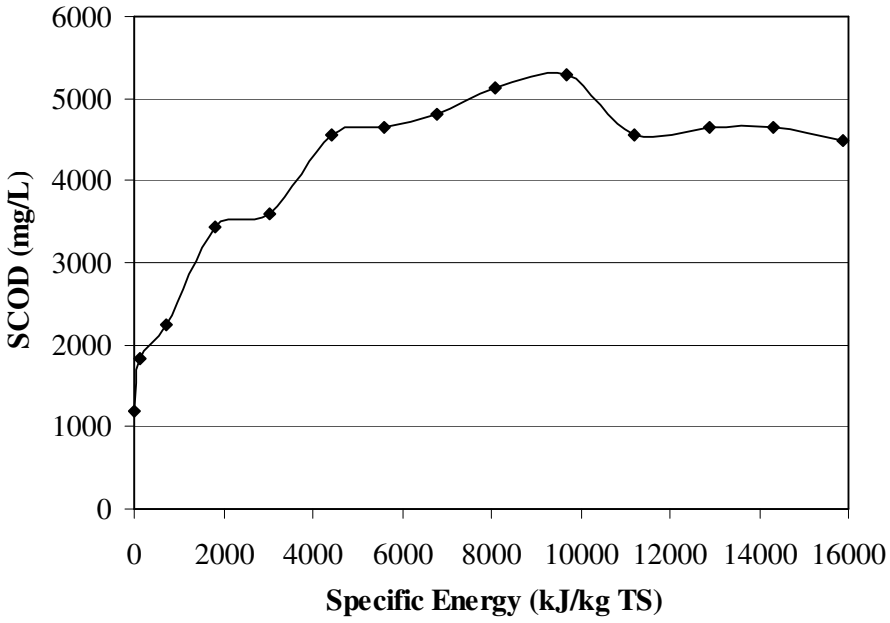


Figure 4.50 Variation of SCOD with specific energy

In fact, it has been reported that the sonication of biological sludge is a multi-stage process (Chu et al., 2001). In the first stage, mechanical forces break down the porous flocs into small particles; in the second stage sonication solubilizes extracellular polymers and causes cell lyses releasing intracellular materials (inactivating the biomass). The transformation of solid-state bound organic compounds into a soluble form could be induced continuously by the elevated bulk temperature during sonication. Therefore, last stage of sonication resulting in decrease in volatile suspended solids further aided by the hydromechanical shear forces and the increase of bulk temperature. Figure 4.51 shows the variation of SS and VSS concentrations with specific energy. Higher decreases in SS and VSS were observed in experiments which specific energy was higher than 8086 kJ/kg TS. Maximum suspended solids solubilization and volatile suspended solids solubilization (these values were calculated using Eq.5 given in Chapter 3.5.7) with ultrasonic treatment were determined as 48.61 % and 46.7 %, respectively for 9690 kJ/kg TS.

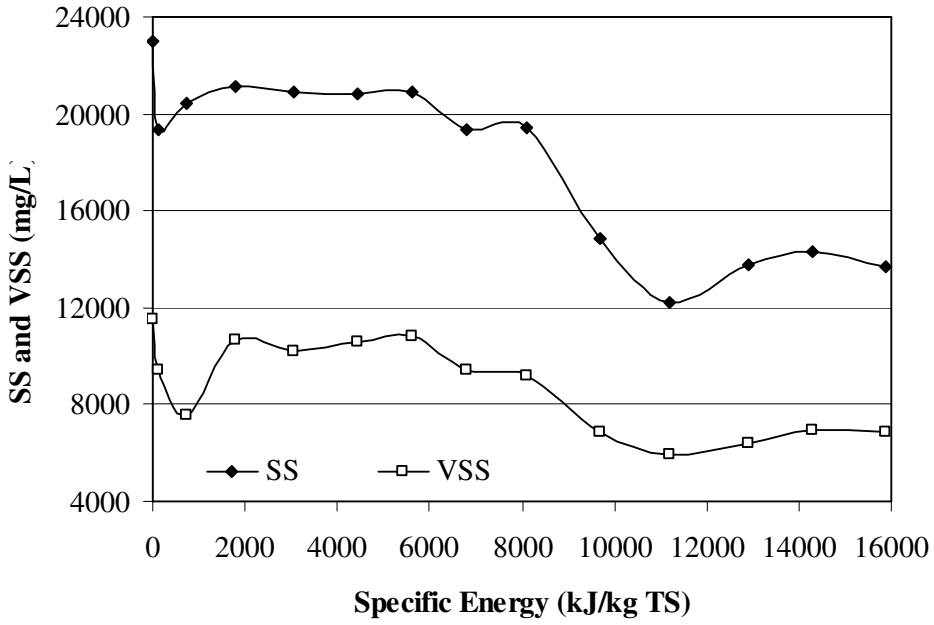
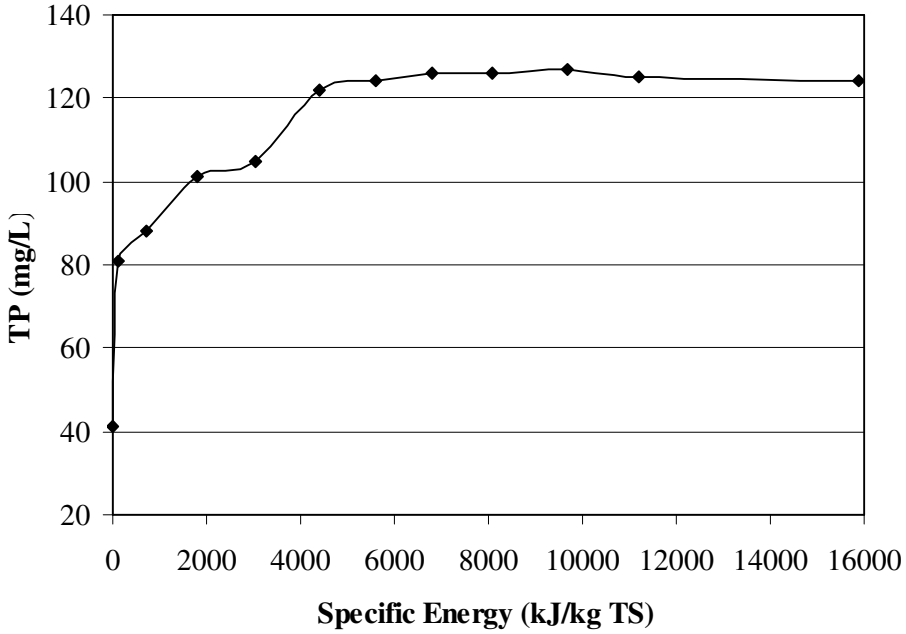
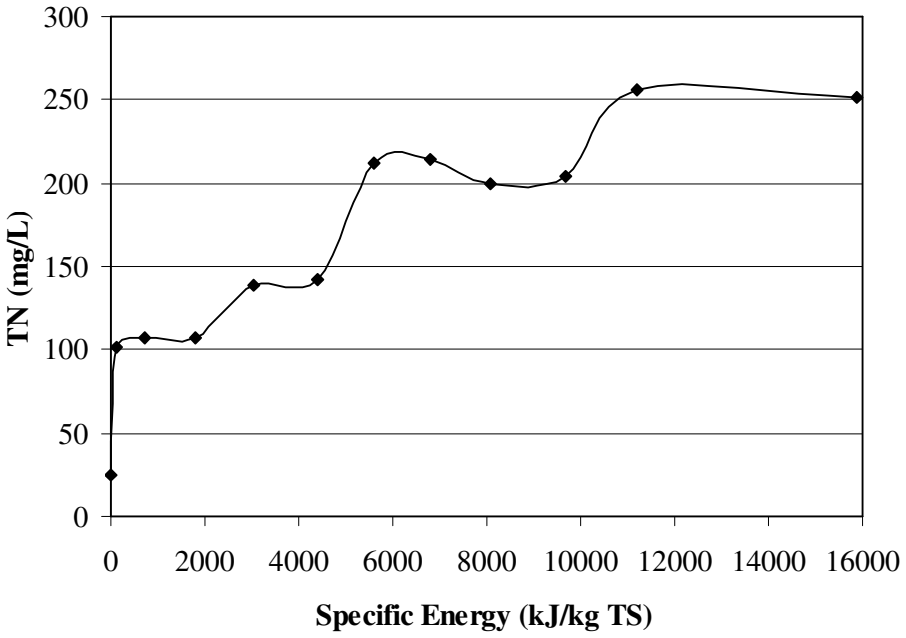


Figure 4.51 Variation of SS and VSS with specific energy

Disintegration causes disruption of microbial cells in the sludge, thereby destroying the cell walls (Vranitzky et al., 2005). The destruction of floc structure and disruption of cells results in the release of organic sludge components into the liquid phase. These components exist in a dissolved phase, e.g. components of intracellular water, or can be liquefied (Muller et al., 2004). Ultrasonic treatment used for the disintegration process was very effective and contributed to the rapid initial increase of nitrogen and phosphorus. Total P and Total N variations with specific energy are given in Figure 4.52 and Figure 4.53, respectively.



4.52 Variation of total phosphorus in sludge's supernatant with specific energy

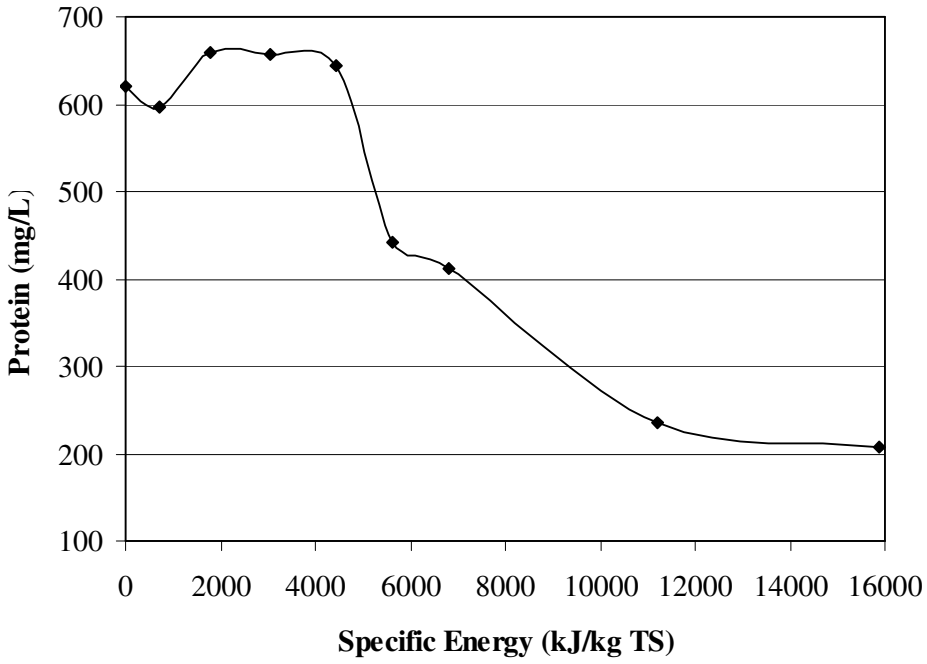


4.53 Variation of total nitrogen in sludge's supernatant with specific energy

Phosphorus released to the sludge supernatant in a few minutes due to ultrasonic pre-treatment, after that it was nearly kept constant. Most of the phosphorus in the

supernatant existed in the form of organic products. Nitrogen concentration in supernatant increased with increasing specific energy. Nitrogen concentration in sludge's supernatant was increased from 25 mg/ L to 256 mg/ L for specific energy of 11204 kJ/kg TS and 45 min of reaction time. For the optimum specific energy (9690 kJ/kg TS) for DD, TN and TP in sludge's supernatant increased by 716% and 207.5%, respectively.

Protein results obtained from ultrasonic treatment experiments are depicted in Figure 4.54. A little increase in protein content was observed up to 4419 kJ/kg TS, after than protein concentration decreased with increasing specific energy. Ultrasonic treatment enhanced the degradation of protein content of sludge. The main purpose of disintegration is the elimination of hydrolysis step to accelerate the anaerobic degradation. Results show that protein hydrolysis was performed successfully by ultrasonic treatment even at very low ultrasonic density levels (lower than 0.1 W/ mL).



4.54 Variation of protein with specific energy

The reduction in particle size generally allows an easier hydrolysis of solids within the sludge due to larger surface areas in relation to the particle volumes. The

result is an accelerated and enhanced degradation of the organic fraction of the solid phase (Muller et al., 2003). So, reduction in particle size is an important parameter for floc disintegration. Table 4.49 shows the particle size changes for different specific energies. Particle size distributions reported in Figure 4.55 were also indicated floc disintegration.

Table 4.49 Particle size changes for different specific energies

Specific energy (kJ/ kg TS)	Particle size (µm)				
	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
0	16.155	107.822	8.010	45.230	265.591
112	12.426	98.091	6.011	36.879	261.668
1794	9.787	73.467	4.647	29.944	191.988
5607	9.583	63.571	4.744	24.407	197.345
9690	8.142	40.644	4.064	18.070	110.642
11204	4.768	47.360	1.858	13.303	121.986
15880	5.867	48.052	2.592	15.561	121.807

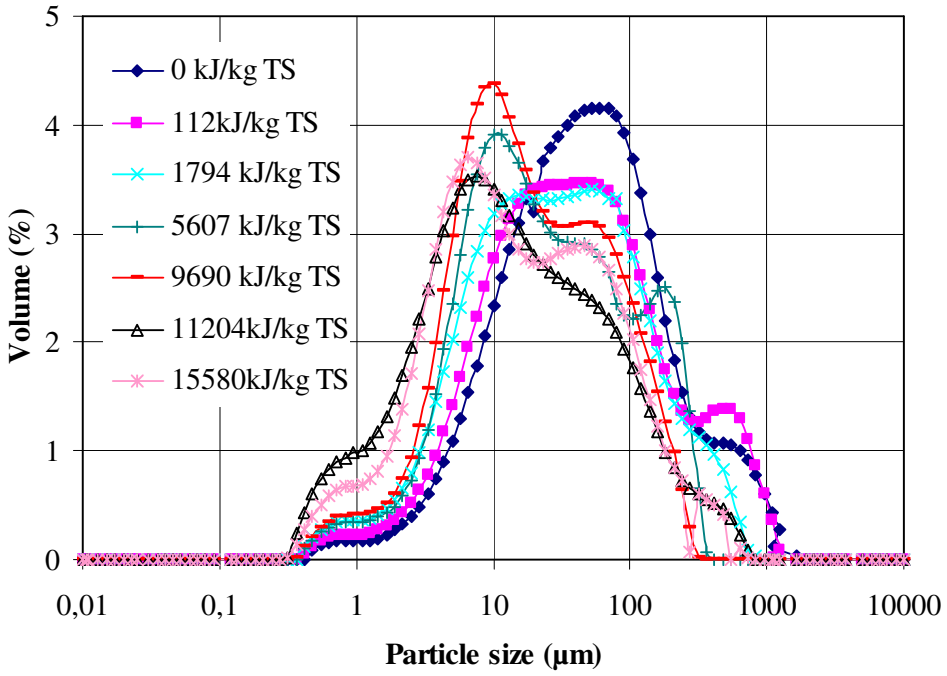


Figure 4.55 Variation of particle size distribution for different specific energies

Particle size in sludge reduced due to ultrasonic treatment and higher reductions were obtained in ultrasonically treated sludge with high specific energies comparing to that in raw sludge. The highest reduction was observed in ultrasonic pre-treated sludge with specific energy of 9690 kJ/kg TS and 62 % of particle size reduction was recorded based on volume weighted mean (D(4.3)). Two peaks were observed especially in raw sludge and ultrasonically treated sludge with low specific energy (Fig.4.55). Second peak could be explained by a re-flocculation phenomenon. Similar results were achieved by Bougrier et al (2005). This re-flocculation was obtained especially due to the release of intracellular or extra-cellular material and second peak was decreased with increasing specific energy.

4.5.2 The Effect of Ozone Oxidation on Dewaterability of Biological Sludge

CST used to evaluate the filterability of sludge. CST variations versus applied specific energy are given in Figure 4.56.

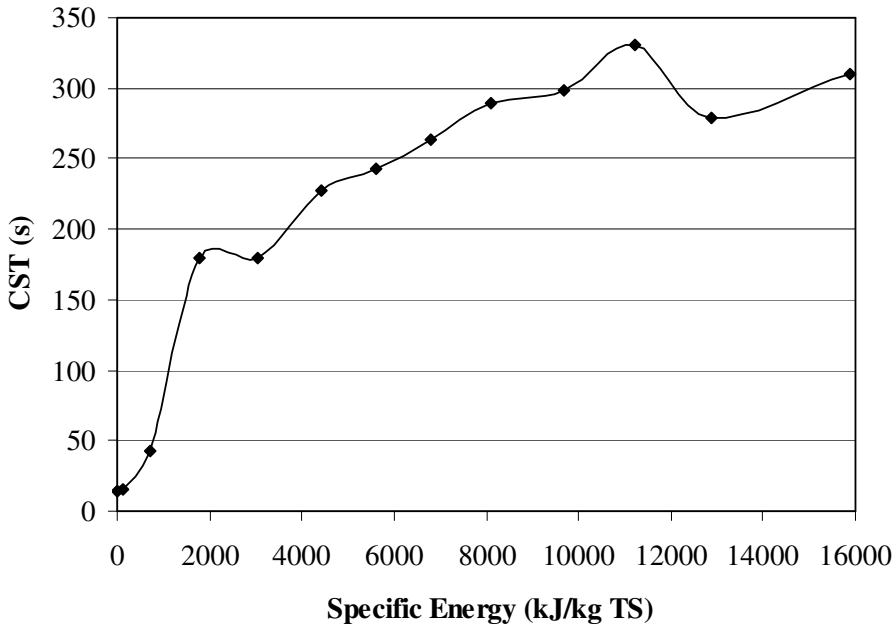


Figure 4.56 Variation of CST with specific energy

CST gradually increased with increasing specific energy. CST results showed that ultrasonic treatment deteriorates the filterability of biological sludge.

4.6 Anaerobic Digestion Study with Ultrasonic Treatment

After optimization study of ultrasonic treatment conditions for biological sludge disintegration, sludge digestion studies were carried out for raw sludge and sonicated sludge. 9690 kJ/kg TS specific energy achieved at the highest DD was chosen as the optimum for biological sludge disintegration. So, 9690 kJ/kg TS of specific energy were applied to sludge preceding anaerobic digestion.

Sludge digestion studies were carried out using two 8.5 L anaerobic reactors. Reactors were operated at 37 ± 2 °C in mesophilic conditions for 30 days of operation period. Reactors operated as batch and semi-batch systems in order to determine optimum operation condition. Different sludge retention times as 5 and 10 days were applied during the operation in order to determine optimum retention time. Sludge digestion procedure was given in detail in Chapter 3.4.

Reactors used anaerobic digestion studies with ultrasonic disintegration were coded according to sludge retention times and presence of ultrasonic application. Control reactors fed with raw sludge were coded as CR_B, CR_5, CR_{10}. Reactors fed with sonicated sludge were coded as UR_B, UR_5, UR_{10} and subscripts in here represents the sludge retention times. Reactor's codes used anaerobic digestion studies with ozone oxidation are given in Table 4.50.

Table 4.50 Reactor's codes used anaerobic digestion studies with ultrasonic treatment

Reactor's code	Ultrasonic treatment	Sludge retention time
CR_B	No applied	Batch operation
UR_B	Applied	Batch operation
CR_5	No applied	5 days
UR_5	Applied	5 days
CR_{10}	No applied	10 days
UR_{10}	Applied	10 days

4.6.1 Control of Anaerobic Digesters Stability

In anaerobic digestion studies with ultrasonic disintegration, pH and temperature parameters were monitored daily while alkalinity and volatile fatty acids (VFA) parameters were analyzed regularly to control anaerobic digester stability.

Temperature was kept at 37 ± 2 °C for all reactors and temperature changes in reactors were given in Figure 4.57. pH values given in Figure 4.58 varied from 7.20 to 8.70 in reactors.

In anerobic digestion studies with ultrasonic treatment, total alkalinity values were measured regularly as a measure of the stability of the digestion unit. An alkalinity range of 1700 – 4920 mg $CaCO_3$/ L were measured during the operation period (Figure 4.59). Especially for semi batch systems, high alkalinity values were recorded in the first operation day and then values decreased and much closed values were observed after 10 days of operation.

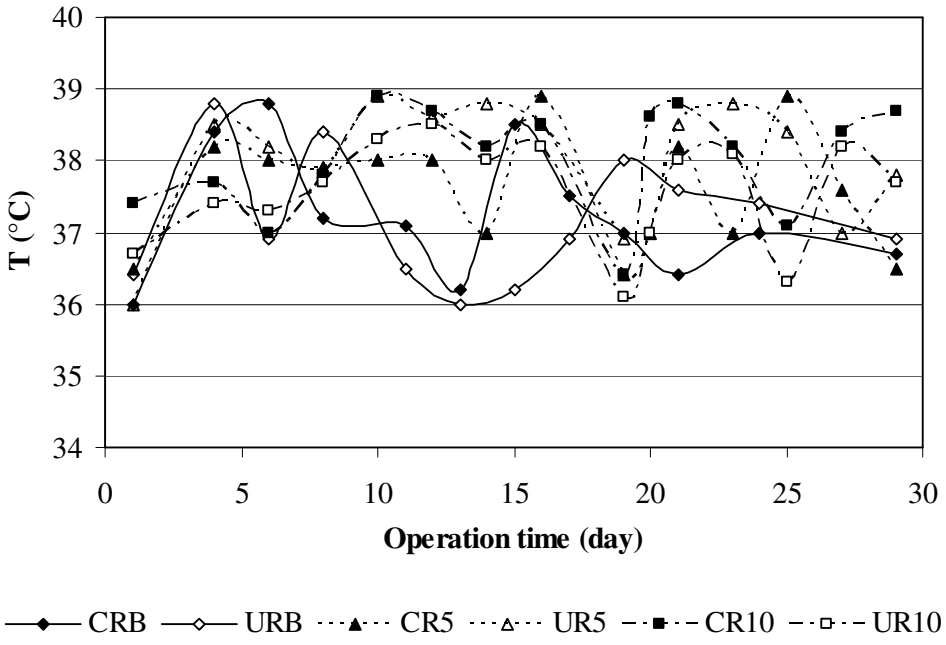


Figure 4.57 Temperature changes in reactor contents of CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} during the operation

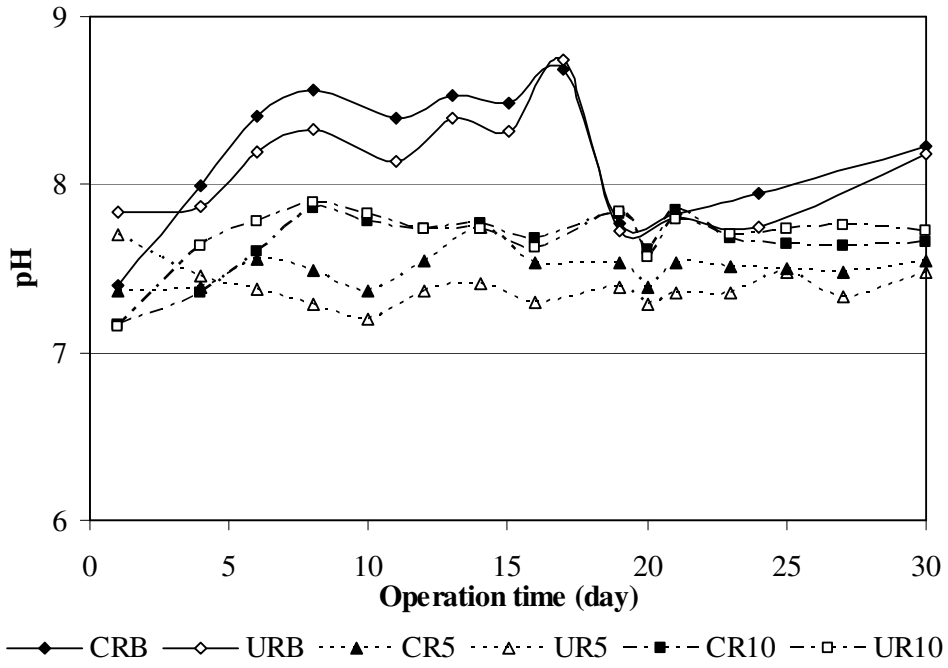


Figure 4.58 pH changes in reactor contents of CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} during the operation

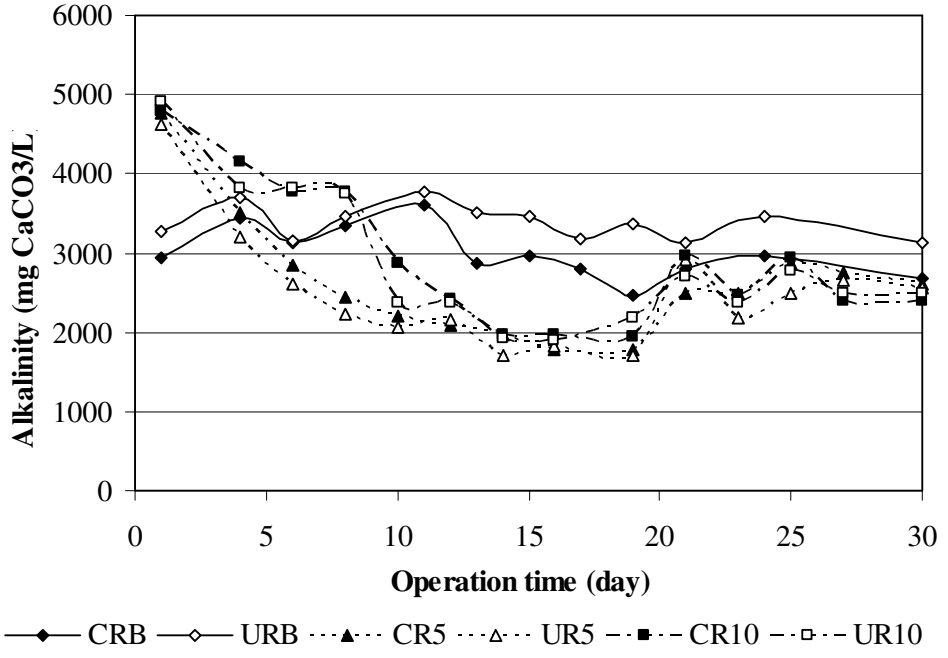


Figure 4.59 Total alkalinity changes in reactor contents of CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} during the operation

VFA content was also checked for reactor stability and results are given in Table 4.51. VFA values above 1000- 1500 mg/L were not recommended for anaerobic methogens (Malina & Pohland, 1992). VFA values did not exceed recommended range even first operation days in batch systems. In semi batch systems, especially in reactors fed with sonicated sludge, VFA values exceed the 1500 mg/L in the first operation day, after that the values were decreased with increasing operation time.

Table 4.51 VFA (Lactic acid, Lc/ Acetic acid, Ac/ Propionic acid, Prc) changes in reactor contents of CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} during operation period

Days	**1**			**4**			**8**			**15**			**24**		
Reactor's code	Lc	Ac	Prc	Lc	Ac	Prc	Lc	Ac	Prc	Lc	Ac	Prc	Lc	Ac	Prc
CR_B	0	0	0	0	1131	373	0	107	90	0	1320	215	0	830	237
UR_B	0	0	0	0	1567	735	0	214	0	0	1467	442	0	1350	164
CR_5	0	2610	488	0	1234	303	0	0	0	0	0	0	0	228	0
UR_5	0	1510	281	0	1273	253	0	0	0	0	0	0	0	199	0
CR_{10}	0	1522	120	0	1460	362	1418	272	0	0	968	142	0	272	0
UR_{10}	0	2115	592	0	1515	405	0	819	137	0	1249	0	0	319	0

4.6.2 Evaluation of Anaerobic Digestion Performance of Sludge

For evaluations of anaerobic digestion performance of sludge, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), protein content, particle size distribution, and gas composition in the biogas (CH_4, CO, CO_2, H_2S) were analyzed during the operation period.

In anaerobic digestion studies with ultrasonic treatment, total solids changes during the operation period are given in Figure 4. 60.

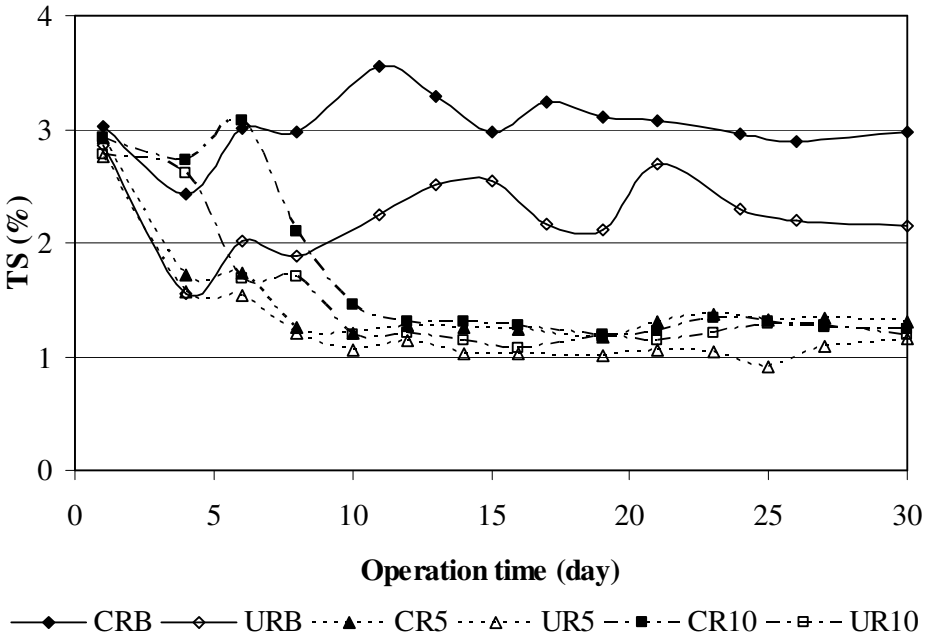


Figure 4.60 Total solids changes in reactor contents of CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} during operation period

Total solids concentrations varied between 1.6 % and 3 % for reactors operated as batch system while those ranged from 0.9 % and 2.9 % for reactors operated with 5 and 10 days of sludge retention times. At the end of the operation period percent decreases in TS in reactor contents according to the first operation day was calculated as 1.7 %, 25 %, 55.6 %, 58 %, 57.5 %, and 57.2 % for CR_B, UR_B, CR_5,

UR_5, CR_{10}, and UR_{10}, respectively. In control reactor operated as batch system (CR_B), it was not observed a significant change in total solids content of the reactors.

In reactor operated as control and fed with sonicated sludge (UR_B), lower decreases were obtained than those reactors operated as semi batch system and fed with sonicated sludge. In other words, lower TS values were obtained in UR_5 and UR_{10} than those in UR_B. TS values decreased drastically especially during the first ten days for these reactors. Minimum TS values were obtained in reactor coded as UR_5. Ultrasonic disintegration preceding anaerobic digestion affected positively TS reduction. It facilitated sludge minimization.

In anaerobic digestion studies with ultrasonic treatment, volatile solids measurement results are given in Figure 4.61.

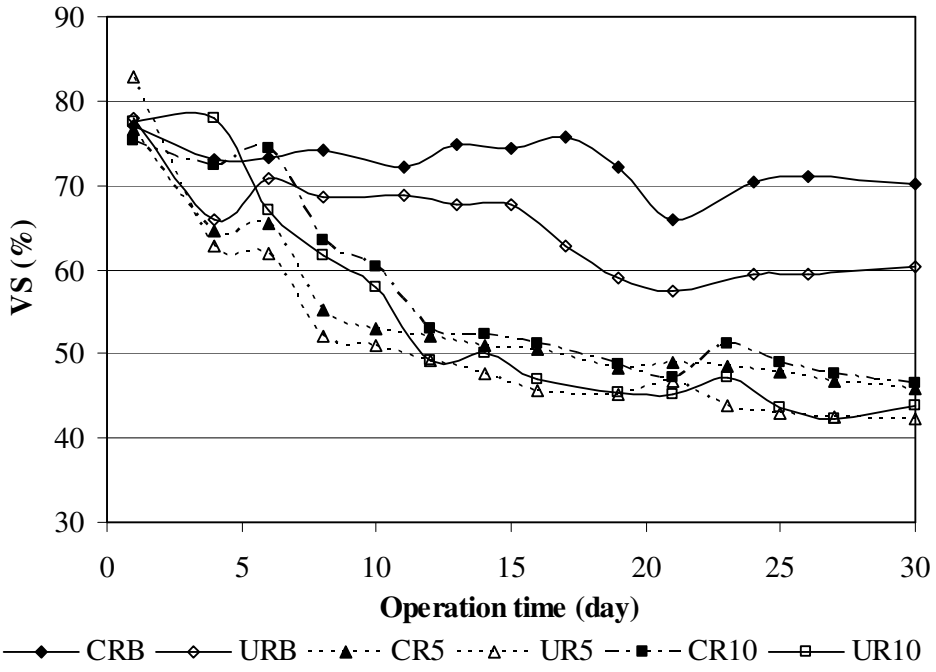


Figure 4.61 Volatile solids changes in reactor contents of CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} during operation period

Anaerobic digestion led to decrease volatile solids in sludge. Lower VS values for reactors operated with 5 and 10 days sludge retention times than those in batch reactors were obtained. VS concentrations in reactors fed with sonicated sludge were

lower than those in control reactors for all sludge retention times. The highest reductions in VS were obtained in reactor coded as UR_5 while the lowest reductions in VS were observed in reactor coded as CR_B. In UR_5 % 49 decrease in VS was observed at the end of the operation comparing to first operation day. The reduction ratio was calculated as 40 % in CR_5. Ultrasonic disintegration preceding anaerobic digestion facilitated high stabilization degree in biological sludge.

Figure 4.62 and Figure 4.63 demonstrates the changes of SS and VSS as a function of operation time, respectively in anaerobic digestion studies with ultrasonic treatment.

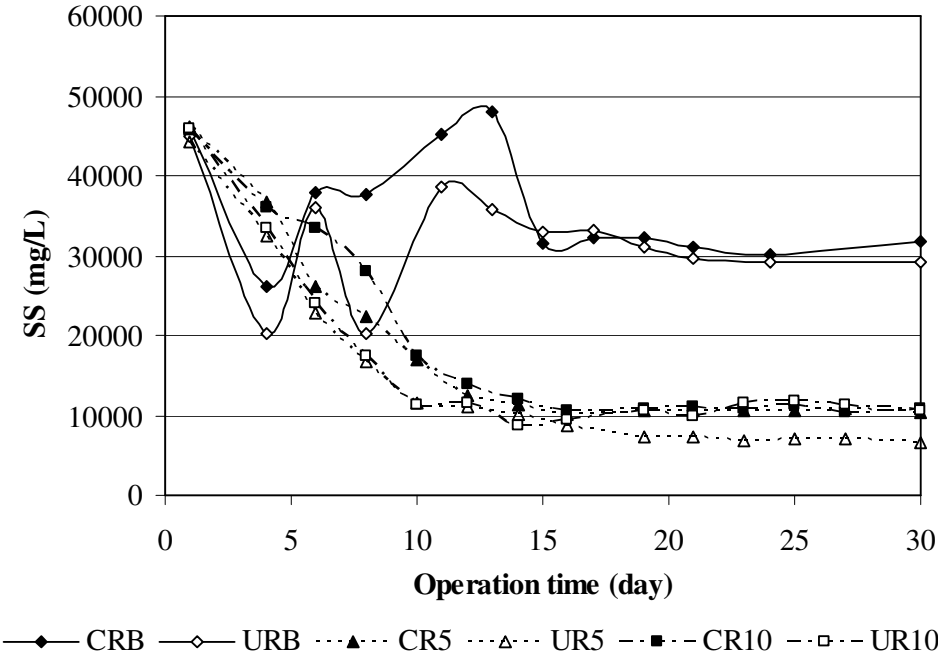


Figure 4.62 Suspended solids changes in reactor contents of CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} during operation period

SS and VSS decreased quickly especially in first week of operation period in reactors operated as semi batch system. After ten days of operation SS and VSS had no change significantly and nearly same values of SS and VSS were observed for 5 and 10 days of SRT. At the end of the first operation day, SS value for CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} was determined as 45800 mg/L, 44900 mg/L, 46200

mg/L, 44300 mg/L, 45700 mg/L, and 46000 mg/L, respectively. The value was 31750 mg/L, 29150 mg/L, 10400 mg/L, 6550 mg/L, 10900 mg/L, and 10700 mg/L at the end of the operation period for CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10}, respectively.

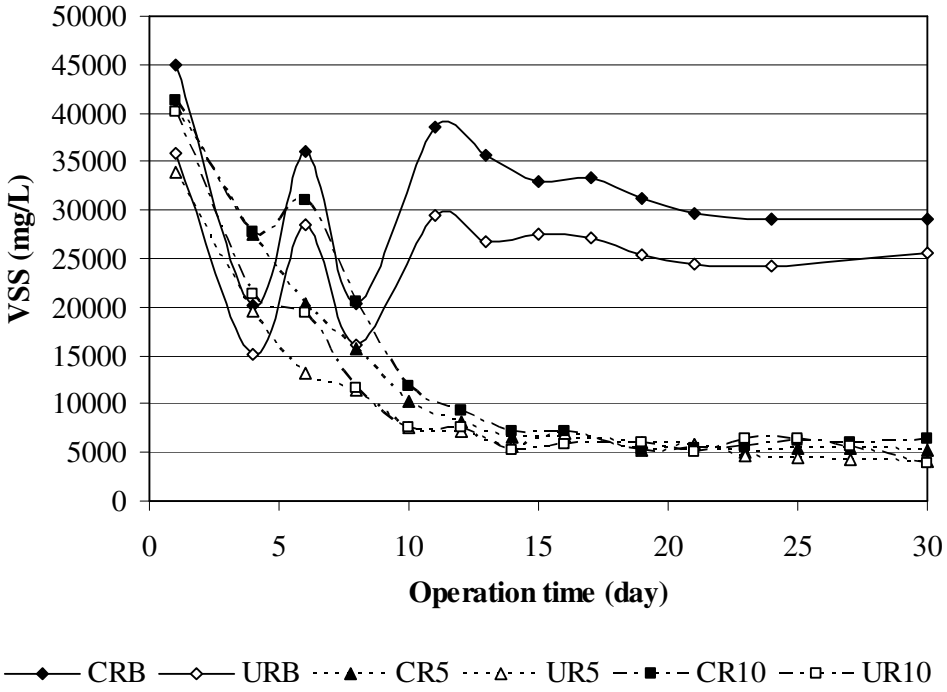


Figure 4.63 Volatile suspended solids changes in reactor contents of CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} during operation period

At the end of the first operation day, VSS value for CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} was determined as 44900 mg/L, 35920 mg/L, 40600 mg/L, 33900 mg/L, 41300 mg/L, and 40200 mg/L, respectively. The value was 29150 mg/L, 25500 mg/L, 5150 mg/L, 4050 mg/L, 6300 mg/L, and 3900 mg/L at the end of the operation period for CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10}, respectively.

Higher reductions in SS and VSS were observed in reactors fed with ultrasonically pre-treated sludge than in control reactors. The lowest SS and VSS were achieved in reactor coded as UR_5. Minimum SS value of 6550 mg/L was achieved at 30^{th} of operation period, while the value was 44300 at the end of first operation day. SS reduction was recorded as 85 % in 30^{th} of operation. The reduction

ratio for VSS was calculated as 89 %. Based on these results it was suggested that the ultrasonic disintegration was effective in improving sludge's solids reduction.

Table 4.52 and Table 4.53 show the CH_4/ CO_2/ H_2S / CO gas composition in CR_B and UR_B, respectively during operation period. For batch systems methane gas and total gas were decreasing during the operation period.

Table 4.52 CH_4/ CO_2/ H_2S / CO gas composition in CR_B during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	27	2	29	2
4	13	1.4	1	0
6	38	1.4	0	0
11	25	1.2	5	11
13	24	0.6	1	0
15	10	1.4	5	0
17	8	0.8	3	0
19	2	0.6	4	3
21	0	0.6	7	5
25	0	0	0	0
30	0	0.4	1	0

Reactor fed with sonicated sludge (UR_B) gave higher methane gas production comparing to the control one (CR_B). Although, H_2S concentrations in UR_B were higher than in CR_B, H_2S values were lower than toxic level (100 ppm) for methanogens during the operation period for both CR_B and UR_B.

Table 4.53 CH_4/ CO_2/ H_2S / CO gas composition in UR_B during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	>100	3.6	12	0
4	72	5.4	42	18
6	49	3.4	12	5
11	29	4.6	43	19
13	16	2.6	5	6
15	12	3.4	0	0
17	4	1.8	0	0
19	5	3.4	0	0
21	4	2.6	0	0
25	0	6	0	0
30	0	1.2	0	0

Table 4.54 and Table 4.55 show the CH_4/ CO_2/ H_2S / CO gas composition in CR_5 and UR_5, respectively during operation period. Reactor fed with sonicated sludge (UR_5) gave higher methane gas and carbon dioxide production comparing to the control one (CR_5).

Table 4.54 CH_4/ CO_2/ H_2S / CO gas composition in CR_5 during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	25	0.0	32.0	0.0
3	18	2.0	14.0	7.0
6	28	2.8	3.0	0.0
8	31	1.6	0.0	0.0
10	38	3.4	1.0	0.0
12	43	2.0	4.0	0.0
14	30	3.0	0.0	0.0
16	28	2.0	2.0	0.0
19	33	1.8	9.0	0.0
21	37	2.8	0.0	0.0
23	29	2.2	0.0	0.0
25	36	2.4	0.0	0.0
30	32	3.2	0.0	0.0

In the first two days of operation, CH_4 concentrations was recorded above 100 ppm, then values decreased and were stable approximately 48 % Lel after 10 days operation for UR_5. In CR_5, methane gas values were much closed for each operation day and the average value was calculated as 31 % Lel.

Table 4.55 CH_4/ CO_2/ H_2S / CO gas composition in UR_5 during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	>100	4.2	38.0	8.0
3	>100	7.4	48.0	17.0
6	79	4.6	39.0	9.0
8	69	3.6	3.0	0.0
10	65	6.8	0.0	0.0
12	55	6.8	0.0	0.0
14	49	8.4	0.0	0.0
16	47	9.0	0.0	0.0
19	45	5.8	0.0	0.0
21	48	8.6	0.0	0.0
23	46	5.2	0.0	0.0
25	59	1.8	4.0	0.0
30	54	6.8	9.0	3.0

Table 4.56 and Table 4.57 show the CH_4/ CO_2/ H_2S / CO gas composition in CR_{10} and UR_{10}, respectively during operation period.

Table 4.56 CH_4/ CO_2/ H_2S / CO gas composition in CR_{10} during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	28	2	13	0
3	14	1.8	8	0
6	30	1.8	0	0
8	28	2.2	0	0
10	30	2.2	0	0
12	39	1.6	3	0
14	28	1.8	3	0
16	25	1.6	2	0
19	29	0.8	0	0
21	35	2	0	0
23	28	1.2	2	0
25	32	8.8	7	5
30	29	1.8	0	0

Reactor fed with sonicated sludge (UR_{10}) gave higher methane gas and carbondioxide production comparing to the control one (CR_{10}). In the first operation day, CH_4 concentrations was recorded as 96 ppm, then values decreased with increasing operation time and very closed values (approximately 44 % Lel) were observed after 10 days operation for UR_{10}. In CR_{10}, methane gas values were much closed for each operation day and the average value was calculated as 29 % Lel.

Table 4.57 CH_4/ CO_2/ H_2S / CO gas composition in UR_{10} during operation period

Days	CH_4 (% Lel)	CO_2 (%)	H_2S (ppm)	CO (ppm)
1	96	3.4	26.0	5.0
3	78	2.0	80	2.0
6	62	2.0	2	0.0
8	56	1.6	0	0.0
10	55	1.2	0	0.0
12	49	1.2	3	0.0
14	46	1.0	3	0.0
16	38	1.4	2	0.0
19	48	0.0	0.0	0.0
21	42	2.0	2.0	0.0
23	49	1.8	7.0	0.0
25	36	4.0	3.0	0.0
30	46	0.6	0.0	0.0

The protein results obtained in anaerobic digestion study with ultrasonic treatment are depicted in Figure 4.64. Protein concentrations of reactor contents decreased with operation time in all reactors, hence anaerobic digestion led to decrease in protein content of sludge. Reduction in protein content according to the first operation day was 82 %, 85.2 %, 87 %, 91 %, 86.7 %, and 88.2 % for CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10}, respectively at the end of the operation period.

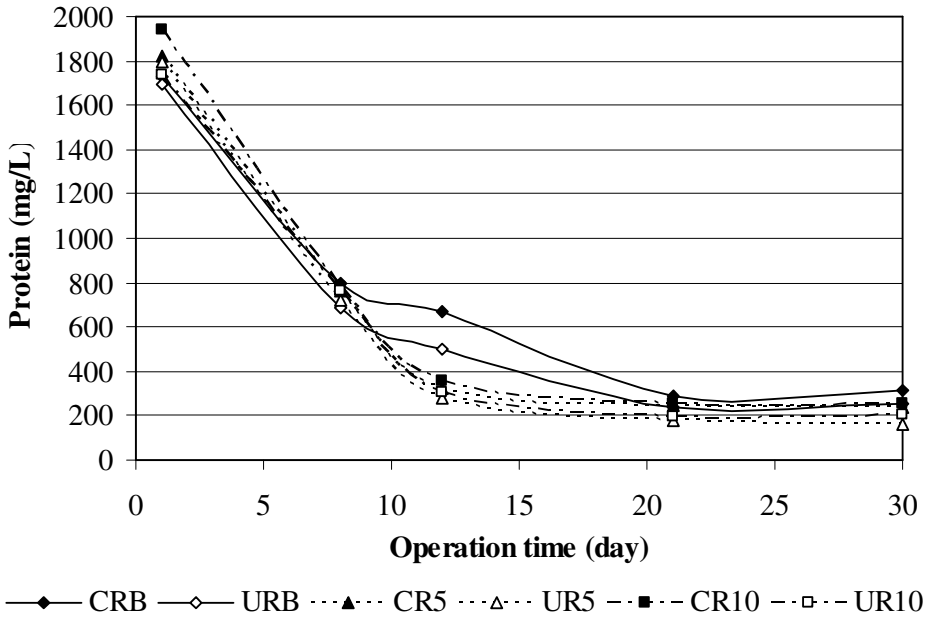


Figure 4.64 Protein changes in reactor contents of CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} during operation period

Higher reductions were observed reactors fed with sonicated sludge comparing the control ones. The highest reductions were observed in reactors fed with sonicated sludge and operated with 5 days sludge retention time (coded as UR_5). On the other hand, in semi batch systems, protein degradation carried out in a shorter time comparing to the batch systems. Protein values were much closed to each other for all reactors after 20 days of operation.

Table 4.39 and Figure 4.40 show the particle size results in control reactor operated as batch system during the operation period. Particle size had no change

significantly during the operation time and disintegration was not observed in reactor coded as CR_B.

Table 4.58 and Figure 4.65 show the particle size results in control reactor operated as batch system during the operation period. Particle size had no change significantly during the operation time and disintegration was not observed in reactor coded as CR_B. First operation day high values of particle size were observed. Then values decreased. Particle size (based on D (4.3)) had no change significantly after ten days of operation in reactor coded as CR_B.

Table 4.58 Particle size changes in CR_B during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	95.891	504.503	39.456	417.726	1152.507
5	90.387	523.160	37.002	419.152	1224.172
10	86.668	517.926	37.018	422.070	1205.669
15	66.979	423.620	36.755	304.429	1002.544
30	51.765	424.737	30.255	296.407	1026.627

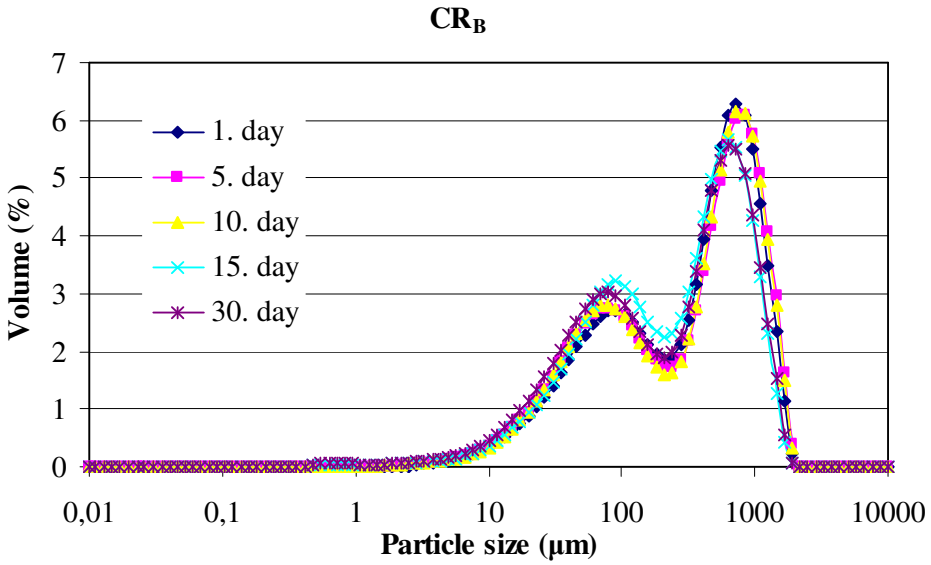


Figure 4.65 Particle size changes in CR_B during operation period

Table 4.59 and Figure 4.66 show the particle size results in reactor fed with sonicated sludge and operated as batch system during the operation period. Particle size (based on volume weighted mean) had no significantly change during first few days for

reactor coded as UR_B, after that values decreased, and highest reductions of particle size were obtained at the end of 30 day operation time.

Table 4.59 Particle size changes in UR_B during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	113.126	567.414	49.116	522.992	1189.777
5	67.663	527.012	43.541	451.462	1173.094
10	42.172	512.116	21.952	437.481	1187.672
15	41.985	466.166	28.208	341.961	1118.176
30	35.966	234.294	27.444	207.973	492.682

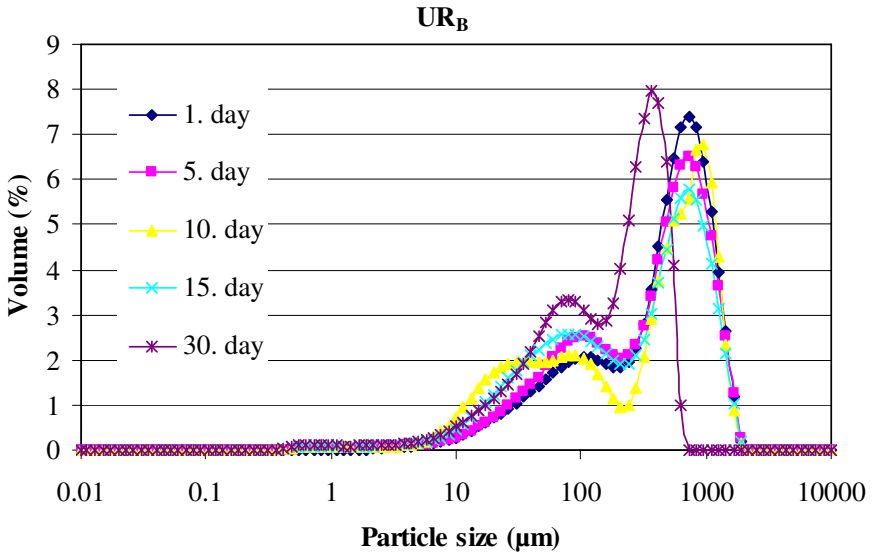


Figure 4.66 Particle size changes in UR_B during operation period

Table 4.59 and Figure 4.66 show the particle size results in CR_5. Particle size decreased within first days of operation, then similar particle size results were obtained for each day.

Table 4.60 Particle size changes in CR_5 during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	104.226	636.451	39.202	605.392	1384.721
5	20.905	70.357	15.250	49.842	124.108
15	23.310	183.569	16.427	54.052	788.552
20	25.755	433.858	16.708	67.602	1441.441
30	21.520	141.016	14.318	48.794	181.983

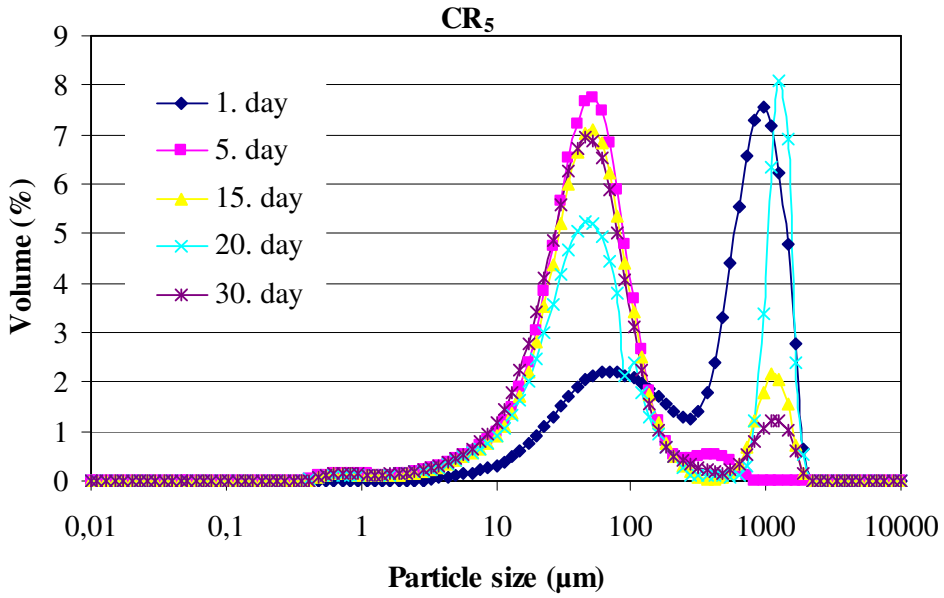


Figure 4.67 Particle size changes in CR_5 during operation period

Particle size changes in reactor coded as UR_5 with operation time are given in Table 4.61 and Figure 4.68. Particle size in the first operation day was recorded as 602.159 µm and the value was 31.180 µm at the end of the operation period, particle size reduced approoximately 95 % in UR_5. Higher reduction in particle size was obtained for UR_5 comparing with control one (CR_5). Ultrasonic disintegration preceding anaerobic digestion led to higher reductions in particle size comparing the classical anaerobic digestion.

Table 4.61 Particle size changes in UR_5 during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	75.216	602.159	25.822	582.124	1333.156
5	34.831	448.763	18.837	171.087	1233.077
15	12.827	39.847	11.111	28.300	39.847
20	14.223	38.691	11.697	29.179	64.379
30	11.080	31.180	9.112	24.138	59.284

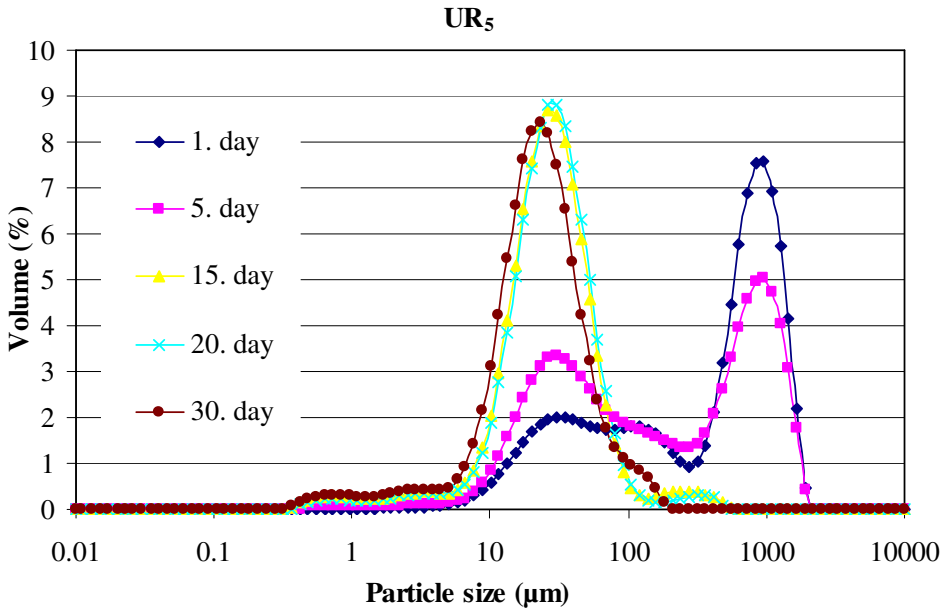


Figure 4.68Particle size changes in UR_5 during operation period

Particle size changes in reactor coded as CR_{10} with operation time are given in Table 4.62 and Figure 4.69. Particle size decreased with increasing operation period. Higher reduction in particle size was observed in CR_{10} than those in control reactor operated as batch system. In addition, for CR_{10} very closed reductions were observed with control reactor operated with 5 days of sludge retention time.

Table 4.62 Particle size changes in CR_{10} during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	67.703	489.610	29.150	204.705	1287.086
5	58.671	287.301	28.151	222.887	621.439
15	24.293	109.219	16.986	17.495	52.94
25	24.116	74.125	17.495	52.94	129.29
30	18.814	60.004	14.293	48.099	111.930

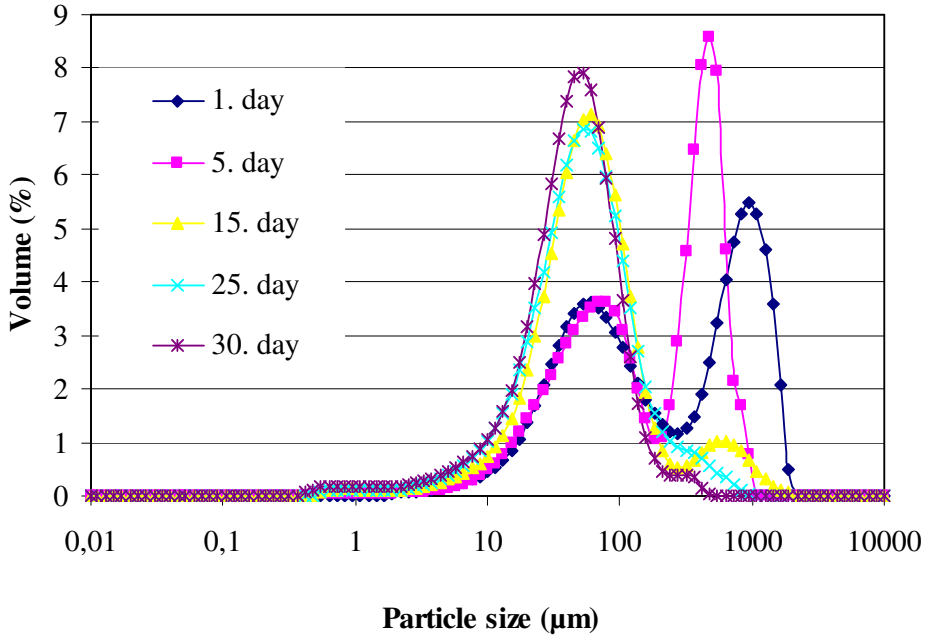


Figure 4.69 Particle size changes in CR_{10} during operation period

Particle size changes in reactor coded as UR_{10} with operation time are given in Table 4.63 and Figure 4.70. Particle size in the first operation day was recorded as 376.989 µm and the value was 45.825 µm at the end of the operation period, particle size reduced approximately 88 % in UR_{10} (reduction ratios were calculated based on D (4.3)). The reduction ratio was calculated as much closed value of 88.7 % for CR_{10}. On the other hand, semi batch systems led to higher reductions in particle size comparing batch system, and 5 days and 10 days of sludge retention times gave very similar particle size distributions during the operation period.

Table 4.63 Particle size changes in UR_{10} during the operation period

Days	Surface weighted mean D(3.2)	Volume weighted mean D(4.3)	d (0.1)	d (0.5)	d (0.9)
1	41.051	376.989	22.048	268.233	959.289
5	29.044	500.605	17.499	159.698	1362.881
15	11.080	31.180	9.112	24.138	59.284
20	12.048	159.946	8.953	26.524	765.910
30	11.308	45.825	8.605	23.547	70.459

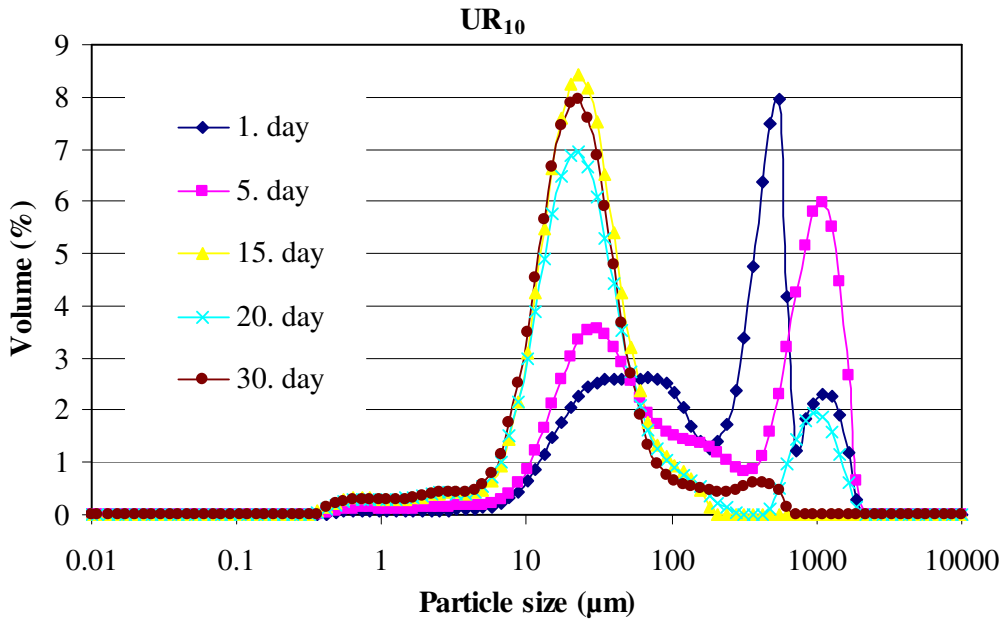


Figure 4.70 Particle size changes in UR_{10} during operation period

4.6.3 Evaluation of Dewatering Performance of Digested Sludge

In anaerobic digestion studies, CST parameter was used for evaluation of filtration characteristics of digested sludge and to see the effect of ultrasonic treatment on dewatering characteristics of sludge in anaerobic digestion units.

CST variations during the operation period are given in Figure in Figure 4.71. For all reactors, CST values were decreased with increasing operation time. Anaerobic digestion increased the filterability characteristics of sludge. Higher CST values were obtained in batch systems comparing to the semi batch systems. In batch systems, ultrasonic disintegration enhanced the filterability of sludge. It was not observed the positive effect of ultrasonic disintegration on sludge filterability in semi batch systems.

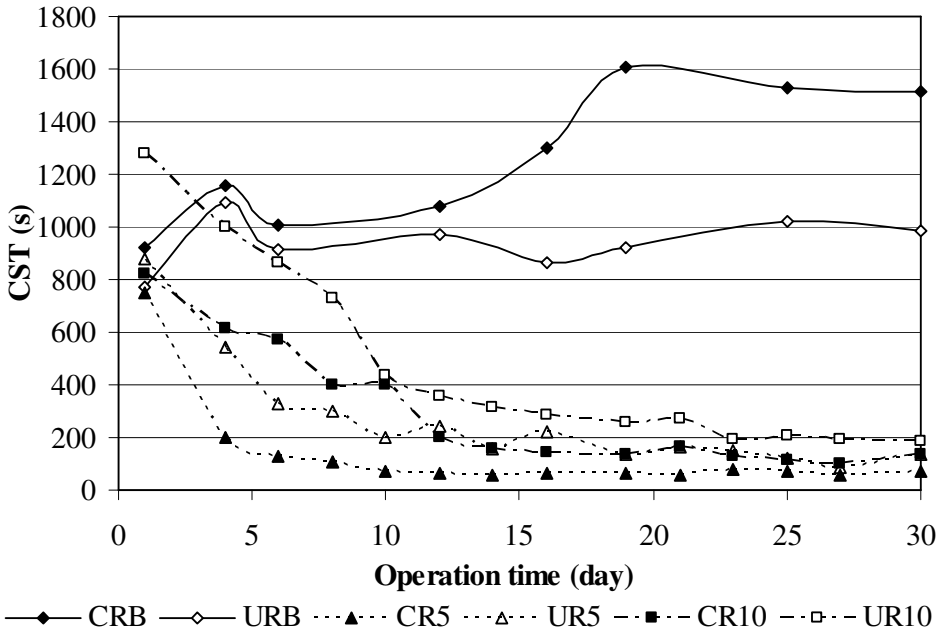


Figure 4.71 CST changes in reactor contents of CR_B, UR_B, CR_5, UR_5, CR_{10}, and UR_{10} during operation

In anaerobic digestion studies, a crown press was used as a simulator of belt press for evaluation of dewatering characteristics of digested sludge. The reactor contents were regularly processed through a crown press during the 30 days of operation period.

Table 4.64 shows the final cake solids obtained from crown press application during the operation period in anaerobic digestion studies with ultrasonic treatment. Final cake solids did not improve with operation time for all reactors.

Table 4.64 Final cake solids obtained from crown press application during operation period in ultrasonic treatment studies

Reactor's code/	Final cake solids, %					
Days	1	5	10	15	20	25
CR_5	12.85	9.20	9.00	9.02	9.51	6.25
UR_5	9.29	8.95	5.27	-	-	-
CR_{10}	10.22	9.81	9.14	8.52	8.96	7.50
UR_{10}	9.99	10.34	8.92	7.65	-	-

In reactors fed with ultrasonically pretreated sludge, it was not observed cake formation after 10 days of operation.

Table 4.65 summarized final drainage volume of sludge after 120 sec of filtration in gravity drainage plow simulator kit. Ultrasonic process preceding anaerobic digestion did not significantly affect of drainage rate during 120 sec of filtration. Ultrasonic disintegration before anaerobic digestion led to little increase in drainage rate during 120 sec crown-press application

Table 4.65 Drainage volume after 120 sec of filtration in gravity drainage plow simulator kit during operation period in ultrasonic treatment studies

Reactor's code /	Drainage volume, mL					
Days	1	5	10	15	20	25
CR_5	110	125	170	170	185	170
UR_5	160	170	190	195	195	195
CR_{10}	100	120	150	160	185	185
UR_{10}	90	120	170	185	190	190

CHAPTER FIVE
CONCLUSIONS & RECOMMENDATIONS

In this thesis, the feasibility of oxidation techniques as biological sludge disintegration purpose was investigated to improve anaerobic digestion performance, to increase stabilization degree and to increase biogas production with experimental studies. Fenton process, ozone oxidation and ultrasonic treatment as advanced oxidation processes were applied to biological sludge samples preceding anaerobic sludge digestion. All applied methods allowed to destruction of microbial sludge cells resulting in an increased biodegradability. Among the methods, ultrasonic treatment gave the maximum disintegration degree. Experimental results showed higher volatile solids reductions and higher biogas productions for the digesters fed with disintegrated sludge. All applied method showed a positive effect on anaerobic sludge biodegradability. When comparing the applied methods in terms of sludge digestion performance, ozone oxidation and ultrasonic treatment gave much closed results and ultrasonic treatment gave the best results in terms of methane production. Fenton process had lower efficiencies then the other two methods in terms of methane production. When comparing the operation types in terms of sludge digestion performance, semi batch systems had better digestion performance than batch system. On the other hand, disintegration processes had no positive effect of sludge dewatering properties.

5.1 Conclusions of Fenton Process Experiments

5.1.1 Optimization Study with Fenton Process

Box-Wilson experimental design was applied to optimize Fenton Process conditions for biological sludge disintegration and to see the effect of Fenton Process on sludge dewatering characteristics. H_2O_2 and Fe(II) concentrations were chosen as the independent variables and designated as X_1 and X_2, respectively. H_2O_2 concentration (X_1) varied between 10 and 100 g/kg dry solids (DS), while Fe(II) concentration (X_2) was ranged from 1 to 5 g/kg DS. Disintegration degree parameter was chosen as the main response for optimization of Fenton Process conditions. The

other responses chosen for determination the effect of Fenton Process on biological sludge disintegration was percent increase in TOC of sludge's supernatant (E_{TOC}) and percent increase in total nitrogen of sludge's supernatant (E_{TN}). Percent decrease in CST (E_{CST}) and percent decrease in SRF (E_{SRF}) after Fenton's application used for determination the effect of Fenton Process on sludge filterability. Observed response values obtained from the experiments were compared with the predicted ones obtained from the response function. Predictions of response function were in good agreement with the experimental data for both responses.

Maximum DD of 25.2 % was achieved at 60 g H_2O_2 / kg TS and 4 g Fe(II)/ kg TS, and optimum Fe(II)/ H_2O_2 ratio was found as 0.067. A ratio of 0.067 g Fe(II) per gram H_2O_2, and 60 g H_2O_2 / kg TS were chosen as the optimum conditions for biological sludge disintegration.

E_{TOC} increased with increasing Fe(II) concentrations up to 4 g Fe(II)/ kg TS, but at higher concentrations E_{TOC} decreased. Similarly, increasing H_2O_2 concentration increased E_{TOC} at 60 g/kg TS, after that point E_{TOC} decreased. Similar results were observed in DD. Decreases in DD and E_{TOC} may be resulted from a competition between the organic substances and H_2O_2 (H_2O_2 acts as a scavenger of the highly potential hydroxyl radicals, and inhibit the disintegration) or high H_2O_2 concentrations (high H_2O_2 concentration may caused the mineralization of organic substances to the final step of water and carbon dioxide). Maximum E_{TOC} of 75.74 % was achieved at 60 g H_2O_2 / kg TS and 4 g Fe(II)/ kg TS.

Fenton process led to break up the microbial cells and cause to release of intracellular compounds into the liquid phase. So, total nitrogen of sludge's supernatant increase after Fenton's application.

As results of the CST and SRF tests, Fenton Process improved the filterability characteristics of sludge, and it can be applied to biological sludge as a conditioning method before mechanical dewatering units.

5.1.2 Anaerobic Digestion Study with Fenton Process

Lower total solids (TS) values for reactors operated with 5 and 10 days sludge retention times than those in batch reactors were obtained and TS values decreased drastically especially during the first ten days for these reactors. At the end of the operation, the highest decrease in TS was observed in reactor operated with 5 days sludge retention time and fed with Fenton processed sludge (FR_5) according to the first operation day. The ratio was 72 % for this reactor. For control reactor (CR_5), this ratio was calculated as 65 %.

The highest decrease in volatile solids (VS) was obtained in reactor operated with 5 days sludge retention time and fed with Fenton processed sludge (FR_5) while the lowest decrease in VS was observed in reactor operated as batch system and fed with raw sludge (CR_B). Very close DS and VS reductions were observed among the reactors fed with Fenton processed sludge and control ones. At the end of operation, decrease in VS was recorded as 49 % according to the first operation day in FR_5. This ratio was determined as 42 % for control one.

Better SS reductions were observed for reactors operated with 5 and 10 days SRT comparing to reactors operated as batch system. SS in reactors fed with Fenton processed sludge were lower than those in control reactors for all sludge retention times. Based on these results it was suggested that the Fenton process was effective in improving sludge's solids reduction.

Reactors fed with Fenton processed sludge gave higher methane gas production comparing to the control ones. The highest methane production was observed in reactor fed with Fenton processed sludge and operated with 5 day of SRT. In addition, Fenton process led to increase H_2S and CO levels in the reactors.

Fenton process enhanced the degradation of extracellular polymeric substances. Protein concentrations of reactor contents decreased with operation time in all reactors and the higher reductions were observed Fenton processed reactors comparing the control ones.

Fenton process led to a little improvement in particle size reduction comparing the classical digestion experiments. In addition, higher reduction in particle size was observed in semi batch systems than those in batch system.

Although Fenton process seems creating positive effect in reactors in terms of CST, this process did not increase drainage rate of sludge and led to a small improvement in cake solids on a crown press application.

5.2 Conclusions of Ozone Oxidation Experiments

5.2.1 Optimization Study with Ozone Oxidation

An oxidative pre-treatment with ozone for the purpose of biological sludge disintegration has been investigated in terms of sludge and supernatant characteristics with laboratory tests. Different ozone dose ranged between 0 and 0.25 g O_3/g TS were used for the process optimization.

When ozone dose was 0.1 gO_3/g TS, maximum disintegration degree (DD) was achieved as 51.1%. Extra ozone dose is unnecessary because it is resulted in mineralization of dissolved organics. Ozone oxidation of biological sludge allows to destruction of microbial sludge cells resulting in an increased biodegradability.

Ozone oxidation changed the supernatant characteristics of sludge. For 0.1 gO_3/g TS, the soluble chemical oxygen demand (SCOD), dissolved organic carbon (DOC), total nitrogen (TN), total phosphorus (TP) and protein content increased by 300 %, 94.2 %, 225 %, 200 %, and 11 %, respectively.

Decreasing of SS and VSS content of sludge during the ozone oxidatin showed that solubilization of sludge's solids can be effectively performed by ozone oxidation.

Ozone oxidation led to a little improvement in particle size reduction comparing the raw biological sludge.

Cell lyses due to ozone oxidation resulted in release of protein content into the liquid phase of sludge and protein content increased in first 25 min reaction time (up to 0.1 gO_3/g TS ozone dose) and then disintegration enhances the degradation of extracellular polymeric substances (EPS) and protein concentration decreased with increasing ozone dose.

Filterability evaluation in terms of CST showed that ozone oxidation does not deteriorate filterability characteristics of sludge and particles size remained nearly constant with ozone oxidation.

5.2.2 Anaerobic Digestion Study with Ozone Oxidation

TS and VS concentrations in reactors fed with ozonated sludge were lower than those in control reactors for all sludge retention times. Lower TS values for reactors operated with 5 and 10 days sludge retention times than those in batch reactors were obtained. At the end of the operation, the highest decrease in TS was observed as 63.7 % in OR_5 (operated with five days retetion time and fed with ozonated sludge) according to the first operation day. For control one, this ratio was calculated as 54 %. At the end of the operation, the highest decrease in VS was observed as 57 % in OR_5 according to the first operation day. For control one, this ratio was calculated as 40.9 %. Similarly, Ozone oxidation preceding anaerobic digestion led to higher reductions in SS and VSS content of sludge comparing the classical anaerobic digestion. Based on the results it was suggested that the ozone oxidation was effective in improving sludge's solids reduction.

Reactors fed with ozonated sludge gave higher methane gas than control reactors. Semi batch operations were more effective on methane production than batch operation. The highest methane gas production was obtained in reactor operated with 5 days of sludge retention time. Ozone oxidation led to increase H_2S concentrations in the reactor contents but H_2S did not exceed toxic level for methanogens.

Ozone oxidation enhanced the degradation of extracellular polymeric substances. Protein concentrations of reactor contents decreased with operation time in all

reactors and the higher reductions were observed reactors fed with ozonated sludge comparing the control ones.

In the first operation day, high values of particle size were observed. Then values decreased. Ozone oxidation process before anaerobic digestion led to little improvement in particle size decrease.

For reactors operated as semi batch system, anaerobic digestion improved the filtration characteristics of sludge and CST values decreased with increasing operation time. But ozone oxidation preceding anaerobic digestion had no a significant effect to increase filterability of sludge. Higher CST values were obtained in batch systems comparing to the semi batch systems. In batch system, ozone oxidation caused a little enhances the filterability of sludge.

5.3 Conclusions of Ultrasonic Treatment Experiments

5.3.1 Optimization Study with Ultrasonic Treatment

Ultrasonic treatment for the purpose of biological sludge disintegration has been investigated in terms of sludge and supernatant characteristics with laboratory tests. The range of the specific energy (SE) varied from 0 to 15880 kJ/ kg TS was used in ultrasonic treatment study.

The maximum disintegration degree of 57.9 % was obtained for specific energy of 9690 kJ kg/ TS and reaction time of 40 min. For specific energies above 9690 kJ/kg TS, DD decreased. Decreasing of DD may be explained by high oxidation effects of radicals. Up to 10000 kJ/kg TS, hydroxyl radicals preferentially attack the organic substances and destruct the activated sludge microorganism's cell walls in biomass and oxidized them to dissolved organic substances and these substances released to the liquid phase and increased the DD. For specific energies above 9690 kJ kg/ TS, as SE increases, more soluble organics were mineralized and DD decreased. High ultrasonic energies promote oxidation by radicals and ultrasound led to mineralization preceding solubilization of sludge.

Ultrasonic treatment led to change of physico-chemical characteristics of sludge. For instance, temperature increased almost linearly with increasing specific energy. Temperature increased from 22°C in raw sludge to 72°C for ultrasonic pre-treated sludge with maximum specific energy input of 15880 kJ kg/ TS. In contrast, pH decreased during ultrasonic pre-treatment. It decreased from 6.95 in raw sludge to 6.16 for ultrasonic pre-treated sludge at 15880 kJ kg/ TS application.

For 9690 kJ/kg TS, the soluble chemical oxygen demand (SCOD), dissolved organic carbon (DOC), total nitrogen (TN), total phosphorus (TP) in sludge's supernatant increased by 340 %, 860 %, 716 %, and 207.5 %, respectively.

Ultrasonic treatment induced sludge reduction due to the solubilization of total and volatile solids. Higher decreases in SS and VSS were observed in experiments which specific energy was higher than 8086 kJ/kg TS. Maximum suspended solids solubilization and volatile suspended solids solubilization with ultrasonic treatment were determined as 48.61 % and 46.7 %, respectively for 9690 kJ/kg TS.

Ultrasonic treatment enhanced the degradation of protein content of sludge. The main purpose of disintegration is the elimination of hydrolysis step to accelerate the anaerobic degradation. Results show that protein hydrolysis was performed successfully by ultrasonic treatment even at very low ultrasonic density levels (lower than 0.1 W/ mL).

Particle size in sludge reduced due to ultrasonic treatment and higher reductions were obtained in ultrasonically treated sludge with high specific energies comparing to that in raw sludge.

CST gradually increased with increasing specific energy. CST results showed that ultrasonic treatment deteriorates the filterability of biological sludge.

5.3.2 Anaerobic Digestion Study with Ultrasonic Treatment

TS and VS concentrations in reactors fed with ultrasonically pre-treated sludge were lower than those in control reactors for all sludge retention times. Lower TS

values for reactors operated with 5 and 10 days sludge retention times than those in batch reactors were obtained.

At the end of the operation, the highest decrease in TS was observed as 58 % in UR_5 (operated with 5 days retention time and fed with ultrasonic pre-teated sludge) according to the first operation day. For control one, this ratio was calculated as 55.6 %. At the end of the operation, the highest decrease in VS was observed as 49 % in UR_5 according to the first operation day. This ratio was calculated as 40 % for control one. Similarly, ultrasonic treatment preceding anaerobic digestion led to higher reductions in SS and VSS content of sludge comparing the classical anaerobic digestion. Ultrasonic disintegration preceding anaerobic digestion affected positively sludge's solids reduction hence it facilitated sludge minimization.

Reactors fed with ultrasonically pre-treated sludge gave higher methane gas than control reactors. Semi batch operations were more effective on methane production than batch operation. The highest methane gas production was obtained in reactor operated with 5 days of sludge retention time. Ultrasonic treatment led to increase H_2S concentrations in the reactor contents but H_2S did not exceed toxic level for methanogens.

Ultrasonic treatment improved the degradation of extracellular polymeric substances. Protein concentrations of reactor contents decreased with operation time in all reactors and the higher reductions were observed reactors fed with ultrasonically pre-treated sludge comparing to control ones.

In the first operation day, high values of particle size were observed. Then values decreased. Ozone oxidation process before anaerobic digestion led to little improvement in particle size decrease.

Ultrasonic treatment preceding anaerobic digestion had no a significant effect to increase filterability of sludge. Higher CST values were obtained in batch systems comparing to the semi batch systems. In batch system, ozone oxidation caused a little enhances the filterability of sludge.

5.4 Recommendations

Experimental studies were done in laboratory scale. To make more conclusive results, full–scale trials should be done.

Dewatering characteristics of digested sludge was evaluated for each disintegration method but any conditioning method has not been applied to sludge taken from the digestion units. Some conditioning methods could be applied to digested sludge for extensive evaluations of final disposal.

Anaerobic digestion studies were carried out in mesophilic conditions. Thermophilic conditions could be applied to determine the effects of temperature differences on anaerobic digestion performance of biological sludge.

As promising technologies for sludge disintegration, Fenton Process, ozone oxidation, and ultrasonic treatment requires inclusive research studies including costs analysis to show whether these technologies are appropriate in practice or not.

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