

**DOKUZ EYLÜL UNIVERSITY
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**MINIMIZATION OF EXCESS SLUDGE
PRODUCTION**

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MINIMIZATION OF EXCESS SLUDGE PRODUCTION

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MINIMIZATION OF EXCESS SLUDGE PRODUCTION

ABSTRACT

Large amounts of waste sludge are produced with the removal of biodegradable compounds and organic or inorganic matter in municipal and industrial wastewater treatment plants for disposal. It is expected that, in near future, sludge production and the regulation limits for disposal alternatives cause an increase in costs for sludge disposal. The current approach to sludge minimization is the reduction of volume of wet sludge and the reduction of dry mass of sludge. The volume of wet sludge for disposal is reduced significantly with the increase of the sludge solid content by dewatering. The reduction of dry mass of sludge leads to the reduction of solid content and volume and this strategy should be favoured, because it allows the immediate reduction of sludge dry mass during its production in the biological treatment stage.

The fundamental aim of this thesis is the reduction of sludge production during the biological treatment. All of the techniques for sludge reduction described in this thesis suitable for implementation during the wastewater treatment plants, not after the sludge production, often by retrofitting the specific additional equipment. Two of these techniques were carried out experimentally and evaluated within the scope of this thesis. The effectiveness of ozonation integrated in activated sludge process and oxic-settling anaerobic (OSA) process were investigated on sludge reduction, especially.

In the first stage of the study, Box-Behnken Statistical Design Program was used in order to determine the optimum operational conditions. Optimum hydraulic retention time (HRT), solid retention time (SRT) and initial COD values for maximum COD removal were determined as 25 h, 25 d and 400 mg/L, respectively. After the determination of optimum operational conditions of activated sludge process, two systems were operated in parallel under these optimum conditions during 45 days until the steady state conditions and the effluent quality and sludge properties of the systems were monitored. When the steady-state conditions were

reached, specific batch tests were carried out in order to investigate the biodegradability of disintegrated sludge and determine optimum ozone dose prior to the modification with the addition of ozonation unit to one of the activated sludge process. Optimum ozone dose for return activated sludge disintegration was determined as 0.05 gO₃/gTS in terms of disintegration degree with 56.2 percent. The higher doses improved disintegration degree, slightly.

After the ozone dose optimization study, the effectiveness of partial ozonation of return activated sludge was investigated for the minimization of excess sludge production using ozonation coupled with activated sludge process in two stages. In the first stage of the ozonation, in ozonated system, 10 percent of return activated sludge (0.1 QR) was ozonated every day during a month with optimum ozone dose and recirculated to the aeration tank. No excess sludge was withdrawn from the ozonation coupled with activated sludge process. The other activated sludge system was remained unmodified and operated as a control run with optimum operational conditions. Excess sludge was withdrawn every day due to SRT. 43 percent observed sludge yield (Y_{obs}) reduction could be achieved in ozone run during the operation period. At the end of the operation, the 56 percent of Y_{obs} reduction was observed in ozone system compared to control system. In ozone run, the effluent quality was weakened slightly in term of COD and NH₄-N removal. Sludge settling properties represented by SVI was improved in ozone run. Ozone run had lower dewaterability characteristics with higher CST values. The filterability of sludge was lower in ozone run than control run in terms of SRF.

In the second stage of the ozonation 800 mL of the return sludge corresponded to 20 percent of the return activated sludge (0.2 QR) was ozonated with optimum ozone dose. 73 percent of Y_{obs} reduction could be achieved in ozone run during the operation period. At the end of the operation, the 62 percent of Y_{obs} reduction was observed in ozone run compared to control run. The effluent quality was weakened slightly in term of COD and NH₄-N removal in ozone run. Sludge settling properties was improved in ozone run in terms of SVI. Lower dewaterability characteristics in

ozone run were proved with CST values. The filterability of ozonated sludge was lower than control run in terms of SRF.

After the application of ozonation to activated sludge system, one of the system was modified by inserting anaerobic tank to comprise OSA system. The other system was remained unmodified as a control system. A specific volume of return activated sludge of OSA system was subjected anaerobic conditions (-250 mV of low ORP level every day. OSA and control system were operated during 45 days. The sludge reduction efficiency and effluent quality were evaluated. After the completion of continuous operation, some batch experiments were conducted in order to investigate sludge reduction mechanisms in OSA process.

In OSA system, 62 percent of reduction efficiency was obtained in yield production in OSA system during the operation. OSA system was also achieved 58 percent reduction efficiency of Yobs compared to control run at the end of the operation. It was found that COD concentrations in the effluent in the OSA system were lower than that in the effluent of the control run due to the additional substrates from the anaerobic tank. The $\text{NH}_4\text{-N}$ removal efficiency in OSA system was lower compared to control run during the operation period due to denitrification. The settleability characteristics of sludge was also found better than that of the control system in terms of SVI. Higher CST values were obtained in control system compared to OSA system during the long term operation. It was revealed that the OSA system enhanced the filterability of sludge.

In order to investigate the sludge decay theory in OSA sistem, two batch experiments with sludge taken from aeration tank of control and OSA systems were carried out. The aim of the first batch experiment was to investigate the relationship among sludge anaerobic reaction time, sludge lysis and sludge yield. The sludge reduction in terms of Yobs caused by sludge decay in OSA batch reactor was 40 percent compared to control batch reactor for the first batch experiment. In the second batch test, the investigation of the energy uncoupling theory was aimed. The sludge reduction in terms of Yobs caused by energy uncoupling in OSA batch reactor was 5 percent compared to control batch reactor.

When the sludge reduction techniques used in this thesis were compared as modified activated sludge processes; the activated sludge process ozonated of 0.2 QR showed better Yobs reduction efficiency than that the first stage of ozonation process (ozonation with 0.1QR) and OSA system during the operation period. The effluent quality of control systems were better than that modified systems in terms of COD and nitrogen removal capacity however, the effluent quality of the modified systems were at satisfactory level. The sludge characteristics of activated sludge were changed even slightly for some parameters after the application of sludge minimization techniques.

Consequently, the ozonation based on cell lysis-cryptic growth mechanism is an applicable and effective technique integrated to the activated sludge process for the minimization of excess sludge production. Besides, it was revealed that the OSA process especially based on sludge decay and energy uncoupling metabolism can be used as another simple effective method for sludge reduction.

Keywords: excess sludge minimization, modification of activated sludge process, ozonation, OSA process.

AŞIRI ÇAMUR ÜRETİMİNİN AZALTILMASI

ÖZ

Evsel ve endüstriyel atıksu arıtma tesislerindeki organik ve inorganik maddelerin ve biyolojik parçalanabilen bileşiklerin giderilmesi sonucunda büyük miktarda atık çamur oluşur. Yakın gelecekte, yönetmeliklerin, çamur uzaklaştırma alternatiflerine sınırlama getirmesi yönüyle, maliyet artışına neden olması beklenmektedir. Oluşan çamur miktarının azaltılması için günümüzdeki yaklaşım, yaş çamur hacminin ve çamur kuru kütlelerinin azaltılmasına yöneliktir. Çamur uzaklaştırmada yaş çamur hacmi, susuzlaştırma ile çamurun katı madde içeriğini arttırmak suretiyle önemli ölçüde azaltılır. Çamurun kuru kütlelerinin azaltılması, oluşan çamur hacminin ve katı madde miktarının azaltılmasına neden olduğundan; biyolojik arıtım kademesinde çamurun kuru kütlelerinin hemen azaltılmasına imkan tanıyan bu stratejinin desteklenmesi gerekmektedir.

Bu tezin temel amacı biyolojik arıtım süreci boyunca, çamur üretiminin azaltılmasıdır. Tez kapsamında çamur miktarının azaltılması amacıyla uygulanan teknikler, mevcut atıksu arıtma prosesinde yapılabilecek küçük modifikasyonlar ile uygulanabilecek tekniklerdir, çamur üretimi aşamasından sonra uygulanan yöntemler değildir. Bu çalışma kapsamında, sözü edilen tekniklerden sadece ikisi deneysel olarak ele alınmış ve değerlendirilmiştir. Aktif çamur sisteminin modifikasyonları olan ozonlama ile bileşik aktif çamur prosesi ve OSA prosesi kullanılmış; bu sistemlerin oluşan çamur miktarının azaltılması üzerine etkileri araştırılmıştır.

Çalışmanın ilk aşamasında, Box-Behnken istatistiksel deney tasarım yöntemi kullanılmıştır. Optimum hidrolik alıkonma süresi 25 saat, çamur yaşı 25 gün ve giriş suyu besleme konsantrasyonu 400 mg/L olarak belirlenmiştir. Optimum işletme koşulları belirlendikten sonra, iki sistem bu optimum şartlar altında paralel olarak 45 gün boyunca kararlı hal koşullarına ulaşılan kadar işletilmiş ve sistemlerin çıkış suyu kalitesi ile çamur özellikleri izlenmiştir.

Aktif çamur proseslerinden birine ozonlama ünitesinin ilavesi ile gerçekleşecek ozonlama ile birleşik aktif çamur prosesi modifikasyonundan önce optimum ozon dozunu belirlemek ve kararlı hal koşullarına ulaşıldığında dezente gre edilmiş çamurun biyolojik olarak parçalanabilirliğini araştırmak üzere kesikli deneyler yapılmıştır. Daha yüksek ozon dozları dezente grasyon derecesini (DD) çok az arttırdığından; Yüzde 56.2 dezente grasyon derecesine göre optimum ozon dozu olarak 0.05 gO₃/gTS belirlenmiştir.

Ozon dozu optimizasyon çalışmasından sonra, aşırı çamur üretiminin azaltılması üzerine geri devir çamurunun kısmi ozonlamasının etkisi iki aşamada araştırılmıştır. Ozonlamanın ilk aşamasında, bir ay boyunca her gün geri devir çamurunun yüzde 10'u (0.1 QR) optimum ozon dozu ile ozonlanmış ve havalandırma tankına geri devir olarak döndürülmüştür. Ozonlama ile birleşik aktif çamur prosesinde aşırı çamur çekilmemiştir. Diğer aktif çamur prosesi modifiye edilmeden bırakılmış ve optimum işletim koşullarında kontrol sistemi olarak işletilmiştir. Çamur yaşına bağlı olarak sistemden hergün çamur çekilmiştir. Sonuçlara göre çamur veriminde yüzde 43 azalma sağlanmıştır. İşletim sonunda ozon sisteminde kontrol sistemine göre çamur üretiminde yüzde 56 azalma gözlenmiştir. Ozon sisreminde, çıkış suyu kalitesi KOİ ve azot giderim verimine göre biraz zayıflamıştır. ÇHI ile temseil edilen çamurun çökeltme özelliği ozon adımıında gelişmiştir. Ozon sistemindeki kontrol sisteminden daha yüksek KES değerleri daha düşük su verme özelliği taşıdığını göstermektedir. SRF dğerlerine göre, ozon sisteminde çamurun filtrelenebilme özelliği kontrol sisteminden daha düşüktür.

Ozonlamanın ikinci aşamasında, geri devir çamurun yüzde 20'sine tekabül eden 800 mL çamur optimum ozon dozu ile ozonlanmıştır. Ozonlu reaktörden deneysel olarak işletim boyunca çamur çekilmemiştir. Kontrol ve ozon sistemlerinin sonuçları, çamur azaltımı göz önünde bulundurularak değerlendirilmiştir. Ayrıca, ozonlanmış sistemin havalandırma tankından ve kontrol sisteminin reaktöründen gelen çamurun özellikleri araştırılmış ve karşılaştırmalı olarak değerlendirilmiştir. Ozonlanmış sistemde işletim süresince çamur üretiminde yüzde 73 azalma elde edilmiştir. İşletim sonunda, ozon sisteminde kontrol sistemine göre bir karşılaştırma yapıldığında ise

yüzde 62 çamur verimi azalması gözlenmiştir. Ozonlama sisteminde, KOİ ve azot giderim verimi dikkate alındığında çıkış suyu kalitesinin biraz zayıfladığı görülmüştür. Ozon adımı, ÇHI ile temsil edilen çamurun çökeltme özelliği gelişmiştir. Ozon sisteminde kontrol sisteminden daha yüksek KES değerleri görülmesi daha düşük su verme özelliği taşıdığını göstermektedir. SRF değerlerine göre, ozon sisteminde çamurun filtrelenebilme özelliği kontrol sisteminden daha düşüktür.

Ozonlama ile birleşik aktif çamur uygulanmasından sonra, sistemlerden birisi anoksik bir tank ilave edip OSA sistemini oluşturmak suretiyle modifiye edilmiştir. Diğer sistem kontrol sistem olarak modifiye edilmeden kalmıştır. OSA sisteminin geri devir çamurunda anaerobik şartları sağlamak üzere her gün kısa süreli olarak azot gazı uygulanarak düşük ORP seviyeleri sağlanmıştır. OSA ve kontrol sistemi 45 gün boyunca işletilmiştir. Çamur üretimindeki azalma ve çıkış suyu kalitesi değerlendirilmiştir. Sürekli işletim tamamlandıktan sonra OSA prosesindeki çamur azaltma mekanizmalarını araştırmak üzere kesikli deneyler yürütülmüştür.

OSA sisteminde, işletim boyunca çamur üretiminde yüzde 62 azalma elde edilmiştir. OSA sisteminde aynı zamanda işletim periyodu sonunda kontrol sistemi ile karşılaştırıldığı zaman çamur üretiminde yüzde 58 azalma elde edilmiştir. OSA sistemindeki NH₄-N giderim verimi işletim boyunca kontrol sisteminden daha düşüktür. OSA sistemindeki çamurun çökebilirliği ÇHI'ne göre kontrol sisteminden daha iyidir. Uzun dönem işletim boyunca kontrol sisteminde OSA sistemine göre daha yüksek KES değerleri gözlenmiştir. Bu durumda, OSA sisteminin filtrelenebilirliği arttırdığını söylemek mümkündür.

OSA sisteminde çamur bozunma teorisini araştırmak için OSA ve kontrol sisteminin havalandırma tankından alınan çamur ile iki kesikli deney yürütülmüştür. İlk kesikli deneyin amacı, çamurun anaerobik reaksiyon süresi, çamur lizisi ve verimi arasındaki ilişkiyi araştırmaktır. Çamur bozunmasının neden olduğu çamur verimindeki azalma kontrol sistemine göre birinci kesikli deney aşaması için yüzde 40 olarak bulunmuştur. İkinci kesikli deneyde, enerji ayırma teorisinin araştırılması amaçlanmıştır. İkinci kesikli deneyde, OSA sisteminde enerji ayırma

mekanizmasının neden olduđu çamur azalması (Yobs) kontrol sisteminde göre % 5'tir.

Bu tez kapsamında, aktif çamurun modifikasyonu olarak çamur azaltma teknikleri karşılaştırıldığında, işletim periyodu boyunca 0.2 QR'nin ozonlandığı aktif çamur prosesi; 0.1 QR'nin ozonlandığı aktif çamur sisteminden ve OSA sisteminden daha iyi Yobs azalma verimi göstermiştir. KOİ ve azot giderim kapasitelerine göre kontrol sistemlerinin çıkış suyu kaliteleri de daha iyidir. Bununla birlikte, modifiye sistemlerin çıkış suyu kaliteleri tatmin edici düzeydedir. Çamur minimizasyon tekniklerinin uygulanmasından sonra aktif çamurun özellikleri çoğu parametre bazında az da olsa değişmiştir.

Sonuç olarak, hücre lizizi ve kriptik büyüme mekanizmasına dayanan aktif çamur prosesine entegre edilmiş ozonlama tekniđi, aşırı çamur üretiminin azaltılması için uygulanabilir etkili bir yöntemdir. Ayrıca özellikle çamur bozunma ve enerji ayırma metabolizmasına dayanan OSA prosesinin çamur azalması için kullanılan basit ve etkili bir metot olduđu ortaya çıkmıştır.

Anahtar Kelimeler: aşırı çamurun minimizasyonu, aktif çamur prosesinin modifikasyonu, ozonlama, OSA prosesi.

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CHAPTER ONE

INTRODUCTION

1.1 The Problem Statement

The transformation of dissolved and suspended organic contaminants to biomass and evolved gases (CO₂, CH₄, N₂ and SO₂) is occurred during biological wastewater treatment. The most widely used biological wastewater treatment method in the world for both domestic and industrial plants is the activated sludge process. However, there are some drawbacks related to the application of activated sludge processes. One of the main drawbacks of conventional activated sludge processes is the high sludge production. A major economic, environmental and legal challenge related to the biological treatment plants is the disposal of excess sludge. One of the ways of overcome sludge problems is to reduce sludge production in the wastewater treatment itself, rather than relying on post-treatment. Wastewater treatment must encourage non-growth activities through biosynthesis in order to reduce the production of biomass (Ahn et al., 2002; Ødegaard, 2004; Wei et al., 2003).

Enormously high cost is required for the treatment and disposal of excess sludge in a biological wastewater treatment system. This cost is approximately equal to half of the whole operational cost for domestic wastewater treatment (Song et al., 2003).

Sludge reduction technologies are based on different strategies include lysis-cryptic growth, uncoupling metabolism and micro-fauna predation (Chen et al., 2002; Egemen et al., 2001; Guo et al., 2007; He et al., 2006; Li et al., 2008; Liang et al., 2006; Saby et al., 2002; Wei et al., 2003; Wei and Liu, 2006). The most promising of these techniques is ozone lysis-cryptic growth that can reduce the waste sludge generation by 50–100 % (Egemen et al., 2001; He et al., 2006; Wei et al., 2003). The effects of introducing ozonated excess sludge into a variety of activated sludge reactors, including traditional activated sludge reactors were studied and evaluated (Yasui and Shibata, 1994; Yasui et al., 1996). A hybrid system of a conventional activated sludge process coupled with ozone treatment process has been widely reported as a significantly effective method for the minimization of sludge

production (Ahn et al., 2002; Yasui and Shibata, 1994). Sludge solubilization can be achieved by the microbial disintegration of sludge into a soluble substrate. This substrate is recirculated to the biological process for subsequent mineralization. Significantly lower production of excess sludge can be obtained as a result of mineralization (Manterola et al., 2008).

The cell walls of microorganisms are destroyed by a strong chemical oxidant such as ozone. The ozonation process has been employed to reduce excess sludge in the activated sludge processes (Ahn et al., 2002; Boehler and Siegrist, 2004; Cui and Jahng, 2004; Yasui and Shibata, 1994) or as a pretreatment technique prior to anaerobic sludge digestion (Scheminski et al., 2000; Muller et al., 1998; Weemaes et al., 2000).

Partial or all sludge in the conventional activated sludge (CAS) system is treated by ozone and recycled into CAS for biological transformation to CO₂ and H₂O in the mechanism of sludge ozonation-cryptic growth (Zhang et al., 2009). The influent of the bioreactor will be altered after the recirculation of ozone-treated sludge consisting of the cell debris and soluble organics released from the disrupted cells to the bioreactor for degradation (Yan et al., 2009a). The cryptic growth is occurred in the presence of a large amount of cell debris and soluble organics in the influent (Wei et al., 2003) when the ozonated sludge solution is returned to the bioreactor. Lysis-cryptic growth may be induced in one of two ways. In the first way, bacteria in the sludge may secrete hydrolysis enzymes and change in the bacterial hydrolysis activity and it leads to a succession in the bacterial population (Mason et al., 1986). The second way that lysis-cryptic growth may be induced is through the direct consumption of cell debris by protozoa and metazoans in the activated sludge, which leads to multiplication of the microfauna (Yan et al., 2009a).

The oxic-settling-anaerobic (OSA) process is a hopeful wastewater treatment technique as a simple modification of a conventional activated sludge process for reducing sludge production and improving the stability of process operation (Wang et al., 2008). Thickened sludge from a final settling tank is returned to an aeration

tank via a sludge-holding tank in an OSA system. The alternate anaerobic–aerobic cycling of activated sludge can stimulate catabolic activity; dissociate catabolism from anabolism, resulting in a minimized sludge yield in OSA system. In sludge holding tank, no additional substrate is added and anaerobic conditions are maintained in it by a closed operation (Perez-Elvira et al., 2006). According to Saby et al., (2003), activated sludge circulation among oxic (aeration tank), settling tank and anaerobic tank can reduced excess sludge production by 40-50 %.

1.2 Purpose of Research

The activated sludge process is commonly used biological wastewater treatment method for both domestic and industrial plants in the world. It is used intensively rather than fixed film processes and can treat up to 10 times more wastewater per unit reactor volume with higher operating costs. High sludge production is one of the drawbacks of conventional activated sludge processes. Currently, production of excess sludge is one of the most serious challenges in biological wastewater treatment.

Sludge-associated problems can be solved by the reduction of sludge production in the wastewater treatment process rather than the post-treatment of the sludge produced. Microbial metabolism liberates a portion of the carbon from organic substrates in respiration and assimilates a portion into biomass. To reduce the production of biomass, wastewater processes must be engineered such that substrate is diverted from assimilation for biosynthesis to fuel exothermic, non-growth activities. Different strategies are currently developed for sludge reduction in an engineering way based on these mechanisms: lysis cryptic growth, uncoupling metabolism, maintenance metabolism and predation on bacteria.

In this thesis, the minimization of excess sludge production was aimed using the modification of activated sludge processes in a lab-scale system. The costs of the treatment and disposal of sludge produced from the activated sludge systems can be decreased or completely removed using these modified systems.

The scope objectives of this thesis are following;

- To investigate the feasibility of ozonation and OSA process entegrated to the activated sludge process for the minimization of excess sludge production,
- To optimize the activated sludge process conditions in terms of effluent quality,
- To operate and stabilize two modiflicated activated sludge processes in parallel under the optimum operational conditions.
- To optimize ozone dose in terms of disintegration degree (DD),
- To determine sludge characteristics of ozonated sludge,
- To investigate the effects of ozonation on sludge reduction using activated sludge process coupled with ozonation process at two stage with different recirculated ozonated sludge volume ,
- To compare the effects of ozonation on sludge reduction, effluent quality and sludge characteristics with control system (without ozoantion).
- To investigate the effects of OSA process on sludge reduction, effluent quality and sludge characteristics.
- To determine the sludge reduction mechanism of the OSA process with batch tests.
- To compare and evaluate the control and OSA systems in terms of sludge reduction efficiencies, the changes of effluent quality and sludge properties

CHAPTER TWO

BACKGROUND INFORMATION & LITERATURE REVIEW

2.1 Sludge Composition and Production

The sources, characteristics and quantities of the sludge to be handled must be known in order to design sludge processing, treatment and disposal facilities properly (Metcalf&Eddy, 2004).

Mechanical, physical, chemical or biological units producing primary, secondary and chemical sludge can be used for wastewater treatment (Foladori et al., 2010). The sources of sludge in a treatment plant vary according to the type of plant and its operation method. Primary sludge is composed of settleable solids from raw wastewater in primary settling tank (Turovskiy and Mathai, 2006). Primary sludge is usually gray and slimy, in most cases has an odor. It can be digested under suitable conditions (Metcalf&Eddy, 2004). Primary sludge has a good dewaterability characteristics compared to biological sludge. Total solids (TS) content of primary sludge is ranged from 2 to 7 %. Secondary or biological sludge is produced by biological processes such as activated sludge or biofilm systems. TS content in secondary sludge is 0.5-1.5 %. Chemical sludge is produced by precipitation of specific substances or suspended solids. A combination of any two or three of the above types of sludge is introduced in the sludge handling units (Turovskiy and Mathai, 2006; Foladori et al., 2010).

In order to operate the wastewater treatment plants (WWTP) with high efficiency, sludge and excess biomass must be treated and wasted (Foladori et al., 2010). A large amount of inert solids contributes sludge production during the biological treatment of municipal wastewater, significantly. The presence of inert organic solids in sludge is due to the endogenous residue produced in microbial decay or to protozoan activity (van Loodsrecht and Henze,1999).

Very high sludge reduction can be achieved by the conversion of a significant part of refractory particulate organic matter into a biodegradable fraction. Therefore, the

composition of sludge should be known to estimate the potential efficiency of a sludge reduction technique (Foladori et al., 2010).

2.1.1 Sludge Composition

The sludge composition is commonly described with the analysis of total solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), total COD or particulate COD.

Total solids can be fractionated as follows:

- i. soluble and suspended fractions, organic (volatile) and inorganic fractions, as indicated in Figure 2.1

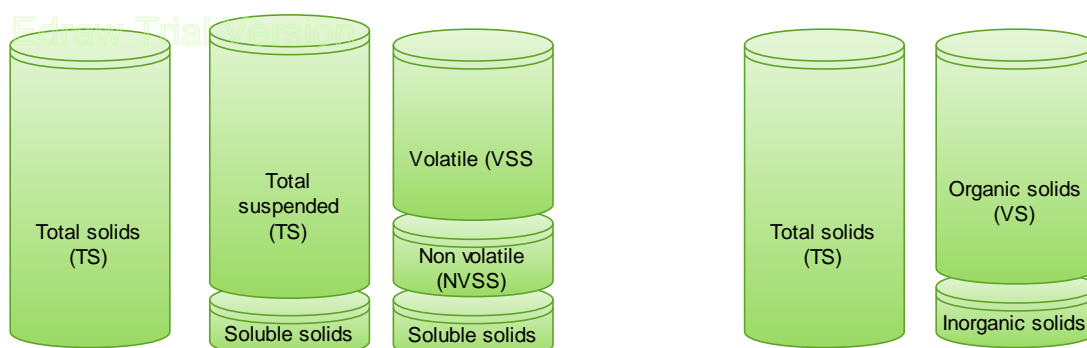


Figure 2.1 Physical fractionation of total solids in sludge (Foladori et al., 2010)

Total COD considers only organic compounds composed of soluble and particulate fractions. Measurements related to solid can be summarized as follows:

- ii. Total Solids (TS): Quantification of solids both in soluble and in particulate form, and both organic and inorganic,
- iii. Volatile Solids (VS): Quantification of organic solids, both in soluble and particulate form,
- iv. Total Suspended Solids (TSS): Quantification of particulate solids, excluding soluble solids both organic and inorganic;
- v. Volatile Suspended Solids (VSS): Quantification of particulate organic solids, excluding soluble solids both organic and inorganic;

- vi. Total COD: Chemical oxygen demand including both particulate or soluble COD,
- vii. Soluble COD: Chemical oxygen demand of soluble compounds.
- viii. Particulate COD: Chemical oxygen demand of particulate compounds: estimated as the difference between total COD and soluble COD (Foladori et al., 2010).

2.1.2 Sludge Production

2.1.2.1 Primary Sludge Production

The amount of settleable solids in raw wastewater with typically 50-60 gTSS/PE.d or 110-170 gTSS/m³ of solid content affects the production of primary sludge (Tchobanoglous et al., 2003). The quantity of TSS in the raw wastewater (typically 90-120 g/PE.d) is considered as the most common approach for calculating the primary sludge production and TSS removal rate usually in the range 50-65 % is assumed (Turovskiy and Mathai, 2006).

2.1.2.2 Biological Excess Sludge Production

In general, the formation of new activated sludge during treatment of wastewater is described as excess sludge production. Starting from this definition, the composition of excess sludge is identical to the composition of the activated sludge. The biological processes are dominated by the growth of heterotrophic bacteria (Günder, 2001). Heterotrophic biomass present in activated sludge grows on organic biodegradable soluble and particulate substrate from influent. Heterotrophic organisms are considered as active biomass and the autotrophic biomass is often neglected in the mass balances (Foladori et al., 2010).

Heterotrophic microorganisms oxidized the organic matter in order to produce H₂O and CO₂ in the process known catabolism. This process requires an electron acceptor (oxygen or nitrate) and lead to the production of energy as ATP. Microorganisms used energy to grow forming new cells and provide maintenance functions (such as the renewal of cellular constituents, maintenance of osmotic

pressure, nutrient transport, motility, etc...) in the process called anabolism. Maximum growth yield is known the ratio between the organic matter forming new cells and the organic matter oxidized in the process. The observed yield is based on the amount of solids production measured relative to the substrate removal (Metcalf&Eddy, 2004). The growth yield can reach 0.6-0.7 g/g in aerobic conditions (Foladori et al., 2010).

$$\text{Biomass yield } Y = \frac{g_{\text{biomass produced}}}{g_{\text{substrate utilized (consumed)}}} \quad (\text{Eq. 1})$$

Simultaneously biological decay of heterotrophic microorganisms occurs, creating two fractions:

- biodegradable particulate COD,
- endogenous residue considered as inert particulate COD, which accumulates in the system.

The biodegradable particulate COD fraction is first hydrolyzed, and is further oxidized to generate new cellular biomass (cryptic growth), while the endogenous residue (8-20 %) remains and accumulates in the sludge (Foladori et al., 2010).

A simplified scheme of these processes leading to sludge accumulation in a biological treatment of influent wastewater is indicated in Figure 2.2.

2.2 Mechanism of Sludge Reduction Techniques Integrated in Wastewater Treatment Plants

Alternative technologies for on-site reduction of sludge production have been studied since 1990s (Foladori et al., 2010). Some approaches can be used for less sludge production based on physical, chemical and biological methods (Mahmood and Elliot, 2006). Solid solubilization and disintegration of bacterial cells in sludge are the main target of these methods. Sludge reduction can be achieved with the following objectives illustrated in Figure 2.3.

- reducing sludge production directly in the wastewater handling units,
- reducing sludge mass in the sludge handling units and simultaneously improving biogas production in anaerobic digestion or in some cases, dewaterability.
- producing an additional carbon source to support denitrification and phosphorus removal in the wastewater handling units (Foladori et al., 2010).

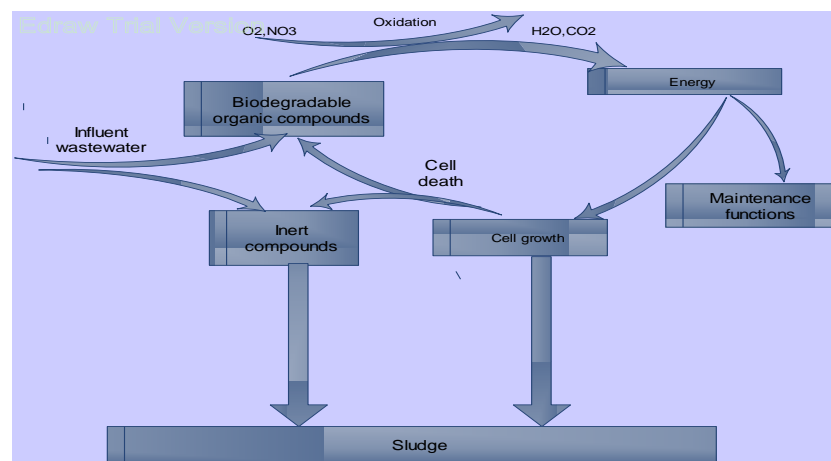


Figure 2.2 Simplified scheme of the processes leading to sludge production in the biological treatment of influent wastewater (Foladori et al., 2010).

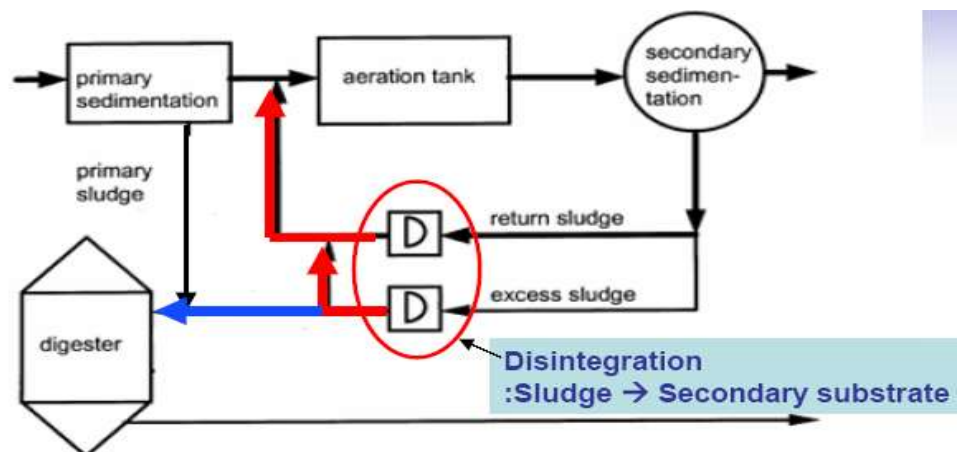


Figure 2.3 Major approaches of excess sludge reduction (Chen et al., 2001)

The mechanisms for sludge reduction techniques can be identified as follows:

- cell lysis and cryptic growth
- uncoupled metabolism
- endogenous metabolism
- microbial predation

The mechanisms indicating main technologies in wastewater handling units classified in Table 1.

Table 1. Sludge reduction mechanisms and techniques in wastewater handling units (Foladori et al., 2010)

Mechanism	Cell lysis and cryptic growth	Uncoupled metabolism	Endogenous metabolism	Microbial predation
	Enzymatic hydrolysis	Addition of chemical metabolic uncouplers	Extended aeration processes, MBRs and granular sludge	Predation by protozoa and metazoa
Techniques	Mechanical treatment	Addition of side-stream anaerobic reactor		
	Thermal treatment			
	Chemical and thermochemical hydrolysis			
	Oxidation with ozone or other oxidants			
	A combination of the above			

In the integration in wastewater handling units, the objective is to reduce sludge production directly in the wastewater treatment units instead of realising post-treatments of sludge after its production.

2.2.1 Cell Lysis and Cryptic Growth

The term “cryptic growth” indicates the reutilization of intracellular compounds (both carbonaceous compounds and nutrients) released from cell lysis. Cell lysis with the consequent solubilization of cellular constituents provided available substrate for further biodegradation caused by several sludge reduction technologies. The cryptic growth process is thus induced which results in an overall reduction of sludge production (Foladori et al., 2010). Under cryptic growth conditions, biomass growth in activated sludge system can be decreased. The cell contents released to the medium by cell lysis, thus, substrate reused in microbial metabolism is produced as an additional organic loading. Besides, a part of carbon content is released as product of respiration and then reduced biomass is produced. This biomass growth on the substrate cannot be discriminated from growth of original organic substrate, thus this growth can be described as cryptic growth (Wei et al., 2003). Lysis cryptic growth composed of lysis and biodegradation stages. Lysis is rate limiting step of the lysis-cryptic growth and the increasing of lysis efficiency causes reduction of sludge production. Sludge lysis and cryptic growth can be developed with physical, chemical and the combination of physical and chemical methods as ozonation, chlorination, combination of thermal/ultrasonic treatment and membrane, combination of alkaline and heat treatment and increasing of oxygen concentration (Wei et al., 2003). The cryptic growth is an applicable approach for the minimization of sludge production (He et al., 2006).

Cell lysis can be obtained with various treatments:

- enzymatic hydrolysis with/without enzyme addition,
- mechanical treatment by means of stirred ball mills, homogenisers or other equipment
- treatment with ultrasound,
- thermal treatment at temperatures between 40 °C and approximately 230 °C
- chemical and thermo-chemical hydrolysis adding acid or alkaline reagents, sometimes coupled with temperature increase,

- oxidation with ozone, H₂O₂ or chlorination;
- electrical treatment

The biological treatment systems can be combined with these treatments in wastewater or sludge handling units. The treatment produces biodegradable carbonaceous matter supporting denitrification in activated sludge stages when the sludge reduction technique is applied to the return sludge. Biogas production can be improved and sludge stabilization in anaerobic digester is obtained when it is integrated in the sludge handling units (Foladori et al., 2010).

2.2.2 Uncoupling Metabolism

The sum total of all the chemical processes of the cell is metabolism. It can be separated into catabolism and anabolism. Catabolism is all processes involved in the oxidation of substrates or use of sunlight in order to obtain energy while anabolism includes all processes for the synthesis of cellular components from carbon sources. Thus, catabolism furnishes the energy required for anabolism and motion and other energy-requiring processes (Rittmann and McCarty, 2001; Liu et al., 2001)

Organic matter in wastewater is used by microorganisms use as a carbon source to obtain energy and produce new cells. The catabolic process transforms organic matter into energy and metabolites. Maintenance requirement meets with this energy and then reused to support the anabolic process. The important role of Adenosine triphosphate (ATP) in the process of substrate oxidation (catabolism) and cell synthesis (anabolism) as briefly indicated in Figure 2.4. ATP is produced by oxidative phosphorylation for most bacteria. Oxidative-phosphorylation is a process contained electrons transported from an electron donor (substrate) to a final electron acceptor (Low and Chase, 1998). Cell anabolism, growth and maintenance functions used the energy released during the conversion of ATP back to ADP+P. The growth yield is directly proportional to the quantity of energy produced (Foladori et al., 2010).

The phenomenon of uncoupled metabolism is encountered in conditions such as presence of inhibitory compounds or some heavy metals (Zn, Ni, Cu, Cr), not optimal temperatures, nutrient limitations, during transition periods in which cells are adjusting to changes in their environment (Chudoba et al., 1992; Mayhew and Stephenson, 1998; Low and Chase, 1999a; Liu, 2000). The overall ATP generation in anoxic or anaerobic catabolism is much lower than in aerobic processes. Consequently, anoxic or anaerobic metabolism is considerably less efficient than aerobic metabolism, resulting in much lower biomass yields (Low and Chase, 1999a).

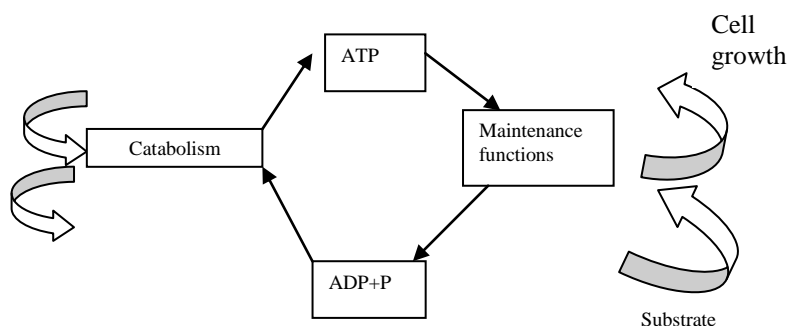


Figure 2.4 Catabolism and Anabolism

Cell composition, growth rate and maintenance requirements are related to the biomass grown per gram of ATP consumed. The uncoupled metabolism in mixed cultures will favour the efficient species in the production and exploitation of ATP (Low and Chase, 1999a). Uncoupled metabolism can be obtained by:

- some metabolic uncouplers are used in order to minimize the excess sludge production such as nitrophenol, chlorophenol, 3,3',4',5-tetrachlorosalysilanilid (TCS), 2,4,5-trichlorphenol(TCP), carbonilcyanide-p trifluorometooksifenilhidrazon, cresol, aminophenol (Liu, 2001).
- subjecting activated sludge to cyclic aerobic and anaerobic conditions by means of side-stream anaerobic reactors. By inserting an aerobic stage the most energy, efficient electron acceptors (such as oxygen and nitrate) are no longer available. An example is the OSA process (Oxic-Settling-Anaerobic), which is made up of a conventional activated sludge stage

integrated with anaerobic digester supplied by the return sludge (Foladori et al., 2010).

Briefly, under energy uncoupling conditions, microorganisms can consume substrate (Liu et al., 2001). As a result, the activated sludge growth will decrease apparently. So, biomass synthesis and the excess sludge production decreases (Gürtekin and Şekerdağ, 2006).

2.2.3 Endogenous Metabolism

Bacteria are used energy obtained from the substrate biodegradation for maintenance requirements and the synthesis of new cellular biomass when external substrate is available. When the external substrate is absent, only a part of cellular constituents can be oxidized to carbon dioxide and water to produce the energy.

Endogenous respiration is the respiration with oxygen or nitrate using cell internal components according to van Loodsrecht and Henze (1999). In other words, the endogenous respiration is the autodigestion of biomass (Perez-Elvira et al, 2006). The endogenous metabolism described the usage of storage compounds for maintenance purposes when the external substrate is completely consumed. The incoming substrate could be finally respired to carbon dioxide and water, while results in a lower biomass production in endogenous metabolism (Gaudy, 1980; Martinage and Paul, 2000). Endogenous metabolism should be defined as a state when no net growth is possible, but cells consume energy to remain viable (Foladori et al., 2010). The control of endogenous respiration would have as much practical significance as the control of microbial growth and substrate removal in wastewater treatment processes (Perez-Elvira et al., 2006). The maintenance and the endogenous respiration concept are mathematically equivalent and these two concepts can not easily be distinguished from each other under experimental conditions. When energy requirements for maintenance functions increase, the amount of energy available for the growth biomass decreases. Therefore, a significant reduction of sludge production can be achieved by maximizing the energy used for maintenance requirements rather than for cellular synthesis (Low and Chase, 1999b).

Several hypotheses explain the phenomenon of endogenous respiration in the absence of external substrate, such as:

- oxidation of the cellular components,
- conversion of intracellular reserve material such as glycogen,
- decay of cells and consumption of the dead cells to synthesize new biomass (cryptic growth) (Foladori et al., 2010).

In activated sludge plants with long SRT operating at low applied loads or low F/M ratios, the sludge production is lower. Biomass production can be reduced in aerobic reactors by 12 % by endogenous metabolism when biomass concentration is increased from 3-6 g/L. When biomass concentration is increased from 1.7 to 10.3 g/L by increasing the SRT, the reduction reaches 44 % (Low and Chase, 1999a). However, there is a limit to the potential increase of sludge concentration in conventional activated sludge systems. Only systems based on membrane filtration (MBR) or biofilm processes (granular sludge) can overcome this limit (Foladori et al., 2010).

The endogenous metabolism is occurred in the following processes:

- low-loaded activated sludge plants extended aeration processes stabilization of sludge in aerobic and anaerobic digestion
- MBR reactors, operating with high concentrations of solids, long SRT and low organic loads. SRT can be controlled independently from hydraulic retention time (HRT) which will result in a higher sludge concentration. When this sludge loading rate becomes low enough, little or no excess sludge is produced (Gyhoot and Verstraete, 1999; Wagner&Rosenwinkel, 2000). In these systems, it would be theoretically possible to reach a balance, in which the energy obtained from substrate biodegradation is equal to the energy required for maintenance. Consequently, the production of new biomass could theoretically reach zero (Gyhoot and Verstraete, 1999; Wagner and Rosenwinkel, 2000).

- granular sludge systems, which are based on a self-immobilization of microorganisms treating wastewater, and are characterized by good settleability, strong microbial structure, high biomass retention and low sludge production (Foladori et al., 2010).

2.2.4 Microbial Predation

Sludge production could be reduced by increasing the microbial predation considering a biological wastewater process as an habitat for bacteria and other organisms (Perez-Elvira et al, 2006; Foladori et al., 2010). Higher organisms such as protozoa and metazoan use bacteria as a food source. The total amount of biomass decreases and the transfer to higher trophic level of the food chain occur when one organism eats another. Part of the biomass and the potential energy is lost as heat. It leads to reduced growth of biomass and lower sludge production. The main drawback of the predation process is the difficulty to ensure stable, long-term, favourable conditions for predator development and reproduction. The most common predators of bacteria, making up around 5 % of the total dry weight of a wastewater biomass are protozoa (Perez-Elvira et al, 2006).

Aquatic oligochaetes may be use for treatment and reduction of excess sludge. Oligochaetes can be used as a predator either in the wastewater handling units or in the sludge handling units. The oligochaetes can be divided into two groups. 1) the large aquatic worms such as Tubificidae, Lubriculidae 2) the small aquatic worms such as Naididae, Aelosomatidae (Foladori et al., 2010).

- ✓ Some cautions are required in the use of predatory activity to reduce the overall biomass production. Advantages (✓) and disadvantages (X) of predation on bacreria are as follows:
- ✓ Large application field today,
- X The worms growth is still uncontrollable, especially in the full-scale application,
- X High capital and operation costs (Perez-Elvira et al, 2006).

2.3 Sludge Minimization Techniques Applied During Wastewater Treatment

Secondary sewage treatment plants are being built rapidly throughout the country especially in developing countries such as China. With the increasing in applications of activated sludge processes, huge amount of excess sludge is produced daily as byproduct of the transformation of dissolved and suspended organic pollutants into biomass and evolved gases (CO_2 , CH_4 , N_2 and SO_2). Due to the fact that separation, dewatering, treatment and disposal of sludge represents major capital and operation cost. Furthermore, the minimization of sludge yield has become more important due to the rising costs and restrictions on sludge disposal (Gyhoot and Verstraete, 1999).

Approximately half the completely operational cost for domestic wastewater treatment should be spent to the treatment and disposal of excess sludge in a biological wastewater treatment systems (Song et al., 2003). Excess sludge produced from the biological treatment process is a secondary solid waste must be disposed of in a safe and cost effective manner. Chen et al., (2003) reported that the treatment of the excess sludge may account for 25 % up to 65 % of the total plant operation cost. Beside this, Saby et al., (2002) also reported that the treatment and ultimate disposal of excess sludge are expensive which usually accounts for 30-60 % of the total operational cost in a conventional activated sludge treatment plant. For the disposal of excess sludge, many treatment process such as dewatering, digestion, burning, landfilling and use in agriculture accounting for nearly 90 % of total sludge production in EU have been used. However, land application of sewage sludge is restricted to prevent to health risks due to potentially toxic elements in the sewage sludge. Difficulties in finding land space and stringent regulations related to the design and operation of new landfills restricted the application of landfilling. Incineration is the final option for sewage sludge disposal with ash generation. Ash cannot be disposed elsewhere due to the high heavy metals content and general toxicity. Hence, the current legal constraints, the rising costs and public sensitivity of sewage sludge disposal have provided considerable impetus to develop new strategies and technologies for minimization of sludge production. So, the studies related to the reduction of sludge produced in the wastewater treatment process become more of an issue (He et al., 2006; Wei et al., 2003).

In recent years, many papers have introduced a series of methods reducing excess biomass production in activated sludge biological treatment system (Zhu et al, 2005). An ideal way to solve sludge-associated problems is to reduce sludge production in the wastewater treatment rather than the post-treatment of the sludge produced (Wei et al., 2003).

In the wastewater handling units, the sludge reduction techniques is used to reduce sludge production directly during wastewater treatment, rather than performing post-treatments of sludge after production. The most widely used techniques are based on cell lysis-cryptic growth, uncoupled metabolism, endogenous metabolism and microbial predation (Foladori et al., 2010).

The reduction techniques based on lysis-cryptic growth are enzymatic hydrolysis with/without added enzymes, mechanical treatments; treatment with ultrasound, thermal treatment, chemical and thermo-chemical hydrolysis, oxidation with ozone or other strong oxidants, electrical treatment and a combination of the above. Addition of chemical metabolic uncouplers and side-stream anaerobic reactor is based on uncoupling metabolism. Extended aeration processes, MBRs and granular sludge techniques and predation by protozoa and metazoan are based on endogenous mechanism and microbial predation, respectively, as mentioned before. In the following sections, a short description is given for each alternative technique presented above.

2.3.1 Enzymatic Hydrolysis with Added Enzymes and by Thermophilic Bacteria

Enzymatic treatment of sludge is based on the mechanisms of solubilization, cell lysis and cryptic growth. Hydrolytic enzymes adsorb the sludge-substrate and the solid solubilization and biodegradation enhancement can be provided by the attack of enzymes to the polymeric substances. The addition of enzymes such as protease, lipase, cellulose, emicellulase and amylase can be used for the hydrolysis of organic matter, for the improvement of sludge biodegradation and for reduction or to enhance organic waste degradation considering the high presence of proteins, carbohydrates and lipids in the composition of excess sludge (Foladori et al., 2010).

In an aerobic reactor, part of the return sludge is subjected to the enzymatic hydrolysis by thermophilic bacteria in this process based on a thermal action and an enzymatic attack occurring at thermophilic temperatures. The lysated sludge is then recirculated in the activated sludge stages where cryptic growth occurs (Foladori et al., 2010).

Enzymatic reactions are the basis of a novel wastewater treatment process, formed by combining the conventional activated sludge system with thermophilic aerobic sludge digester in which the excess sludge is solubilized by thermophilic bacteria. In this process, a portion of return sludge injected to the thermophilic aerobic digester and sludge is solubilized by thermophilic bacteria and mineralized by mesophilic bacteria. The solubilized sludge is returned to the aeration tank to further degradation. The results showed 93 % overall excess sludge reduction and high BOD removal efficiency (Sakai et al., 2000; Shiota et al., 2002).

The sludge can be mechanically thickened in order to save energy when heating the sludge before entering the thermophilic reactor. Thermophilic bacteria produce hydrolytic enzymes such as thermostable extracellular protease, responsible of the enhancement of sludge solubilization compared to the thermal action alone in the thermophilic reactor at temperatures of 55-70 °C (HRT:1-3 d). Thermophilic bacteria then pass from the thermophilic aerobic reactor to the activated sludge stage, where they become inactive and form spores which return to the thermophilic aerobic reactor. The thermal affect also render the cells in sludge more susceptible to enzyme attack under thermophilic temperatures. VSS solubilization is 30-40 % and causes a high strength lysate, recirculated in the activated sludge stage (Foladori et al., 2010).

Biolysis E developed by Ondeo-Degremont consists of drawing mixed liquor from activated sludge basin, thickening it and then passing it through a thermophilic enzymatic reactor operating at about 50-60 °C. A particular type of microbe was developed under these conditions. The microbes attacked the outer membrane of the bacteria. The enzymes released by the bacteria. The heated and degraded sludge passed through a heat exchanger to recover a part of its energy prior to activated

sludge tank. Results showed 30-80 % sludge reduction with no external enzyme (Perez-Elvira et al., 2006).

2.3.2 Mechanical Disintegration

The process is based on the cell lysis-cryptic growth. In the mechanical disintegration sludge is disintegrated and lysate obtained is recirculated into the activated sludge reactors. Several systems aimed to enhance sludge solubilization with bacteria cell disintegration and disaggregation of biological flocs have been proposed for the mechanical disintegration of sludge. In these systems, energy is supplied as pressure or translation movements. In general, at low applied energy only floc disintegration is observed, while high energy is required to damage microbial cells (Foladori et al., 2010).

2.3.3 Ultrasonic Disintegration

The basic mechanism of ultrasonic disintegration is cell lysis cryptic growth. The most important mechanism of ultrasonic disintegration is ultrasonic cavitation. It is advantageous to apply ultrasounds at low frequencies and at high energy levels. The ultrasonic disintegration treatment consists of an ultrasound generator operating at frequencies of 20-40 kHz and in a device, which usually is a sonotrode, to transmit mechanical impulses to the bulk liquid. In the application of ultrasounds, pressure waves lead to cavitation bubbles forming in the liquid phase. Then released high energy cause sludge disintegration and the rupture of microbial cells. A part of the return sludge is treated continuously or in batch mode in a contact reactor equipped with sonotrodes in the ultrasonic disintegration integrated in the wastewater handling units. The subsequent biodegradation of lysate is completed in the activated sludge stage (Foladori et al., 2010).

A reduction of sludge production of up to 90 % can be achieved applying Es of 108,000 kJ/kgTS in a lab-scale SBR system fed with synthetic wastewater and integrated with an ultrasonic treatment (Zhang et al., 2007). This Es is very high,

causing an equally high-energy consumption. This operational cost is not economic and such high reduction efficiency is not possible with real wastewater.

In an activated sludge system operated with intermittent aeration, 30 % of the daily sludge was sonicated and the lysate recirculated to the activated sludge tank to improve denitrification. 25 % of excess sludge reduction was obtained and the dewaterability of the sludge was improved 2 % (Neis et al., 2008).

Pham et al., (2009) studied the pre-treatment of wastewater sludge by ultrasonic waves at frequency of 20 kHz using fully automated lab-scale ultrasonication equipment. The optimal conditions of ultrasonic pre-treatment were $0.75\text{W}/\text{cm}^2$ 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.

Aerobic and anaerobic digestions were compared in reactors fed with sonicated activated sludge by Salsabil et al., (2009). Sludge sonication prior to aerobic digestion in the aim of enhancing sludge reduction was inconclusive. Under anaerobic conditions, the enhancement of sludge reduction due to sonication depended on the disintegration degree of the sludge. The combination of high disintegration degree of sonicated sludge prior to an anaerobic digestion led to very good results in term of sludge reduction (80 %).

Hirooka et al., (2009) used nozzle-cavitation treatment to reduce excess sludge production in a dairy wastewater treatment plant. During the 450-d pilot-scale membrane bioreactor (MBR) operation, when 300 L of the sludge mixed liquor was disintegrated per day by the nozzle-cavitation treatment with the addition of sodium hydrate and returned to the MBR. The amount of excess sludge produced was reduced by 80 % compared with that when sludge was not disintegrated. It was concluded that the nozzle-cavitation treatment did not have a negative impact on the performance of the MBR. The estimation of the inorganic material balance showed that when the mass of the excess sludge was decreased, the inorganic content of the

activated sludge increased and some part of the inorganic material was simultaneously solubilized in the effluent.

He et al., (2011) studied the influences of operational parameters to improve the energy efficiency during ‘ultrasonic lysis–cryptic growth’ sludge reduction. Subsequent batch reactor with a HRT of 8 h was used to treat urban sewage, and ultrasound wave with a specific energy of 20 kWh/kg TS was employed for sludge lysis. Results showed that the most important operational parameter was the proportion of sonicated sludge (SP), which determined the energy consumption and significantly impacted the energy efficiency. Higher SP caused heavier sludge reduction but more energy consumption; when SP was 30 %, the excess sludge reduction was the greatest (67.6 %) and the energy consumption was the highest (0.101 kWh/d).

2.3.4 Thermal Treatment

The disaggregation of sludge flocs, high level of solubilization, cell lysis and release of intracellular bound water can be provided by the application of thermal treatment of sludge. The main parameter for thermal treatment is temperature. The highest sludge solubilization is confirmed around 180 °C and higher temperatures do not causes significant increase of sludge biodegradability by several investigations. However, the thermal treatment at $T < 100$ °C integrated in the activated sludge systems causes a significant reduction of excess sludge production related to an immediate decrease of biological activity and an increase of maintenance requirement. In the thermal treatment applied for sludge reduction, the sludge is heated by steam and/or by heat exchangers prior to enter a contact reactor, then lysated sludge is recirculated in the activated sludge system (Foladori et al., 2010).

The application of a mechanical treatment induce the following changes in sludge properties (Muller et al., 2004).

- damage of microorganisms: damaged microorganisms undergo a rapid lysis and the loss of intracellular compounds followed by hydrolysis. This

phenomenon favours the sludge reduction due to the mechanism of cell lysis-cryptic growth.

- floc size reduction,
- sludge solubilization,
- improvement/worsening of settling and dewatering
- foaming reduction: in some cases, in anaerobic digester
- increased flocculant demand: reducing particle size and increasing the specific surface could lead to a greater electrical charge on particle surfaces; this lead to a greater demand for chemicals to neutralize the charges during conditioning of sludge. As a result, a greater quantity of flocculants are needed for sludge dewatering,
- viscosity reduction.

2.3.5 Chemical and Thermo-Chemical Hydrolysis

The process of cell lysis-cryptic growth is promoted by an increase in temperature with a strong change in pH, cell breakage in chemical or thermo-chemical treatments based on alkaline or acid reagents. The thermo-chemical treatment has a higher efficiency in sludge solubilization when applied at the same temperature compared to the simple thermal treatment due to the effect of reagents. Alkaline reagents such as NaOH most effectively used, are considered to be more efficient than the acids (HCl or H₂SO₄). pH>10, temperature>50-60 °C, contact time less than 1h are the optimal conditions to induce sludge solubilization and reduce costs are, since longer time do not improve solubilization effectively. The lysate is recirculated in the activated sludge for further biodegradation after the hydrolysis. The biodegradability of excess sludge increases with the thermo-chemical treatment and when lysate is recirculated the cryptic growth caused the reduction of excess sludge production (Foladori et al., 2010).

Sludge reduction by alkaline treatment achieved at 60 °C, pH:10 for 20 min in a lab scale plant fed with synthetic wastewater. A 37 % reduction of sludge production was obtained compared to the control (Rocher et al., 2001). However, the integration

of a thermo-chemical treatment in the wastewater handling units at full scale is rare and it is difficult to find successful results in the literature. The waste energy for heating a low concentrated return sludge and increased reagent dosage for changing pH restricted the application of process.

To enhance nutrient removal performance and reduce disposal amount of waste activated sludge (WAS), a pilot-scale continuous system consisting of a 2-step sludge alkaline fermentation process and an A²O reactor was proposed by Gao et al., (2011). The feasibility of WAS reducing and resourcing by alkaline fermentation was investigated. Volatile fatty acids (VFA) yield was higher under alkaline condition than that under acidic condition. The results showed that 38.2 % of sludge was hydrolyzed, 19.7 % was finally acidified into VFA, and as high as 42.1 % of WAS was reduced. Sludge reduction and enhanced nutrient removal could be achieved simultaneously in the proposed system.

Paul et al., (2006) evaluated of the efficiency and the economics of disintegration techniques that have demonstrated their potential to reduce the excess sludge production when combined to an activated sludge plant fed with a real urban wastewater. A high ESP reduction rate is achievable (more than 40 %) by using disintegration technique such as a thermal (95°C), an ozonation or a hydrogen peroxide treatment. The ozone appeared to be the most interesting route for sludge reduction but the heating route is also economically competitive with conventional sludge treatment and disposal especially if stringent constraints on the sanitary quality of the sludge are imposed.

2.3.6 Oxidation with Ozone (Ozonation)

The treatment based on ozone integrated in the wastewater handling units for sludge reduction has been proposed the mid 1990s. Up to date, sludge ozonation has been successfully applied at full-scale both in industrial and municipal WWTPs. Sludge ozonation causes disintegration, cell lysis, organic matter solubilization and mineralization (Foladori et al., 2010). The mechanism of ozonation will be explained in the following sections in details.

2.3.7 Oxidation with Strong Oxidants (Different from ozone)

The ozonation treatment increases operational cost significantly because of the expensive ozone generation and application (Saby et al., 2002). The advanced oxidation processes include other oxidants such as hydroxide peroxide or chlorine require less expensive equipment and less qualified personnel compared to ozonation (Foladori et al., 2010).

In order to improve the cost of sludge minimization, chlorination can be tried to replace ozonation as a strong oxidizer in reducing the excess sludge. The chlorination operation cost is only 10 % of that of ozonation in terms of disinfection practice. Beside this, the trihalomethanes (THMs) will be produced and may appear in treated water but an acceptable level for effluent discharge. Saby et al., (2002) investigated the possibility of using chlorination to achieve excess sludge minimization. A batch operation of sludge chlorination with a certain amount of excess sludge was conducted at various chlorine doses once per day. The chlorinated sludge liquor was then returned to a continuous activated sludge system upon the completion of sludge chlorination. Two identical activated sludge membrane bioreactors (MBRs) were operated with a continuous supply of synthetic wastewater for cultivation for 2 months. The MBRs combined a biological process with a membrane separation technique, claiming the advantages of a complete dissociation between hydraulic and sludge retention times so that sludge production rate can be determined precisely. The systems used a 10 L single column system with an inner membrane separator are shown in Figure 2.5.

The formation of THMs is the main disadvantage of the sludge chlorination. Because of the detection of effluent low THMs concentration such as 200 ppb due to the volatilization of THMs during the chlorine treatment, the THMs formation in water did not become an issue in the process; nevertheless, it seemed necessary to investigate the gas emission during the chlorination step. A treatment of the gas produced in the chlorine reactor could be investigated to limit the impact on VOC. Furthermore, soluble COD in the sludge increased significantly in the initial stage of the operation of the system. However, after a few weeks of operation, the soluble

COD concentration decreased but still remained too high compared to the reference system. Because of the operational problems related to sludge chlorination step can limit the application of chlorination-based sludge minimization technique in conventional treatment plants (Saby et al., 2002). The excess sludge minimization can be achieved 65 % sludge reduction with a dose of $0.066 \text{ gCl}_2/\text{gMLSS}$. However, this process has some disadvantages such as THMs formation, deterioration of sludge settleability and increasing of effluent COD contents (Wei et al., 2003).

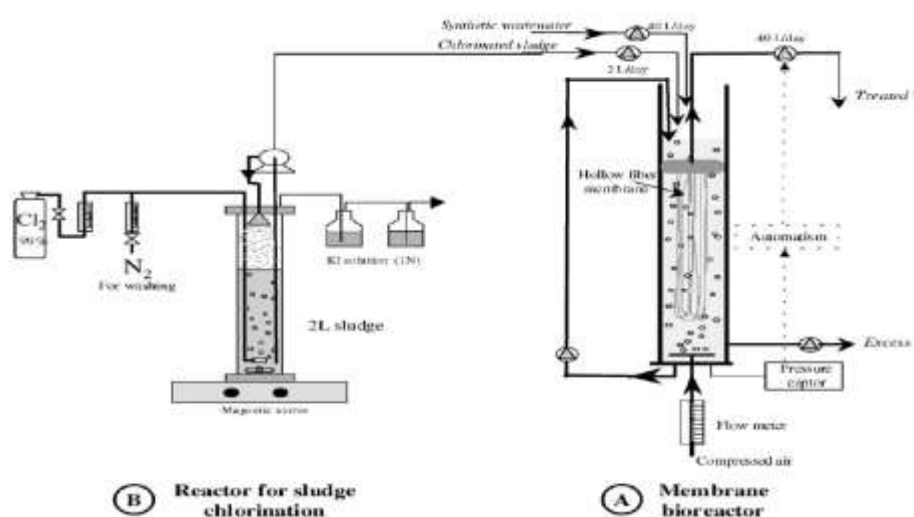


Figure 2.5 Membrane biological reactor (A) and chlorination setup (B)

2.3.8 Electrical Treatment

For treating sludge in wastewater handling units due to the breakage effect on microbial cells, the pulsed electrical field (PEF) has been proposed by Heinz (2007). After the application of PEF, treating part of the return sludge is then recirculated in activated sludge system. In order to increase the solid concentration up to 60 gTSS/L , while maintaining pumpability, thickening of sludge before PEF is advised. 27-45 % of TSS reduction was achieved at a specific energy of $100,000 \text{ KJ/m}^3$ depending on the type of sludge. However, this application is still at pilot-scale and further investigation is needed to fully understand the process (Foladori et al., 2010).

2.3.9 Addition of Metabolic Uncouplers

The mechanism of oxidative phosphorylation can be effectively uncoupled by the addition of chemical metabolic uncouplers such as 2,4-dinitrophenol (dNP), para-nitrophenol (pNP), pentachlorophenol (PCP) and 3,3',4',5-tetrachlorosalicylanilide (TCS) for the reduction of sludge production (Perez Elvira et al., 2006; Foladori et al., 2010). Growth efficiency of activated sludge is lower in the presence of uncouplers. In biological wastewater treatment processes, a decreased biomass yield per unit mass of substrate removed demonstrated uncoupled metabolism (Low and Chase, 1999).

The process is based on the simple addition of the chemical metabolic uncouplers to the wastewater handling units; the effect of the compounds added occurs directly during contact with activated sludge (Foladori et al., 2010).

Biomass population dynamics, biomass surface chemistry and consequently settling characteristics are affected by reactor conditions. Variations in settleability have been related to the ratios of floc-forming and filamentous microorganisms. Extracellular polymer production and cation concentration have also been correlated with settleability. Metabolic uncoupling may influence growth rates of individual species in the population differently and population dynamics may be altered (Low and Chase, 1999).

Uncoupler-induced energy spilling process was investigated for minimization of excess sludge production by several researchers. In a laboratory scale activated sludge system, Low and Chase (1999), reported that biomass production was reduced by 49 % when pNP was added to the culture. At a pNP concentration of 120 mg/L, no sludge production was observed. However, it was found that most of the organic protonophores are xenobiotic and potentially harmful to the environment and the application of this study in wastewater treatment practice would not be very safety. TCS seems to be more environmentally among these uncouplers. Cook and Russell (1994) found that the majority of organic substrate was oxidized via energy spilling and did not go to biosynthesis functions in TCS-containing microbial culture. In a

batch culture of activated sludge, Chen et al., (2000) also reported that the observed growth yield was reduced by 78 % at a TCS concentration of 0.8 mg/L as compared with control culture without addition of TCS, but no significant effect on substrate removal kinetics. It seems that the loss of energy by uncoupling metabolism can be used for reduction of excess sludge production (Liu et al., 2001).

Loomis and Lipmann (Okey and Stensel, 1993) studied 2,4-dinitrophenol (dNP) in 1948. Several chlorinated and nitrated phenols and benzoates were tested for their short-term effects on cell yield, COD consumption, and respiration of activated sludge. 2,4-dichlorophenol (DCP) concentration of 30 mg/l achieved about 50 % biomass reduction compared with no uncoupler 2,4,5-trichlorophenol (TCP), o-nitro-p-chlorophenol, 2,4,6-tribromophenol, 2,6-dibromo-4-nitrophenol, and DCP were strongest uncouplers. The effects of 12 chemical uncouplers on biomass yields were compared in batch cultures for screening commercially available chemical uncouplers by Strand et al., (1999). The most effective uncouplers, 2,4,5 trichlorophenol (TCP) was tested in a bench scale, continuous flow and completely mixed activated sludge system treating simulated municipal wastewater, respectively. Initially, TCP addition reduced average yield by approximately 50 %, but sludge yield increased as TCP levels in the reactor decreased after 80 days. According to the results, the addition of chemical uncouplers to biological wastewater treatment systems can significantly reduce sludge production, however, long term application of uncouplers cannot demonstrate significantly reduction effect (Wei et al., 2003).

Chen et al., (2001) studied the feasibility of using 3,3',4',5-tetrachlorosalicylanilide (TCS) as a metabolic uncoupler to reduce the sludge growth in activated sludge cultures. The results have confirmed that TCS is an effective chemical agent in limiting the sludge growth when its concentration is > 0,4 mg/L. It was demonstrated that TCS was able to reduce sludge growth rate by around 40 % when the TCS concentration was 0.8 mg/L.

Yang et al., (2003) compared the effectiveness of four metabolic uncouplers (p-chlorophenol, m-chlorophenol, m- nitrophenol and o-nitrophenol) in reducing sludge

production from an activated sludge process. A series of batch experiments fed with different concentrations of individual metabolic uncouplers were conducted at constant initial biomass and glucose concentrations. Results showed that sludge production was reduced with the increase of metabolic uncoupler concentration. Among four metabolic uncouplers studied, m-chlorophenol was the most effective in reducing sludge production, and had less effect on the process performance e.g. 86.9 % of sludge reduction was achieved at a m-chlorophenol concentration of 20 mg/L with the COD removal efficiency was lowered only by 13.2 % as compared to the control test. It appears that selection of metabolic uncoupler and optimization of its dosage should be based on a compromise of the desired sludge reduction and system performance.

2.3.10 Anaerobic Side-Stream Reactor

The anaerobic side-stream reactor (SSR) process draws attention because of the significant sludge reduction without causing negative effects on sludge settling and effluent properties among several sludge reduction strategies (Novak et al., 2007). There are some configuration variations in the anaerobic SSR activated sludge process consist of an aeration basin, a settling tank, and an anaerobic SSR. A portion of return sludge or excess sludge is recycled through the anaerobic SSR with intentionally minimized sludge wasting. It has been reported that the solids retention time (SRT) of this anaerobic SSR is usually maintained at 10 days under ambient temperature conditions (Novak et al., 2007; Johnson et al., 2008). A few studies have analyzed the reduced sludge yield in the anaerobic SSR process by performing overall solids and COD measurements. For example, Goel and Noguera (2006) showed from their laboratory enhanced biological phosphorous removal (EBPR) process that the incorporation of an anaerobic SSR into EBPR led to 63 % sludge reduction (sludge yield at 0.16 mgVSS/mgCOD). Novak et al., (2007) also showed that activated sludge with an anaerobic SSR resulted in about 60 % less sludge generation (sludge yield from 0.11 to 0.15 mgVSS/mgCOD depending on the sludge interchange rate) than the control activated sludge system. Novak et al. (2007) proposed that reduction of iron in the anaerobic SSR cause release of ironbound organic matter, primarily proteins that are then rapidly degraded under aerobic

conditions when anaerobic sludge is recycled back to the aeration basin for the possible mechanism of sludge reduction in the anaerobic SSR process. Recently, Chon et al. (2011a) demonstrated that about half of overall sludge reduction occurred in the aeration reactor through a long SRT condition while the other half was directly achieved by the anaerobic SSR. The anaerobic SSR process, which should show extremely long SRT due to minimal sludge wasting, has been reported to operate well without any evidence of the upset conditions (i.e., settling properties and effluent quality). Furthermore, determining SRT itself is also rather complicated for this process due to continuous recirculation of sludge between the mainstream and the side-stream reactor and gradual accumulation of some truly inert solids in the system. To gain a better insight of the anaerobic SSR activated sludge process and to further identify the mechanism of sludge reduction in this process, Chon et al., (2011b) compared five activated sludge systems with different side stream or conventional sludge treatment schemes under control, parallel reactor operation. They are the activated sludge systems with: 1) aerobic SSR, 2) anaerobic SSR, 3) aerobic digester, 4) anaerobic digester, and 5) no sludge wastage. A combination of synthetic wastewater and real wastewater was used as a feed substrate to better mimic real operation system. Since solids are the one most important parameter to assess the anaerobic SSR system. Sludges from each system at the end of operation were subjected to both batch anaerobic and aerobic digestion to investigate the remaining pools of digestible materials within activated sludge flocs even after vigorous sludge reduction via side-stream treatment. Among the five different processes, the anaerobic SSR process produced the lowest sludge generation. Only the anaerobic SSR process led to sound operational performances seen with good effluent TSS and SVI data. The anaerobic SSR process degraded both aerobically and anaerobically digestible materials and continuously refreshed the floc composition leading to effective flocculation and good effluent quality. Reduced sludge yield obtained from an extended SRT operation. Another SSR system (activated sludge with aerobic SSR) still produced better sludge reduction than the control activated sludge with conventional digestion and the extended SRT system, suggesting that cyclic feast/fasting conditions even under the same aerobic environment could bring further sludge reduction. The settling property, however,

became challenging as the system was operated for a longer period. Therefore, recirculation of sludge under aerobic feast and anaerobic fasting condition was the necessary setting to achieve the most effective sludge reduction with sound operational performances (Chon et al., 2011b).

Oxic-Settling-Anaerobic (OSA) process composed of the integration of an anaerobic reactor fed with part of the return sludge in an activated sludge process has been known a successful process for significant sludge reduction. The sludge reduction phenomenon can be explained with the cyclic alternation of aerobic/anaerobic conditions uncouples catabolism and anabolism, decreasing in growth yield. However, the mechanisms causing sludge reduction with the OSA systems have not yet fully understood. The OSA system will be discussed in the following sections in details.

The process known as Cannibal system is based on physical treatments and a biological anaerobic reactor. This process requires the addition of a mixed tank which has to operate without oxygen (only short periodic aeration), at a high biomass concentration, a sufficiently long retention time (SRT:8-15 d), an interchange rate between 4 % and 7 %, without any wastewater feeding and maintaining a low redox potential (ORP) set approximately at -250 mV. A reduction of the observed sludge yield of 60 % was demonstrated in pilot-scale plants fed with synthetic wastewater. Field operations indicate that the Cannibal process allows a significant reduction of sludge, but only a few studies have been conducted to fully understand and explain the mechanisms causing sludge reduction (Foladori et al., 2010).

2.3.11 Extended Aeration Process

The excess sludge production is generally reduced due to lower observed biomass yield, which depends by SRT when activated sludge system operates at a sufficiently long sludge age and low F/M ratio, such as in extended aeration processes (Foladori et al., 2010). Extended aeration processes are known to produce little sludge, as they extend the oxidation to the stabilization of the sludge (Perez-Elvira et al., 2006).

Extended aeration processes require long aeration times and low applied organic loads ($0.04 \text{ kgBOD}_5/\text{kgTSS.d}$) compared to conventional activated sludge processes ($0.08\text{-}0.15 \text{ kgBOD}_5/\text{kgTSS.d}$). Due to inert solid part of sludge, entering the system with the effluent wastewater, which accumulates in the sludge, theoretical zero sludge production is not possible even for long SRT. However, in practice, a significantly lower quantity of excess sludge is produced compared to conventional activated sludge processes (Foladori et al., 2010). However, these processes have a very high footprint and energy demands (Perez-Elvira et al., 2006).

2.3.12 Membrane Biological Reactors (MBR)

Membrane bioreactors present an alternative process for activated sludge process for sludge retention and separation. Activated sludge process coupled with membrane process replaces sedimentation tank for solid/liquid separation and serves as an advanced treatment unit for coliform bacteria, which cannot remove with conventional processes (Yoon et al., 2004). In MBR systems, the sludge and effluent separate in a highly efficient membrane module rather than in a conventional gravity settler (Foladori et al., 2010). The second sedimentation tank is eliminated in membrane bioreactors and the use of membrane process provides supernatant separation. MBR presents some advantages such as solid retention physically, elimination of sedimentation tank and related problems, the controlling of sludge retention time and the degradation and retention of higher molecular weighted compound (Mahmood and Elliot, 2006). Due to higher sludge concentration ($7\text{-}20 \text{ gTSS/L}$), lower F/M ratio and longer SRT, the sludge production in the MBRs is usually expected to be lower than in conventional activated sludge processes (Foladori et al., 2010). The high SS concentration caused long sludge retention time and low food/microorganisms (F/M) ratio can be achieved in a membrane bioreactor by retention sludge with membrane process. Low F/M ratio with long sludge retention time leads to less sludge production. In other words, less sludge production can be obtained with longer sludge retention time and the higher loading rate in MBRs. In MBR, sludge production is reduced by increasing sludge age (Mahmood and Elliot, 2006). It was found that MBR was operated for 300 days without sludge discharged at prolonged SRT condition (Sun et al., 2007). However, a MBR easily

satisfies a long SRT condition even at a high organic loading without deteriorating the effluent quality (Yamamoto, 2001). Ghyoot and Verstraete, (1999) studied two-stage systems consist of a completely mixed reactor and an activated sludge system. The results indicated that the MBR systems yielded a 20-30 % lower sludge production than the conventional activated sludge system under similar conditions. Beside this, sludge reduction capacity of MBR can be increased with addition of some process such as Fenton and ozone oxidation and addition of thermal treatment. The integration of MBRs with some disintegration techniques (alkaline treatment, ozonation, ultrasonic disintegration) have also been proposed, with the aim to increase the decay rate of biomass, maintaining a relatively low TSS concentration in MBRs (Foladori et al., 2010). He and Wei, (2010) studied the minimization of excess sludge produced in the MBR coupled with Fenton oxidation process. It is reported that the addition of Fenton process to MBR could reduce the sludge production. The sludge yield decreased from 0.15 gSS/gCOD to 0.006 gSS/gCOD. He et al., (2006) investigated the effects of ozonation on sludge yield and reported that the average sludge yield were 0.130, 0.082 and 0.039 kgSS/kgCOD when the amount of ozonated sludge was 0 %, 2 %, 4 % of the reactor volume. According to Wang et al., (2008), a zero sludge yield coefficient could be achieved in a MBR coupled with a sludge ozonation process for 8000 mg/L MLSS concentration. Goma et al., (1997) studied a MBR considering the maintenance and cryptic growth phenomena of *Pseudomonas fluorescence* cultures in order to reduce the excess sludge. In the same study, the biomass extracted from a continuous culture and the results showed that thermal treatment induces biomass death and a partial biomass lysis. The sludge production yield was 0.19 g/g with thermal treatment compared to 0.57 g/g without thermal treatment.

MBR cannot be considered as an attractive method from economical perspective. The high cost of supply, maintenance and operation and fouling are some disadvantages of MBR application (Mahmood and Elliot, 2006). In practice, adverse effects on membrane, such as fouling, increased cleaning requirements, oxygen transfer limitations, increased sludge viscosity, worsening in sludge filterability and reduction of biological activity are the drawbacks of MBR due to the high TSS concentrations (Foladori et al., 2010).

2.3.13 Granular Sludge

Granular sludge systems based on a self-immobilization of microorganisms treating wastewater present some advantages compared to conventional activated sludge: 1) very high biomass concentration in the reactor (15-60 kgTSS/m³); 2) very high treated organic loads, up to 10 kgCOD/m³.d; 3) very low sludge production.

The mechanisms of the formation of granules have not fully understood yet. The compact and dense aerobic granules have a strong microbial structure and generally good settleability. The observed sludge yield in granular sludge reaches only 0.27-0.35 kgTSS/kgCOD. Denitrification occurs in the internal part of the granules and the energy available of anabolism is very low, resulting in a limited bacterial growth. The low sludge production is probably due to the endogenous metabolism and the high maintenance requirements (Foladori et al., 2010).

2.3.14 Predation on Bacteria

The presence of protozoa and metazoan in aerobic wastewater treatment processes keep the effluent clear by consuming dispersed bacteria. Protozoa and metazoan were important indicators of process performance and efficiency in biological wastewater treatment processes in the past. Recently, many researchers have focused on sludge reduction induced by grazing on bacteria (Wei et al., 2003). Sludge minimization techniques based on the microorganism predation are attractive methods due to the less energy requirement and no additional pollution (Huang et al., 2007). High-level organisms can predate on bacteria such as protozoa and metazoan. Using these organisms in the activated sludge process is an applied method in order to minimize the sludge production (Wei et al., 2003). Sludge reduction by predation using protozoa and metazoan due to grazing effect is based on the loss of energy in the food chain (Foladori et al., 2010). The energy is lost during the energy transferring from low energy level to high energy level due to the inefficient biomass transformation (Wei et al., 2003). The dissipation of energy is occurred between bacteria and higher organisms in the food chain. The maximum dissipation of energy makes the sludge production minimum (Gürtekin and Şekerdağ, 2006). The total

energy loss will be maximal and total biomass production will be minimal under optimal conditions. The presence of these organisms suppresses the dispersed bacteria growth in the conventional aerobic wastewater treatment processes and encourages the growth of refractory floc and film bacteria which are more protected against predation to degradation (Wei et al., 2003). To manage predators directly within activated sludge is very difficult despite efforts to control the growth and reproduction of predators in the biological systems. Thus, some experiences developed predator-reactors separate from activated sludge stages in order to favour the growth of predators. The performance of metazoan in sludge reduction is higher than protozoa (Foladori et al., 2010). Two stages developed in order to tackle this problem. First stage bacterial stage; is operated with a short sludge retention time as a chemostat to provide the dispersed bacteria growth. Second stage is designed as a ripper with long sludge retention time to provide growth of protozoa and metazoan (Wei et al., 2003). In practice, this two-stage system greatly increases the operational costs due to high volume requirement and thus it is generally not feasible to apply for municipal wastewater (Foladori et al., 2010).

Most protozoa have small size in the activated sludge process. Worms are the biggest organisms observed in activated sludge microscopic survey and they are widely used in the practical application related to the sludge reduction due to their big size compared to protozoa. The most important worm's species are *Aelosomatidae*, *Naididae*, *Pristina*, *Dero* ve *Tubificida* in the activated sludge and trickling filter. *Tubifex tubifex* is preferred in practical application of sludge reduction to micro fauna species (Huang et al., 2007).

Huang et al., (2007) investigated a conventional activated sludge (CAS) process combined with a recycled sludge reactor where *Tubifex tubifex* (one of *Oligochaeta*) was inoculated for sludge reduction. The results showed sludge production could be reduced by *T. Tubifex*'s predation on sludge reactor. The results demonstrated that the existence of *T. Tubifex* did not affect COD and $\text{NH}_4\text{-N}$ removals in the process but led to a slight decrease in TP removal.

Liang et al., (2006) tested sludge reduction in a conventional activated sludge (CAS) process where *Aelosoma Hemprichi* (one species of Oligochaeta) inoculated micro-fauna. The factors affecting the growth of *A. Hemprichi* and the influence of *A. Hemprichi* on treatment performance were investigated. The relative sludge reduction by *A. Hemprichi* was estimated to be about 39-65 %, and the apparent sludge reduction rate per unit weight of *A. Hemiprichi* was from 0.53 to 6.32 mg-USS/mgA. Hemiprichi day. The existence of *A. Hemiprichi* was beneficial to stabilize the sludge settleability and TP removal but did not affect COD and NH₄-N removal in the process. The results indicated that using *A. Hemiprichi* could be used in order to reduce sludge in wastewater.

A method to scale the rate of sludge reduction caused by micro fauna was proposed by Liang et al., (2006). Four micro faunas were compared for sludge reduction rates. The principle of this method is based on the change of carbon forms. The rate of sludge reduction was correlated with the rate at which solids were changed into liquid and gas. Four micro faunas, including *Aeolosoma hemprichi*, *Daphnia magna*, *Tubifex tubifex* and *Physa acuta*, were cultured with sterilized sludge in a covered sterilized bottle and were then isolated from the atmosphere above the liquid phase. The rates of sludge reduction using the four micro faunas were 0.8, 0.18, 0.54 and 0.1 mg-sludge/ (mg-Micro fauna d), respectively, changing with the micro faunas phylum or class and body size. Based on the change of carbon (C) forms, the proposed method produced accurate results similar to those produced using the direct measuring method

Lin et al., (2009) studied the gravel contact oxidation reactor (GCOR) and a conventional activated sludge reactor (ASR) at a molecular level in order to evaluate the variation and structure of the microbial community and their functions to excess sludge reduction. GCOR showed much superior to ASR in terms of biomass consumption with environmental bacteria and other biological parameters for wastewater treatment. MLSS in the sediment tank of GCOR was only 4.5 mg/L, 25 times less than that in ASR 115.4 mg/L at the 60th day, the time of two reactors' normal operation. Diverse microbes and a large amount of biomass attached on the carriers are one of the main functions to excess sludge reduction in GCOR.

A novel Tubificidae-reactor with special porous carrier and combined aeration system was designed to investigate the sludge reduction by Tian et al., (2010). The influences of change in frequency of high-intensity aeration (FHIA), dissolved oxygen (DO) content, initial sludge concentration (ISC) and sludge retention time (SRT) on the immobilization of Tubificidae and sludge reduction were evaluated. In order to optimize the process conditions using the sludge reduction rate and stable immobilization of worms as the target parameters to optimize, and DO as the control factors to be optimized with the fluctuation of influent ISC, while keeping FHIA and SRT at optimum level, the response surface method was applied. Attractive sludge reduction rate (470 mg/L/d) can be obtained using the strategies indicated by the highly correlated model. The optimum conditions were found to be DO of 1.0–1.6 mg/L and ISC of 3000–4000 mg/L respectively, while keeping FHIA at 12 times/d and SRT at 2 d.

Hendrickx et al., (2010) can achieve reduction of the amount of waste sludge from WWTPs with the aquatic worm *Lumbriculus variegatus* in a new reactor concept. The results showed that an aquatic worm reactor has most potential for smaller WWTPs. Decreasing the volumetric load on sludge handling and transport operations will have most impact, even at a relatively low TSS reduction (21 %) by the worms.

Hendrickx et al., (2011) designed a new configuration of the reactor which allows for easy aeration and faeces collection, thereby making it suitable for full scale application. A continuous worm reactor directly treated the daily waste sludge from a lab-scale activated sludge reactor and was successfully operated during a period of nearly eight weeks. The results showed a higher worm growth rate compared to previous experiments with the old configuration, whilst nutrient release was similar. Net growth of worm biomass clearly took place in the worm reactor at a rate of 0.014 d⁻¹.

The secondary sludge degradation by the aquatic Oligochaete worm *Aulophorus furcatus* in a 125 m³ reactor and further sludge conversion in an anaerobic tank were studied by Tamis et al., (2011) via the system operation fed with secondary sludge from a low loaded activated sludge process over a period of 4 years at WWTP

Wolvega, the Netherlands. The surface specific conversion rate reached 140-180 g TSS/m²d and the worm biomass specific conversion rate was 0.5-1 gTSS sludge/gdry weight worms per day. The sludge reduction under optimal conditions in the worm reactor was 30-40 %. Anaerobic digestibility was increased with the worms' activity allowing for future optimization of the total system by maximising sludge reduction and methane formation besides reducing the sludge amount. In the whole system it was possible to reduce the amount of sludge by at least 65 % on TSS basis. This is a much better total conversion than reported for anaerobic biodegradability of secondary sludge of 20-30 % efficiency in terms of TSS reduction.

Wang et al., (2011) operated two submerged anoxic/oxic membrane bioreactors (MBRs) in parallel under same conditions but different aeration intensities. The *Aeolosoma hemprichi* and *Tubificidae* proliferated in the MBR operated under high aeration intensity but were never observed in the MBR with low aeration intensity. Results showed that the presence of aquatic worms decreased the total phosphorus removal efficiency while it had no impacts on chemical oxygen demand and nitrogen removal. High aeration intensity could decrease the floc size and increase dispersed bacteria population, thus providing more feed for the worms. The worm growth led to a reduction of the sludge production, an increase of soluble microbial products, an improvement of sludge settleability and a deterioration of sludge dewaterability. The excess growth of worms resulted in a higher membrane fouling rate in the MBR.

2.4 Mechanism of Sludge Ozonation

A new process for reducing excess sludge production was developed by Yasui and Shibata (1994). The process consists of a sludge ozonation stage and a biodegradation stage (Low and Chase, 1999a; Yasui and Shibata, 1994). A fraction of recycled sludge passes through the ozonation unit and then the ozonated sludge is returned to the bioreactor. The ozonation of sludge results in both solubilization (due to disintegration of suspended solids) and mineralization (due to oxidation of soluble organic matter). The recycling of solubilized sludge into the aeration tank will induce cryptic growth. It was reported that throughout the operation periods of full-scale plants with sludge ozonation process, no excess sludge was withdrawn and no

significant accumulation of inorganic solids occurred in the aeration tank at optimum ozone doses. The operation costs of this process were estimated to be lower than those of conventional sludge treatment process, including sludge dewatering and disposal (Wei et al., 2003).

A combined system of activated sludge process and intermittent ozonation has been successfully developed in order to solve sludge problems at roots. It was reported that ozonation coupled with activated sludge process would be a useful technology for reducing excess sludge production (Liu et al., 2001). The process consists of sludge (biomass) ozonation stage followed by a biodegradation stage. A part of recycled sludge passes through the ozonation unit. Solubilization to biodegradable organics due to disintegration of suspended solids and mineralization to CO₂ and H₂O due to oxidation of soluble organic matter were occurred in ozonation step. The ozonated sludge is then recycled to the aeration tank (Dytczak et al., 2007).

Kamiya and Hirotsuji (1998) have proposed a working principle for the ozonation-combined activated sludge process as follows:

- A part of activated sludge is ozonated in the ozone reactor. Most activated sludge microorganisms in the ozonation reactor would be killed by ozone and oxidized to organic substances,
- Additional organic substances comes from ozonation can be degraded in biological treatment.

The flow sheet of the activated sludge coupled with ozonation is shown in Figure 2.6.

2.4.1 How Sludge Ozonation Works

Bacterial cell is illustrated in Figure 2.7. Bacteria cell is ozonated in the basin. Ozone contacts and penetrates the cell wall. Then ozone oxidizes cellular compounds

causing lysis. Lysed cell is returned to the basin where COD is released. Solid waste effectively transformed to “food” for biomass in basin.

2.4.2 Mineralization and Lysis

Cell contents are released into the medium by cell lysis. Autochthonous substrate is provided contributed to the organic loading with the releasing of cell contents. In microbial metabolism, this organic autochthonous substrate is reused and a portion of the carbon is liberated as products of respiration, and then results in a reduced overall biomass production. The biomass growth occurred on this autochthonous substrate cannot be distinguished from growth on the original organic substrate. Therefore, this growth is termed as cryptic growth. Lysis and biodegradation are the stages of lysis-cryptic growth. The lysis stage is the rate-limiting step of lysis-cryptic growth, and enhances of the lysis efficiency can therefore lead to an overall reduction of sludge production. There are several methods applied for sludge disintegration; (Fabiya et al.,2008). Ozonation is summarized systematically in Figure 2.8. Mineralization and lysis are shown in Figure 2.9.

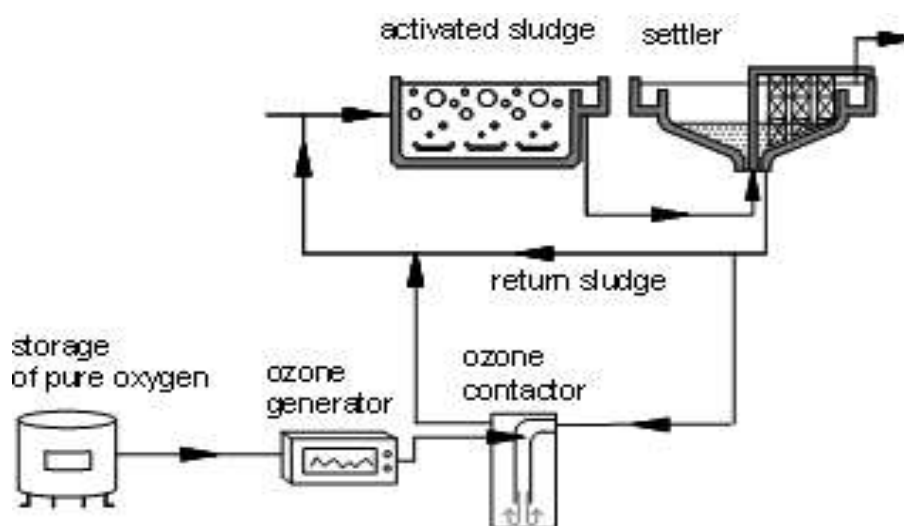


Figure 2.6 Process concept reduction of waste activated sludge by ozonation (Kamiya and Hirotsuji, 1998)

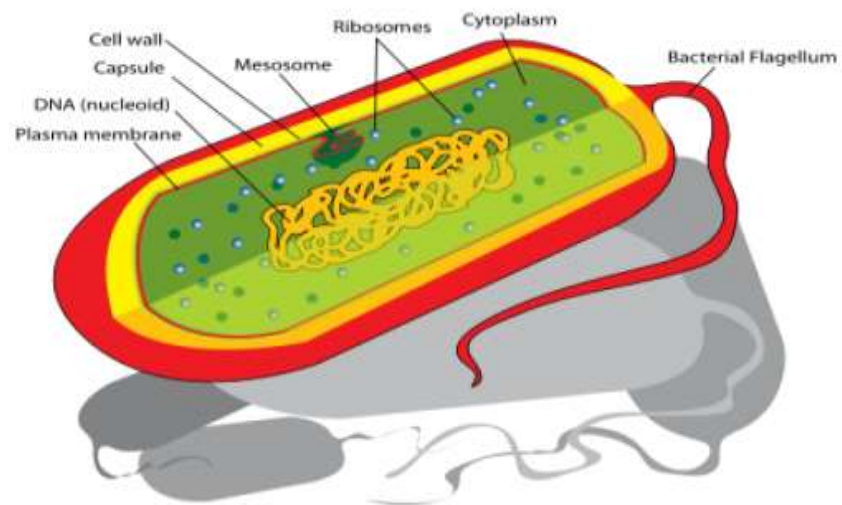


Figure 2.7 Bacterial cells (Fabiya et al., 2008)

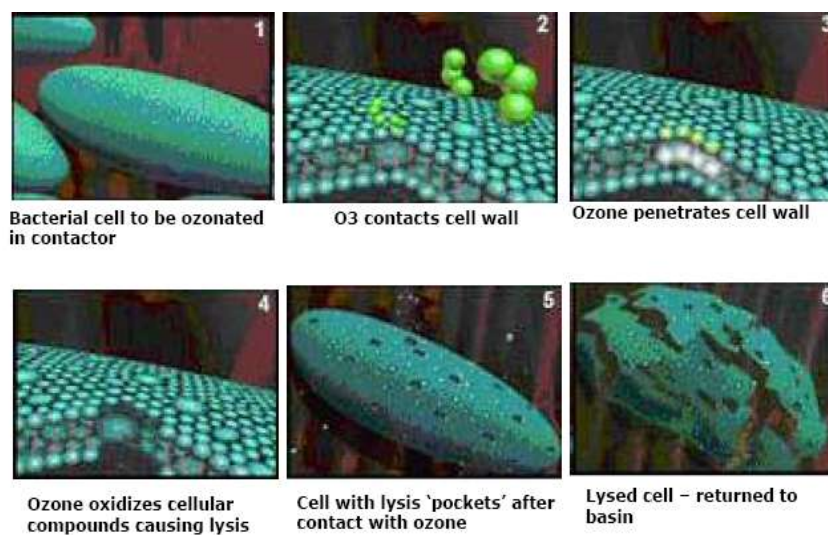


Figure 2.8 Sludge ozonation (Fabiya et al., 2008)

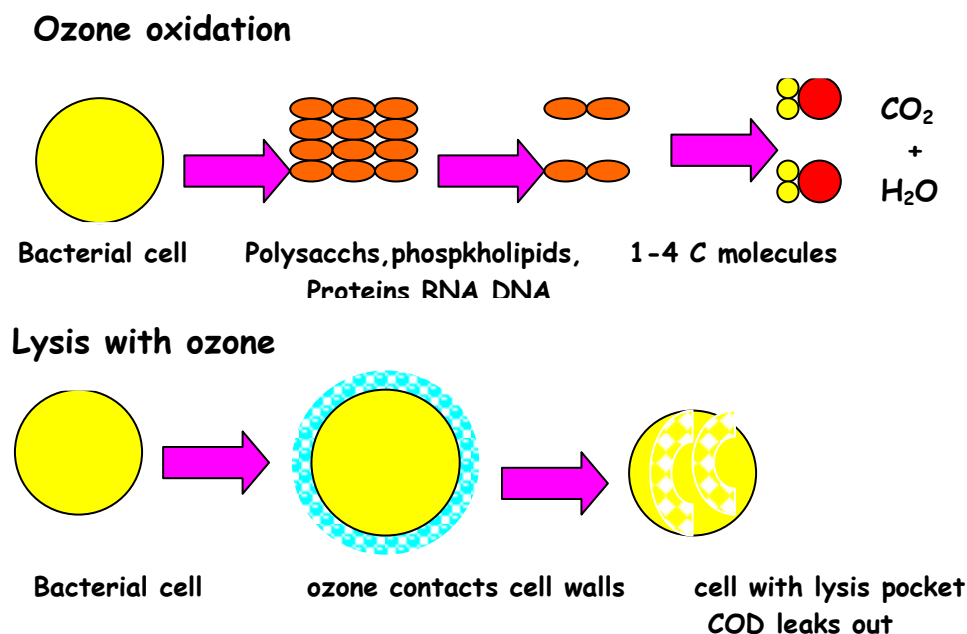


Figure 2.9 Mineralization and lysis (Fabiya et al., 2008).

In order to promote the sludge lysis and subsequently cryptic growth physical, chemical and combined ways in order to reduce sludge production, such as ozonation, chlorination, integration of thermal/ ultrasonic treatment and membrane, integration of alkaline and heat treatment, an increase of oxygen concentration can be used (Wei et al., 2003). Research shows that microbial cell lysis can be amplified by prolongation of sludge retention time (SRT) or through physicochemical treatments of sludge, such as thermal, alkaline or acid (He et al., 2006).

It was reported that the sludge ozonation process could be applied to membrane bioreactor (MBR) system for minimization of excess sludge production. Due to the relatively high biodegradability, organic matter in the ozonated sludge can be effectively used as a carbon source in a biological nutrient removal (BNR) system under low organic loading condition. MBR process has supremacy compared to CAS processes. Excellent effluent quality, small footprint, less sludge production and flexibility of operation and becomes a promising alternative for wastewater treatment can be considered as advantages. However, because of the small, weak, and open sludge flocs, high viscosity and high sludge volume index (SVI) sludge settling and dewatering properties of sludge are poor in MBR. High SRT operation of MBR can

overcome the problems despite of increased aeration cost, and excessive membrane fouling. To operate MBR with complete sludge retention is not feasible in practice, and there must exist a minimal rate at which excess sludge is wasted in order to keep an optimal range of sludge concentration in MBR (Song et al., 2003).

Ozonation combined activated sludge process is already established in full-scale plants (Yasui et al. 1996). Ondeo-Degre'mont is developed "Biolysis O" process to reduce sludge generation using ozone. In this process, liquor extracted from the activated sludge basin is contacted with ozone in a reactor and returned to the activated sludge tank. A demonstration of Biolysis O in France produced sludge reductions of between 30 and 80 %. Future research should be focused on optimization of ozone dosage, dosing mode (continuous or intermittent), and reactor configuration (bubble or airlift reactor). Positive (✓) and negative (X) aspects of the ozonation technology are:

- ✓ At optimal ozone dose rates there is no significant accumulation of inorganic solids occurred in the aeration tank
- ✓ The sludge settleability was highly improved as compared with control test
- ✓ Successful full-scale experience.
- X Sludge ozonation causes TOC slight increase in the effluent
- X High costs involved in ozonation.
- X Consumption of ozone in the degradation of other possible organic materials that may be present (Perez-Elvira et al., 2006).

Dytczak et al., (2006) examined the effectiveness of partial ozonation of return activated sludge for enhancing denitrification and waste sludge minimization. Denitrification rate improved up to 60 % due to additional carbon released by ozonation. Overall, ozonation provided the expected benefits in denitrification and had less impact on nitrification in the alternating reactors.

Performances of ozonation integrated in wastewater treatment plants for sludge reduction by many researches are summarized in Table 2.2.

Table 2.2 Performances of ozonation integrated in wastewater treatment plants for sludge reduction

Experimental Details	Sludge Reduction (%)	Observations	References
Laboratory scale Ozone dose = 0.04 gO ₃ /gSS, Biomass concentration=4200 mg/ L in the aeration tank, Recirculation rate=0.3/day, BOD loading = 1.0 kgBOD/ m ³ /d.	100	Biomass required is 1.2 times the influent BOD for sludge yield to be zero, Total organic carbon content were slightly higher than the conventional activated sludge process	Yasui and Shibata, 1994
Full scale plant operation of pharmaceutical wastewaters Ozone dose= 20 to 30 g/Nm ³ (gas), BOD loading= 550 kg/d, sludge recirculation= 3 times higher than the sludge withdrawal rate of the control experiment, aeration tank volume= 1900m ³ .	100	Improved SVI, Slight increase of inorganic solid content in MLSS such as Si, Al and Fe.	Yasui et al., 1996
Full scale activated sludge process operated at 10 d of SRT with raw wastewater, Ozone dose: 0.136 gO ₃ /gTSS	100		Sakai et al., 1997
Laboratory scale, Synthetic sewage with meat extract and peptone, Continuous ozonation, ozone dose = 30 mgO ₃ /gMLSS/day. Yield coefficient= 0.5 Intermittent ozonation, ozone dose = 11 mgO ₃ /gMLSS day.	50 70	Improved sludge settling characteristics	Kamiya and Hirotsuji, 1998

Table 2.2 Performances of ozonation integrated in wastewater treatment plants for sludge reduction (Continued)

Lab scale SBR process operated at 10 d of SRT with raw wastewater, Ozone dose: 0.048gO ₃ /gTSS	50		Huysmans et al.,2001
Pilot Scale wastewater treatment system Ozone dose= 0.2 gO ₃ /g dissolved solids Ozone dose= 0.5 gO ₃ /g dissolved solids	45 34	Total nitrogen (TN) removal efficiency increased about 10 % without deteriorating effluent quality, significant improvement in settleability and dewaterability	Ahn et al., 2002
Laboratory Scale, Domestic wastewater after primary sedimentation Continuous ozonation, ozone dose = 0.05 gO ₃ /gVSS treated, Y _{obs} =0.28 gVSS/gCOD	70	Slight increase in COD in the effluent. Significant improvements in sludge settling characteristics	Deleris et al., 2002.
Two modified Ludzack-Ettinger type MBR systems with or without batch-type sludge ozonation.Ozone dose=0.1 gO ₃ /gSS MLSS=8000 mg/L	Significantly effective	In control run, the daily sludge production=1.04 g/d In ozone run, the daily sludge production is negligible. The MBR system with sludge ozonation showed relatively better nutrient removal than without sludge ozonation	Song et al., 2003
A pilot scale activated sludge system coupled with ozonation process. Period:112 days MLSS:5000 mg/L SS:10 mg/L		While Sp is mainly subject to the COD loadings sludge concentration is affected by the temperature.	Lee et al., 2005
3 MBRs with different amounts of activated sludge ozone dosage 0,16 kg O ₃ /kg MLSS Period:120 days		Excellent quality of permeate. Small quantity of sludge production.	He et al., 2006

Table 2.2 Performances of ozonation integrated in wastewater treatment plants for sludge reduction (Continued)

SBR with synthetic wastewater, 0.08 gO ₃ /gTSS	25		Dytczack et al.,2007
Two nitrifying sequencing batch reactors, one control and one ozonated under alternating anoxic/aerobic conditions	95–136 d, f wasted solids decreased up to 25 %, 190–232 d solids destruction decreased by 50 %.	Prolonged operation of partial sludge ozonation, an increase in ozone dose may be required to continuously maintain the expected solids destruction level.	Dytczack et al.,2008
Two lab-scale bioreactors	Without excess sludge	The protease activity and intracellular ATP concentration of ozonated reactor increased compared to control reactors an indicator of better ability to digest proteins and cell debris. The dissimilarity of bacterial population in the reactors was 40 %.	Yan et al., 2009b
Laboratory Scale, Synthetic waste water, Yield coefficient of the control reactor=0.26 gSS/g SCOD, Yield coefficient =0.25 g SS/g SCOD.	40-60		Egemen et a.l, 2009
The full-scale application The recommended ozone dose ranges from 0.03 to 0.05 gO ₃ /gTSS		Improvements in the biodegradability of the ozonated sludge Unaffected effluent quality but improved the settling properties of the sludge	Chu et al. 2009a

Table 2.2 Performances of ozonation integrated in wastewater treatment plants for sludge reduction (Continued)

<p>A seafood industry WWTP (two coagulation-flocculation units and a biological unit) 0.03 gO₃/gTSS to sludge coming from flotation units during batch tests. 0.007 to 0.02 g O₃/ g TSS were also applied to the raw wastewater</p>	<p>A reduction of Y_{obs} of biomass from 0.14 to 0.07 gTSS/gCOD_{re} moved</p>	<p>During batch tests, no solids solubilization being observed. Ozonation caused a and a slight improvement of COD removal efficiencies</p>	<p>Campos et al., 2009</p>
<p>Activated sludge exposed to low-dose ozone at less than 20 mg O₃/gTSS</p>		<p>The efficiency of sludge solubilization initially changed a little and then increased rapidly to around 30 % at an ozone dose of 20 mg O₃ /g.TSS</p>	<p>Chu et al., 2009b</p>
<p>Ozone optimization study The ozone dose of 50 mgO₃/gDS was found optimal</p>	<p>50 mgO₃/gDS, the sludge disintegration degree was 46.7 % after 105 min. The TS concentration and VS concentration decreased by 49.1 % and 45.7 %, respectively.</p>	<p>The supernatant soluble chemical oxygen demand, total nitrogen, total phosphorus, protein, polysaccharide, and deoxyribonucleic acid increased by 699 %, 169 %, 2379 %, 602 %, 528 %, and 556 %, respectively.</p>	<p>Zhang et al., 2009</p>

2.4.3 Sludge Reduction and Changes of Characteristics After Ozonation

Ozone is capable of oxidize the organic and inorganic compounds as a powerful oxidant. Ozone kills the microorganisms of activated sludge with strong cell lytic activity and further oxidize the organic substances released from the cells (Cui and Jahng, 2004; Saktaywin et al., 2005). The process of sludge ozonation is generally composed of the sequential decomposition reactions of floc disintegration, solubilization, and the subsequent oxidation of the released organics into carbon dioxide (mineralization) (Ahn et al., 2002; Lee et al., 2005). When the ozone dose was 50 mgO₃/gDS, the sludge disintegration degree was 46.7 % after 105 min in the study by Zhang et al., (2009).

A decrease in the ratio of volatile suspended solid VSS/TSS and pH value is occurred in case of the sludge ozonation. The ratio of VSS/TSS decreased from 78 % in raw sludge to 73 % in ozonated sludge with a dose of 0.16 gO₃/gTS (Bougrier et al., 2006), and pH decreased from 6.2 to 3.0 at an ozone dose of 0.5 gO₃/gTS (Deleris et al., 2002). In addition, the water content of sludge decreased with increased ozone dose (Zhao et al., 2007). Sludge decomposition can change the water distribution in the biomass. The bound water content decreased rapidly and then leveled off at an ozone dose of higher than 0.5 gO₃/gTS (Bougrier et al., 2006). Zeta-potential increased according to ozone dose and was enhanced at doses above 0.5 gO₃/gTS (Bougrier et al., 2006).

Following ozonation, the characteristics of the sludge are greatly changed. Floc disintegration and solubilization produces a large number of micro-solids dispersed in the supernatant in addition to soluble organic substances (Chu et al., 2008). Particle size was also modified after ozonation. Ozonation did not appear to greatly affect particle size at lower ozone doses (Zhang et al., 2009). In the study by Bougrier et al. (2006), the medium diameter of particles before and after ozonation (0.16 gO₃/gTS) was 36.3 μm and 32.6 μm, respectively. Zhao et al. (2007) reported that the media diameter of sludge particles reduced from 6 μm to 4μm at an ozone dose of 0.04 gO₃/gTSS. Higher ozone doses resulted in an increase in small particles

due to sludge destruction by ozonation, which occurred due to disruption of the biomass during sludge treatment. Park et al. (2004) demonstrated that the mean particle size decreased from 70 μm to 40 μm with an ozone dose of 0.5 gO_3/gTSS . With further ozone dose of 5 gO_3/gTSS , the highest peak of particle size distribution was identified around 5 μm .

Dytczak et al. (2008) examined partial ozonation of return activated sludge for waste sludge minimization and soluble COD production. Two nitrifying sequencing batch reactors were operated under alternating anoxic/aerobic conditions. One of them was control and the other one was ozonated reactor. During the first steady-state period of 95–136 d of ozonation, the amount of wasted solids decreased with the ozone dose up to 25 % by cell lysis. However, during a subsequent period of 190–232 d of continuous ozonation, the effect of solids destruction and COD production decreased by 50 %.

Song et al. (2003) investigated the effects of sludge ozonation on excess sludge minimization and enhancement of nutrient removal in membrane bioreactor (MBR). The study was carried out with two modified Ludzack-Ettinger (MLE) type MBR system contained a flat type microfiltration membrane (pore size 0.4 μm). The reactors were operated in parallel with or without a batch-type sludge ozonation process and 0.1 gO_3/gSS of ozone dosage was used. In the control run (without sludge ozonation), the daily sludge production was about 1.04 g/d. However, in the ozone run (with sludge ozonation), the daily sludge production was negligible. MLSS and MLVSS concentrations in the reactor maintained constant around 8000 mg/L and 0.75, respectively, without excess sludge. The concentration of effluent was maintained at a satisfactory level in both runs. It was concluded that ozonated sludge could be used for enhancement of nutrient removal due to the relatively better nutrient removal efficiency in MBR system with sludge ozonation than without sludge ozonation. It was also expected that floc size for the ozone run was smaller than that for control run due to disintegration of sludge by ozonation. However, the result was quite interesting. The floc size in the reactor for the control run was smaller compared to that for the ozone run. It was attributed to the reflocculation of disintegrated sludge particles occurred over a certain limit of ozone dose as reported

by Kwon et al., (2001) that the mean size of ozonated sludge particles bounced up with increases of ozone doses.

Lee et al. (2005) operated a pilot-scale activated sludge system integrated with sludge ozonation process for 112 days of a winter without excess sludge wasting. In this process, the excess sludge is first disintegrated by ozone oxidation and then recirculated to a bioreactor in order to mineralize the particulate and soluble organic compounds. The aim of operation was to determine either the optimal amount of sludge in kg SS ozonated each day (SO) or the optimal ozonation frequency under the variable influent COD loading and temperature conditions considering energy cost. Using the theoretically estimated sludge production rate (SP), the optimal SO was obtained.

Dytczak et al. (2008) investigated the effects of partial ozonation of return activated sludge for enhancing denitrification and waste sludge minimization. A control and an ozonated sequencing batch reactor were operated in either aerobic or alternating anoxic/aerobic conditions. The production rate of solid was increased with ozone dose. The destruction of biomass in the anoxic/aerobic reactor was easier than in the aerobic one. The SCOD production by cell lysis in the anoxic/aerobic reactor is higher than aerobic reactor. Due to additional carbon released by ozonation denitrification rate improved up to 60 %. Because of the destruction of nitrifying autotrophs as well as competition created by growth of heterotrophs receiving the additional COD, nitrification rates deteriorated much more in the aerobic than in the alternating reactor. It was revealed that, ozonation had less impact on nitrification in the alternating reactors and it is beneficial for denitrification.

He et al., (2006) were carried out the experimental period in two stages consist of a series of batch studies to get an understanding of the effect of ozonation on sludge properties and three membrane bioreactors (MBRs) to evaluate the influence of sludge ozonation on sludge yield and permeate quality. It was proved that the combination of ozonation unit with MBR unit could achieve an excellent quality of permeate as well as a small quantity of sludge production. The results of economic

analysis indicated that an additional ozonation operating cost for treatment of both wastewater and sludge was only 0.096 Yuan (US \$ 0.0115)/m³.

2.4.4 Effluent Quality After Ozonation

After the addition of ozonation unit to activated sludge process, the effluent quality is not influenced significantly in terms of COD concentration; however, the sludge settleability in terms of SVI was highly improved as compared with control test without ozonation (Kamiya and Hirotsuji, 1998).

The influence of sludge ozonation on effluent quality draws significant attention in the biological treatment process. Inert dissolved and colloidal COD is released into the solution, resulting an increase in inert SCOD in the effluent during long-term operation during ozonation (Chu et al., 2009a). Dytczak et al. (2008), proved the increasing of soluble COD in the ozonated part of the return sludge.

The nitrogen loading increased with the recirculation of ozonated sludge to the reactor and slightly higher TN concentration value of the effluent were observed in ozonated system compared to the control run without sludge ozonation (Chiavola et al., 2007; Sakai et al., 1997).

The supernatant soluble chemical oxygen demand, total nitrogen, total phosphorus, protein, polysaccharide, and deoxyribonucleic acid increased by 699 %, 169 %, 2379 %, 602 %, 528 %, and 556 %, respectively (Zhang et al., 2009).

With sludge ozonation, the settling properties of the sludge are improved and a reduction in bulking and foaming are occurred (Caravelli et al., 2006; Deleris et al., 2002; Kamiya and Hirotsuji, 1998; Paul and Debellefontaine, 2007; Vergine et al., 2007; Weemaes et al., 2000). Smaller flocs and a turbid supernatant were produced after sludge disintegration. Equalization in particle size distribution resulting improvement of sludge settling with the recirculation of the ozonated sludge (Bohler and Siegrist, 2004).

It is proved by researches that ozonated sludge present low dewatering and filterability capacity compared with raw activated sludge. Sludge dewatering affected negatively by the releasing of protein via cell lysis due to their surface charge and cations are needed for the destabilization of sludge flocs. Moreover, an adverse influence on sludge filtration by the unsettled micro-particles leading to a more compact filtration layer with reduced permeation of liquids was observed. At a dose of 0.1 gO₃/gTSS provided a strong increase in the capillary suction time (CST) value from 151 s to 382 s after ozonation (Bougrier et al., 2006). The ozone dose is important for the filtration of sludge. At ozone dose up to 0.2 g O₃/g TS, the specific resistance to filtration (SRF) value rapidly increased and then decreased dramatically at a dose of 0.5 g O₃/g TS (Deleris et al., 2002).

The negative impact of ozonation on dewaterability is minimal for the biological wastewater process combined with ozonation. According to Dytczak et al. (2006), the average CST of sludge increased slightly from 5.9 s to 6.2 s in a combined SBR and ozonation system after ozonation.

2.4.5 Application of Sludge Ozonation Technology

The major limitation of ozone production for sludge treatment in full-scale plants is cost. In the near future, the main research objectives of ozonation must be optimization. The most important parameter in evaluating the performance of sludge ozonation is the efficiency of sludge solubilization. 30–60 % of sludge solubilization efficiency for ozone oxidation was reported. A decrease in the rate of sludge solubilization was observed at a higher rate of ozone consumption due to complexity of sludge ozonation. It has been reported that ozone may first react with the soluble fraction of the activated sludge and then attack the particulate fraction (Cesbron et al., 2003).

The importance of gas flow rate on ozone mass transfer affirmed by Manterola et al., (2008). For those higher gas flow rates that corresponded to lower ozone gas concentrations, an increase in COD solubilization affirmed that higher flow rates increased the ozone mass transfer from gas to liquid. Another parameter should be

considered in sludge-ozonation processes is initial TSS concentration. Manterola et al. (2008) reported that the initial TSS concentration affected sludge solubilization during the ozonation process at ozone doses of 10–20 mg O₃/g TSS. The degree of solubilization increased when the sludge concentration to be treated was increased (Deleris et al., 2000).

2.5 Oxic-Settling Anaerobic Process (OSA Process)

Conventional activated sludge process can be modified by inserting an anaerobic reactor in the recycling bypass of sludge to form oxic-settling-anaerobic process employed successfully limiting the growth of filamentous organisms and provide a cost-effective way to reduce excess sludge production in activated sludge process. (Chen et al., 2003; Liu et al., 2001). With the insertion of the sludge-holding tank, that retains thickened sludge from the settling tank under the no air supply condition, which results in an “anaerobic” sludge zone in an OSA process. In the sludge-holding tank, few external organic substrates are left since they have already been utilized in the clarifier prior to entering the sludge-holding tank (Chen et al., 2003). Possibly for the first time, Westgarth et al., (1964), reported the insertion of a period of anaerobiosis in the high-rate activated sludge process as a method could reduce excess sludge production as compared with that conventional process without anaerobic reactor. Since then, oxic and anaerobic cycling has been evaluated as minimization technique for excess sludge production in the activated sludge process. ATP is generated from the oxidation of exogenous organic substrate for aerobic microorganisms and when the microorganisms are subject to anaerobic condition without food supply, they can not produce energy and use their ATP reserves as energy source. ATP would be exhausted during the anaerobic starvation period. After microorganisms return to food-enriched aerobic reactor, they have to rebuild necessary energy reserves prior to biosynthesis because cellular synthesis could not proceed without a certain intracellular stock of ATP. In this case, to satisfy the energy requirement of microorganisms, the substrate consumption should thus go to catabolic metabolism. Therefore, it appears that alternative aerobic± anaerobic cycling of activated sludge would stimulate catabolic activity, and make catabolism dissociate from anabolism. Maximized energy uncoupling would result in a

minimized sludge yield. Oxic-settling-anaerobic technique is especially based on energy uncoupling induced by alternative aerobic and anaerobic treatment. Chudoba and Capdeville (1991) compared sludge production in oxic-settling-anaerobic and conventional activated sludge processes and found that in the oxic-settling-anaerobic process, the specific sludge production was reduced by 20-65 % as compared with conventional process. On the other hand, the SVI value in the oxic-settling anaerobic process was much lower than that observed in conventional process. The oxic settling-anaerobic process could also improve the settleability of activated sludge. Another successful application of oxic-settling-anaerobic strategy is in sequencing batch reactor (SBR) system obtained lower sludge production and excellent settleability. The sludge production in conventional activated sludge process increases with increasing sludge loading rates however, the sludge production in the oxic-settling-anaerobic process shows a reducing trend (Chudoba et al., 1992). The oxic-settling-anaerobic process provides a promising technique for efficiently reducing sludge production, while improving the stability of process operation (Liu et al., 2001).

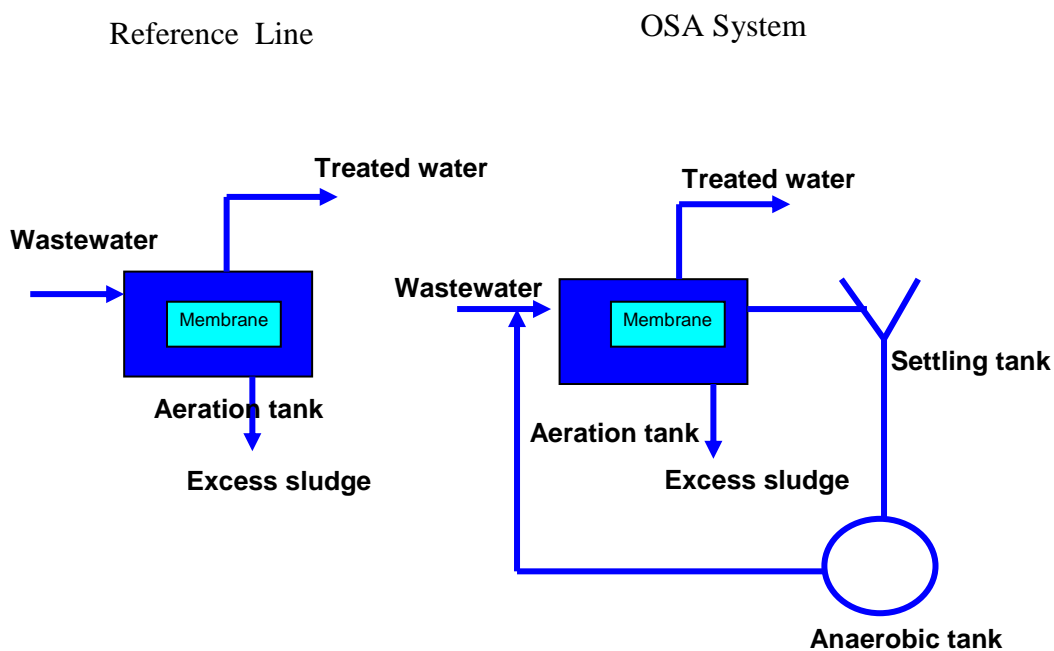


Figure 2.10 Schematic diagrams of two experimental systems by Saby et al. (2003)

In the study by Saby et al. (2003), in OSA process, membrane bioreactor served as aeration tank (Figure 2.10). OSA and reference system (without sludge holding tank) were operated with synthetic wastewater for 9 months. The OSA system was operated with different ORP levels (+100 to -250 mV) in its anoxic tank during the operation and produced much less excess sludge than the reference system. A lower ORP level than +100 mV in the anoxic tank supported the excess sludge reduction. The sludge reduction efficiency was increased from 23 % to 58 % when the ORP level decreased from +100 to -250mV (Saby et al., 2003). The OSA process does not require any physical-chemical pretreatment and adding any chemical. Therefore, it is a promising and cost effective technique for efficiently reducing sludge production (Wang et al., 2008).

It is of significance to realize the mechanism of reducing excess sludge in the OSA process, which will be in favor of controlling the operational parameters of minimizing excess sludge production without affecting effluent quality, optimizing the process running condition, and exploring industrial scale application of the OSA process (Wang et al., 2008).

2.5.1 Sludge Reduction Mechanism of OSA Process

Oxic-settling-anaerobic aimed to repress the growth of filamentous organisms. The insertion of a period of anaerobiosis in the high-rate activated sludge process could reduce the rate of excess sludge production by half as compared with that conventional process without anaerobic reactor reported by Westgarth et al. (1964).

ATP is produced from the oxidation of exogenous organic substrate for aerobic microorganisms. The microorganisms are no longer able to produce energy when they subject to anaerobic condition without food supply and have to use their ATP reserves as energy source. ATP would be completed during the anaerobic starvation period. Microorganisms have to rebuild necessary energy reserves prior to biosynthesis because cellular synthesis could not proceed without a certain intracellular stock of ATP when they return to food-enriched aerobic reactor. In order to satisfy the energy requirement of microorganisms, the substrate consumption

should thus go to catabolic metabolism (Chudoba et al., 1991). Therefore, alternative aerobic± anaerobic cycling of activated sludge could stimulate catabolic activity, and make catabolism dissociate from anabolism. The maximized energy uncoupling could achieve the minimized sludge yield. It can be concluded that the alternative aerobic and anaerobic treatment with energy uncoupling can be the basis of oxic-settling anaerobic systems.

The ORP level as function of the sludge exposure time, sludge concentration, and the concentration of oxidizing substances in the tank can be considered in controlling the anoxic exposure degree treatment of sludge in OSA system. In order to maximize the excess sludge reduction in an OSA system, an appropriate ORP level should be identified and the effect of the ORP level in the anoxic tank must be investigated.

Chen et al., (2003) investigated the following possible mechanisms that may explain the reduction of excess sludge in the OSA process. They are ranged as follows:

- energy uncoupling,
- domination of slow growers,
- soluble microbial products (SMPs) effect,
- sludge decay in the sludge-holding tank under a low oxidation–reduction potential (ORP) condition.

Results showed that only the final scenario might reasonably explain this reduction. It has also been found that the sludge decay process in the sludge-holding tank may involve the reduction of the cell mass.

Wang et al., (2008) were also investigated the possible factors of sludge reduction in the OSA process such as sludge decay, uncoupled metabolism, and anaerobic oxidation with low sludge production. It has been confirmed that sludge decay is the certain cause in the OSA process, with 66.7 % of sludge reduction efficiency. Sludge

decay includes hydrolysis and acidogenesis of dead microorganisms and particle organic carbon adsorbed in sludge floc and endogenous metabolism. Energetic uncoupling leads to about 7.5 % of sludge reduction in the OSA system proved by batch experiments since microorganisms were subjected to alternative anaerobic and aerobic environment. In the OSA process, SCOD released from the anaerobic sludge tank was used as the substrate for cryptic growth. The substrate was used for anoxic denitrifying, anaerobic phosphorus release, sulfate reduction, and methane production. These anaerobic reactions in the sludge anaerobic tank have lower sludge production than in the aerobic oxidation when equivalent SCOD is consumed, which may lead to approximately 23 % of sludge reduction in the OSA process.

Ye and Li (2010) investigated the effect of 3,3,4,5-tetrachlorosalicylanilide (TCS) on OSA process to reduce excess sludge production. TCS was dosed into aeration tank with 0.05, 0.10 and 0.15 g every other day in three lab-scale OSA processes, respectively to form the TCS and OSA combined processes. 21–56 % of sludge yield reduction could be achieved under the same sludge retention time in sludge anoxic in the OSA and TCS combined processes.

It has been concluded that multiple causes resulted in the minimization of excess sludge in the OSA system.

CHAPTER THREE

MATERIALS & METHODS

3.1 Experimental Setup

The reactor system used in the study was depicted in Figure 3.1. The system consists of two activated sludge systems. Each activated sludge system contains an aeration tank and a settling tank. Reactors made by stainless steel and equipped with electrical control panel. Beside this, a feeding tank was integrated to processes. For the further modification, a tank for ozonated sludge and an anaerobic tank for OSA process were added to the reactor systems.



Figure 3.1 Experimental set up consists of two activated sludge reactor system

3.2 Sludge Properties

In the experimental study, the activated sludge processes were fed synthetic wastewater prepared for C/N/P ratios as 100/5/1. In the start up period of the operation, the activated sludge taken from aeration tank of Pakmaya Kemalpaşa Production Plants in İzmir was used as inoculum sludge. Firstly, the analyses were done in order to determine the sludge properties and all parameters were measured according to the Standard Methods (APHA, 2005). The properties of activated sludge used in cultivation were given in Table 3.1.

Table 3.1 The properties of activated sludge taken from Pakmaya Treatment Plants

Parameter	Average Value
pH	7.26
Temperature (°C)	27.8
Oxidation Reduction Potential (ORP) (mV)	68
SVI (mL/g)	123
MLSS (mg/L)	6325
MLVSS (mg/L)	2675
TS (mg/L)	11205
TOM (mg/L)	3175
NH ₄ -N (mg/L)	58
PO ₄ -P (mg/L)	51
NO ₃ -N (mg/L)	128
CST (s)	69

3.3 Influent

The reactor was fed with 6.75 L/d of synthetic wastewater composed of different compounds given in Table 3.2. The concentrations of the inorganic components were proportionally adjusted with the carbon source (being molasses) to maintain a constant C/N/P ratio. The synthetic wastewater composition is determined according to COD=400 mg/L, N=20 mg/L and P=4 mg/L (C/NP=100/5/1).

Table 3.2 Composition of synthetic wastewater

Component	Concentration (g/L)
Molasses (mL)	48
NH ₄ Cl	0.076
KH ₂ PO ₄	0.0176
MgSO ₄ ·7H ₂ O	0.0225
CaCl ₂	0.05426
FeCl ₃	0.00025

3.4 Box-Behnken Statistical Design Program

All aerobic treatment systems are operated on some principles. Mixing regimes, SRT, HRT are important factors for the activated sludge process. There are two parameters related to time in the system. The link between SRT and HRT is neither proportional nor linear and depend on the wastewater organic concentration (COD or

BOD₅) and the reactor suspended solids concentration (TSS) (Ekama and Wentzel, 2008). Because, the optimum values of these parameters should be determined for the successful operation of activated sludge process. Behnken Statistical Design Program was used in order to determine the optimum operational parameters and minimize the number of parameter should be analyzed. Experiments were carried out according to the Box-Behnken Statistical Design. The independent variables were chosen as initial COD concentration (COD_i), HRT and SRT. The low, center and high levels of each variable designated as -1, 0 and +1, respectively are presented in Table 3.3.

Table 3.3. The minimum and maximum values of the variable parameters in this study

Variable	Symbol	<i>Coded variable level</i>		
		Low level	Center level	High level
		-1	0	+1
Solid retention time (SRT)	X ₁	5	17,5	30
Hydraulic Retention time (HRT)	X ₂	5	15	25
Initial COD concentration	X ₃	300	400	500

It can be realized from the Table 3.3, HRT:5-25 h, SRT:5-30 d and COD_i concentration (300-500 mg/L) were determined as variable parameters. Experimental data points used in Box-Behnken Statistical Design are given in Table 3.4. The mathematical relationship connecting the variables and the response can be calculated by the quadratic polynomial equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2$$

(Eq. 1)

Where; Y=predicted response; b₀=constant, X₁=COD_i (mg/L), X₂= HRT (hours), X₃= SRT (days), b₁,b₂,b₃-linear coefficients, b₁₂,b₁₃,b₂₃=cross product coefficients. The design experiments were carried out for analysis using the Stat-Ease Design Expert 7.0.3 computer program for this study. Box-Behnken design requires 17 runs for a 3-factor experimental design.

Table 3.4. Experimental data points suggested by Box-Behken statistical design program

	Factor 1	Factor 2	Factor 3
	A:Initial COD	B:HRT	C:SRT
	mg/L	hour	day
1	300.00	5.00	17.50
2	400.00	5.00	5.00
3	300.00	15.00	30.00
4	300.00	25.00	17.50
5	400.00	15.00	17.50
6	500.00	15.00	5.00
7	400.00	15.00	17.50
8	400.00	15.00	17.50
9	400.00	15.00	17.50
10	400.00	25.00	5.00
11	400.00	15.00	17.50
12	400.00	5.00	30.00
13	400.00	25.00	30.00
14	500.00	25.00	17.50
15	500.00	5.00	17.50
16	500.00	15.00	30.00
17	300.00	15.00	5.00

3.5 Operation of Activated Sludge Processes Prior to Modification

After the determination of optimum operational conditions of activated sludge process, two systems were operated in parallel under the optimum conditions during 45 days until the steady state conditions and the effluent quality, sludge properties of the system were monitored.

3.6 Determination of Optimum Ozone Dose

The balance between sludge reduction efficiency and cost must be considered in the determination of ozone dose. Cost of production and full-scale application of ozone in plants are the disadvantages of ozone usage. Since, the optimization of the sludge ozonation stage must be one of the main research objectives. The efficiency of sludge solubilization is the most important parameter in evaluating the performance of sludge ozonation.

The necessary ozone dose for sludge reduction has been reported to range from 0.02 to 0.5 g O₃/g TSS (Bohler and Siegrist, 2004; Caffaz et al., 2005; Deleris et al., 2002; Lee et al., 2005; Sakai et al., 1997; Sievers et al., 2004; Vergine et al., 2007; Wolff and Hurren, 2006; Yasui et al., 1996).

In present study, when the steady-state conditions were reached, specific batch tests were carried out in order to investigate the biodegradability of disintegrated sludge and determine optimum ozone dose. The sludge ozonation experiments were conducted for seven different ozone doses ranged between 0.007-0.06 gO₃/gTS. 400 mL sludge sample volume was used for each experiment. OZO 1VTT model ozone generator with a maximum ozone production capacity of 5 g/h was used for ozone production. The ozone produced from pure oxygen with a purity of 99.5 % was bubbled through the ozone reactor using a diffuser with the diameter of 15 mm and with the height of 25 mm (Erden and Filibeli, 2010). The ozone reactor was made of Pyrex-glass with a total reactor volume of 2 L. Initial ozone concentrations (4.7 g/h) and residual ozone concentrations after reaction were measured by the standard potassium iodide absorption method (APHA, 2005). The experimental setup for ozonation was illustrated in Figure 3.2.

After ozonation, the sludge and supernatant were analyzed in order to investigate the effect of ozonation on DD as an achievement of sludge solubilization at the end of the cell lysis for each ozone dose. The sludge lysis efficiency is represented by DD_{COD} by Zhang et al., (2009) which is calculated as follow (Eq. 2):

$$DD_{COD} = (SCOD_{ozone} - SCOD_o) / (TCOD - SCOD_o) \quad (Eq.2)$$

Where, SCOD_{ozone}: is the supernatant COD of the ozonated sludge (mg/L). SCOD_o is the supernatant COD of raw sludge (mg/L) and TCOD is the total COD of raw sludge (mg/L).



Figure 3.2 Experimental setup for ozonation

3.7 Modification of Activated Sludge Process Using Partial Ozonation

An activated sludge process coupled with ozonation for sludge reduction proposed and developed by Yasui and Shibata (1994). Kamiya and Hirotsuji (1998) reported that excess sludge production was reduced by 50 % per day at an ozone dose of 0.01 g O₃/g TSS in the aerobic tank. No excess sludge was produced when the ozone dose was kept as high as 0.02 g O₃/g TSS.

3.7.1 Modification with 0.1 of Return Activated Sludge (Q_R)

The effectiveness of partial ozonation of return activated sludge was investigated for the minimization of excess sludge production using ozonation coupled with activated sludge process. The SRT of the activated sludge was approximately 25 d and the HRT was 25 h. The dissolved oxygen (DO) was controlled at 3 mg O₂/L in the two bioreactors. The internal recycling rate (R) of the sludge from the settling tank to the bioreactor was controlled at about 0.75. The temperature of the reactors changed from 23 to 27 °C. 10 % flowrate of return activated sludge of the system (Q_R) was ozonated during a month with dose of 0.05 g O₃/g TS. The performance of the ozonation system was evaluated considering sludge reduction and dewatering capacity compared to control run (without ozonation). Furthermore, dewaterability, filterability and settling properties of the ozonated sludge were analyzed in terms of

capillary suction time (CST), specific resistance to filtration (SRF) and sludge volume index (SVI), respectively.

3.7.2 Modification with 0.2 of Return Activated Sludge (Q_R)

In the second stage of the ozonation, for start-up phase of the two reactors, the activated sludge of the Pakmaya Kemalpaşa Production Plants was inoculated and cultivated with synthetic wastewater to domesticate the two reactors for about 30d. After the domestication, one of the reactors was operated in parallel with determined optimum conditions and served as a control run without ozonation. 240 mL of excess sludge was withdrawn from the bioreactor once a day. The other reactor contained a batch ozonation unit that was used to ozonate 800 mL of the return sludge corresponded to 20 % of the return activated sludge ($0.2 Q_R$) at an optimum dose of $0.05 \text{ gO}_3/\text{gTS}$ during a month. There was no excess sludge wastage from ozone reactor during the experimental period. The results of control and ozone runs were evaluated considering sludge reduction. Furthermore, sludge properties of ozonated sludge and activated sludge from control run were compared.

3.8 Modification of Activated Sludge Process (OSA Process)

After the modification activated sludge process with ozonation, two activated sludge process were operated in parallel with optimum operation conditions. When the treated water quality and sludge production became stable in these systems, one of them was modified by inserting anaerobic tank to comprise OSA system. The other system was remained unmodified as control system. A specific volume of return activated sludge of OSA system was subjected anaerobic conditions every day. -250 mV . Low ORP level was maintained for anaerobic condition. Sometimes pure nitrogen was used in order to achieve low ORP level in a short period. OSA system and control system were monitored during a month considering sludge reduction, effluent quality and sludge characteristics. After the completion of continuous operation, some batch experiments were conducted in order to investigate sludge reduction mechanisms and growth kinetics of control and OSA systems.

3.8.1 Batch Experiment I: Sludge Decay

In order to investigate the sludge decay theory, batch experiments with sludge taken from aeration tank of control and OSA systems were carried out. Two 2 L volume reactors were filled 1 L return activated sludge of control and OSA systems, respectively. The batch reactors were operated with a 24 h cycle: 6 h aerobic reaction and 18 h anaerobic reaction for sludge at -250 mV of low ORP level. The aim of this batch experiment was to investigate the relationship among sludge anaerobic reaction time, sludge lysis and sludge yield. At the beginning and at the end of the anaerobic cycle, MLSS, COD, PO₄-P, NH₄-N and TP concentrations and OUR were monitored.

3.8.2 Batch Experiment II: Energy Uncoupling

In order to investigate the energy uncoupling theory, a batch test was conducted. During an alternative exposure between a food-sufficient oxic condition and food-insufficient anaerobic condition, the sludge yield will decline according to the energy uncoupling theory (Chen et al., 2003). 1 L of sludge sample was taken from the aeration tank of the control system and aerated for 7 h. At the beginning and at the end of the aerobic treatment MLSS and COD concentrations measured. On the other hand, 1 L of sludge sample taken from the aeration tank of the control system was subjected to anaerobic conditions under -250 mV ORP level for 7 h via pure nitrogen injection. After the anaerobic cycle, the synthetic wastewater was added to the anaerobic sludge. SCOD of mixed sludge and MLSS concentration were measured at the beginning and at the end of the anaerobic cycle. Sludge yield was calculated based on the changes in MLSS and COD concentrations.

3.9 Analytical Methods

In the first optimization study, to determine the optimum conditions of the activated sludge process, the COD removal efficiencies were considered as response. Therefore, during the 17 runs of experiments suggested by Box-Behnken Statistical Design Program, the COD concentration of influent and effluent were measured. In

addition to, pH, temperature (T), DO, conductivity (EC) and oxidation and reduction potential (ORP) of the activated sludge processes were monitored daily.

After the optimization study of operational conditions, during 45 days of stabilization period, COD and $\text{NH}_4\text{-N}$ removal efficiencies, $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ concentrations of the effluent, $\text{PO}_4\text{-P}$ concentrations of influent and effluent, MLSS, MLVSS, total nitrogen (TN) and total phosphorus (TP) concentrations of aeration tank were measured for both systems three times in a week. Furthermore, SVI, SRF, CST and particle size were measured for activated sludge of both systems. pH, T, DO, EC and ORP were monitored daily.

In order to determine optimum ozone dose, the return sludge of one of the activated sludge process was used. Seven ozone doses were applied for return activated sludge. For each batch ozone application, 400 mL of return activated sludge was used. After the each ozone application, soluble COD (SCOD), protein, TSS and VSS, TN and TP, CST, SRF, SVI and particle size were measured. The changes in carbon, nitrogen and phosphorus in the supernatant were evaluated. The sludge was centrifuged at 4000 rpm for 30 min (Figure 3.3) in order to obtain supernatant analyzed for SCOD, TN and TP. SCOD were measured according to Standard Methods using Open Reflux Method (APHA, 2005).

After the ozone optimization study, partial ozonation of return activated sludge was conducted with two stages. All above analysis were done both first and second continuous operation with activated sludge from ozone and control run.

MLSS and MLVSS concentrations were measured for aeration tanks. COD and $\text{NH}_4\text{-N}$ removal efficiencies, $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ concentrations of the effluent, $\text{PO}_4\text{-P}$ concentrations of influent and effluent, TN and TP concentrations of aeration tank were measured for both systems three times in a week. Y_{obs} values for the systems were calculated as described in Section 3.9.6. Furthermore, SVI, SRF, CST and particle size were measured in order to characterize the ozonated sludge. pH, T, DO, EC and ORP were monitored daily.



Figure 3.3 Centrifuge

In the continuous operation of OSA system compared to control run, COD and $\text{NH}_4\text{-N}$ removal efficiencies, $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ concentrations of the effluent, $\text{PO}_4\text{-P}$ concentrations of influent and effluent, TN and TP concentrations of aeration tank were also measured for both systems three times in a week. Y_{obs} values for the systems were calculated and evaluated. Furthermore, SVI, SRF, CST and particle size were measured in order to characterize the ozonated sludge. OUR was monitored periodically. pH, T, DO, EC and ORP were monitored daily. In the first batch experiment, at the beginning and at the end of the anaerobic cycle, MLSS, COD, $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$ and TP concentrations and OUR were monitored. ORP level in anaerobic period was observed continuously. For the second batch experiment, MLSS and COD, SCOD, MLVSS concentrations were analyzed and ORP levels monitored.

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.

3.9.1 Degree of Disintegration (DD)

The degree of disintegration is a widely applied parameter to evaluate the efficiency of physico/mechanical treatments for sludge reduction. DD can be determined on the basis of COD solubilization or oxygen consumption. The soluble COD allows us to understand how organic compounds are released in the bulk liquid, while oxygen consumption is due to the metabolism of bacterial biomass and the availability of biodegradable substrate. In the extreme situation where all the bacterial biomass is destroyed, there will be a high concentration of soluble COD in the sludge (Foladori et al., 2010). The degree of disintegration should be determined in terms of soluble COD concentration of sludge for the determination of optimum ozone dose. COD concentration of return activated sludge, supernatant and ozonated sludge should be determined for the calculation of disintegration degree.

$$DD_{\text{COD}} (\%) = \frac{SCOD_t - SCOD_o}{SCOD_{\text{NaOH}} - SCOD_o} \times 100 \quad (\text{Eq. 3})$$

Where;

$SCOD_o$ = concentration of soluble COD in the untreated sludge (mg/L),

$SCOD_t$ = concentration of soluble COD in the pre-treated sludge (mg/L),

$SCOD_{\text{NaOH}}$ = maximum COD concentration that can be solubilized and corresponds to the soluble COD after alkaline hydrolysis (mg/L),

The concentrations of $SCOD_o$ and $SCOD_t$ in the sludge are determined after filtration at 0.45 μm (alternatively on the supernatant after centrifugation). Alkaline hydrolysis can be performed by using 0.5 mol/L or 1 mol/L for 22-24 h at room temperature (Tiehm et al., 2001; Gonze et al., 2003; Bougrier et al., 2005; Nickel and Neis, 2007).

The sludge lysis efficiency represented by the disintegration degree (DD_{COD}) developed by Zhang et al. (2009), which is calculated as follow was used in this thesis:

$$DD_{\text{COD}} (\%) = \frac{SCOD_{\text{ozone}} - SCOD_o}{TCOD - SCOD_o} \times 100 \quad (\text{Eq. 4})$$

Where,

$SCOD_{\text{ozone}}$ = supernatant COD of the ozonated sludge (mg/L),

$SCOD_o$ = supernatant COD of untreated sludge (mg/L),

$TCOD$ = total COD of untreated sludge (mg/L).

The supernatant samples were obtained by centrifuging the sludge at 4000 r/min for 30 min. (Zhang et. al., 2009).

3.9.2 Protein Analysis

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

3.9.3 SCOD Analysis

The ability of sludge reduction technique to solubilize the particulate fraction can be evaluated either through the degree of COD solubilization or through the degree of TSS solubilization (or TSS disintegration).

The TSS disintegration is defined by the following expression, as percentage:

$$\text{TSS disintegration (\%)} = \frac{TSS_o - TSS_t}{TSS_o} \times 100 \quad (\text{Eq. 5})$$

Where;

TSS_o = concentration of TSS in the untreated sludge (mg/L),

TSS_t = concentration of TSS in the sludge after treatment (mg/L),

The COD solubilization is calculated with the following expression, as a percentage (Cui and Jahng, 2006; Yan et al., 2009a) :

Where;

$$\text{COD solubilization} = S_{\text{COD}} (\%) = \frac{SCOD_t - SCOD_o}{COD_o - SCOD_o} \times 100 \quad (\text{Eq. 6})$$

SCOD= concentration of soluble COD in the untreated sludge (mg/L),

$SCOD_t$ =concentration of soluble COD in the pre-treated sludge (mg/L),

COD_o =concentration of total COD in the untreated sludge (mg/L),

COD parameter was analyzed using Open Reflux Method. In SCOD measurements, soluble part of sludge was obtained by centrifuging of sludge samples at 10000 rpm for 20 minutes.

3.9.4 pH, T, DO, EC and ORP Measurements

WTW model 340i multi analyzer was used for the measurement of pH, T, DO, EC and ORP.

3.9.5 Measurement of MLSS and MLVSS

The concentration of suspended solids in the aeration tank, commonly known as the mixed liquor suspended solids (MLSS) concentration, is a crude measure of the biomass available for substrate removal. It is the most basic operational parameter and is used to calculate other important operating parameters. Expressed either in mg/L or g/m³ some of the MLSS may be inorganic, so by burning the dried sludge at 500°C in a muffle furnace the MLSS can be expressed as the mixed liquor volatile suspended solids (MLVSS) which is a more accurate assessment of the organic fraction and hence of the microbial biomass. However, neither the MLSS nor the

MLVSS can distinguish between the active and non-active microbial fraction, and the level of sludge activity.

10 mL samples from aeration tanks were filtered using apparatus shown in Figure 3.4. In addition, kept roughly an hour inside an oven at 105 °C (Figure 3.5). Aluminum dishes should be used to support the filters. After that, the filters are kept for a while inside a desiccator until they reach room temperature before weighting them again. With the weight obtained in the following formula has been used to calculate the MLSS.

$$\text{MLSS} = \frac{1000 * (a - b)}{V} \quad (\text{Eq. 7})$$

Where a: is the mass of filter after filtration, in milligrams,

b: is the mass of filter before filtration, in milligrams,

V: is the volume of sample, in milliliters

After this stage, the filters were then kept again for roughly an hour inside a muffler at 550 °C shown in Figure 3.6. Again, they were allowed to reach room temperature afterwards so that their weight could be measured. With the values thus obtained, the following formula has been used to calculate the MLVSS.

$$\text{MLVSS} = \text{MLSS} - \frac{d - b}{V} \quad (\text{Eq. 8})$$

Where d: the mass of the filter and residue, in milligrams

b: the mass of the filter before the filtration, in milligrams

V: the volume of sample, in milliliters



Figure 3.4 Set-up for the measurement of MLSS and MLVSS



Figure 3.5 Drying oven for operation at 103-105 °C



Figure 3.6 Muffle furnace for operation 550 °C

3.9.6 Observed Sludge Yield (Y_{obs})

Considering a mass balance of carbonaceous substrate in a chemostat system, Pirt (1965) proposed that a portion of the carbon source be used for maintenance and a portion used for anabolism. When the entire substrate is used for anabolism, the maximum growth yield (Y_H for heterotrophic bacteria), Y_H is theoretically obtained.

In a system containing a given amount of biomass, part of the carbon source is always used for maintenance. Therefore, the “observed biomass yield (Y_{obs}) is a function of the maximum growth yield (Y_H and SRT through coefficient from maintenance (m_s) or endogenous respiration (k_e) as described by van Loosdrecht and Henze (1999), resulting in the following expression:

$$Y_{obs} = Y_H \cdot \frac{1}{1 + SRT \cdot m_s \cdot Y_H} \quad (\text{Eq. 9})$$

$$Y_{obs} = Y_H \cdot \frac{1}{1 + SRT \cdot k_e} \quad (\text{Eq. 10})$$

Where; Y_H is 0.67 gCOD/gCOD (0.45 gVSS/gCOD) under aerobic conditions. The observed biomass yield Y_{obs} is always lower than Y_H .

In the practical approaches in WWTPs, the parameter Y_{obs} is used more general way, to evaluate the specific sludge production, and not only describe the net growth of bacterial biomass.

In this case, the parameter Y_{obs} is defined as “observed sludge yield” and corresponds to the ratio $\Delta VSS/\Delta COD$. It is different from the observed biomass yield because it contains other organic solids from the wastewater that are measured as VSS, but are not biological (Tchobanoglous et al., 2003).

It can be calculated as the total solid mass of sludge generated per unit of COD removal and corresponds to the slope of the lines shown in Figure 3.7 (a). A change (decrease) in the Y_{obs} coefficient is expected after the integration of a sludge reduction technique in an activated sludge process (Figure 3.7 (b)) demonstrating that the amount of sludge can be effectively reduced.

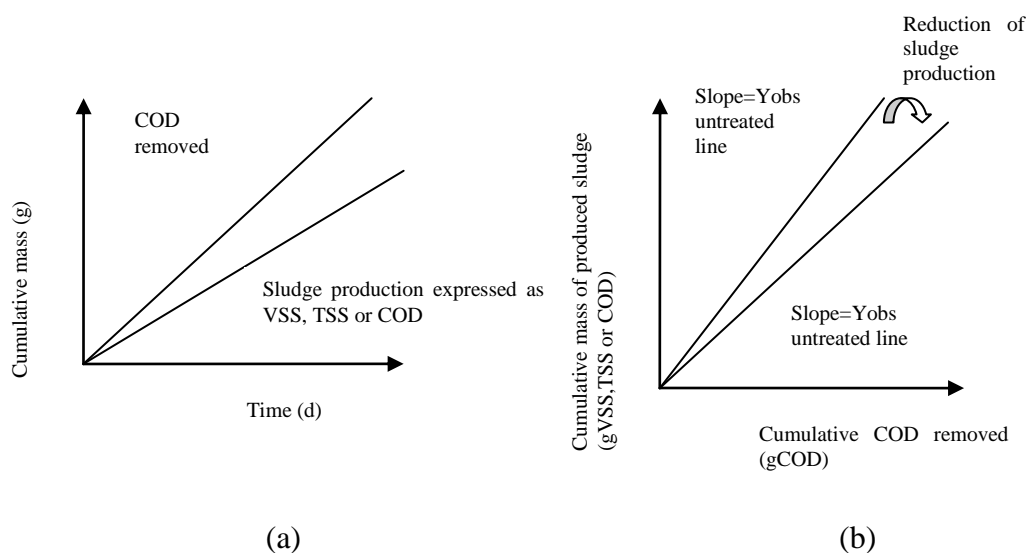


Figure 3.7 (a) Comparison between the mass of COD removed in the process and the production of excess sludge (b) relations between the cumulative sludge increase and COD removed, for untreated and treated line

3.9.7 NH_4-N , NO_3-N and NO_2-N Analysis

NH_4-N of supernatant were analyzed by using spectroquant cell test supplied by Merck (Kit number: 14763). NO_3-N of supernatant were analyzed by using spectroquant cell test supplied by Merck (Kit number: 14773). NO_2-N of supernatant were analyzed by using spectroquant cell test supplied by Merck (Kit number: 00609).

3.9.8 Sludge Volume Index (SVI)

The sludge volume index (SVI) is the volume in milliliters occupied by 1 g of a suspension after 30 min settling. SVI typically is used to monitor settling characteristics of activated sludge and other biological suspensions.

The suspended solids concentration of a well-mixed sample of the suspension and 30 min settled sludge volume were determined and calculated using following formula.

$$SVI = \frac{\text{settled_sludge_volume}(m/L) * 1000}{\text{Suspended_solids}(g/L)} \quad (\text{Eq. 11})$$

The settled sludge can be seen in Figure 3.8.



Figure 3.8 View of settled sludge

3.9.9 Oxygen Uptake Rate (OUR) and Specific Oxygen Uptake Rate (SOUR)

The Specific Oxygen Uptake Rate (SOUR), also known as the oxygen consumption or respiration rate, is defined as the milligram of oxygen consumed per gram of VSS per hour. This quick test has many advantages; rapid measure of influent organic load and biodegradability, indication of the presence of toxic or inhibitory wastes, degree of stability and condition of a sample, and calculation of oxygen demand rates at various points in the aeration basin.

This test was originally developed as a plant control parameter. SOUR is now also used as an alternative test method to meet the vector attraction reduction requirement

imposed by 40 CFR Part 503 standards for the use or disposal of sewage sludge. This requirement reduces the potential of spreading infectious disease agents by vectors (e.g. insects, rodents, and birds). SOUR is defined as milligram of oxygen consumed per gram of total solids (TS) per hour (APHA, 2005).

The oxygen uptake rate measures the rate by which the oxygen is used by the microorganisms to oxidize the organic matter present in the wastewater and it is closely related to their growth rate (Metcalf & Eddy, 2004). Sample container was filled to overflowing with a representative sample. Monitoring of the dissolved oxygen was begun. After the meter reading has stabilized, initial DO or manometric or respirometric reading was recorded and timing device was started. Appropriate DO, manometric or respirometric data was recorded at least once per minute, depending on rate of consumption. Over a 15 minute period or until DO levels drop below 1 mg/L, data was recorded.

Low DO (<2.00 mg/L) at the start of the test) may limit oxygen uptake by the sample. This phenomenon will be indicated by a decreasing rate of oxygen consumption as the test progresses. Reject such data as being unrepresentative of oxygen-consumption rate and repeat the test beginning with a sample having a higher initial DO level.

Observed readings (mg/L DO) versus time (minutes) were plotted on graph paper and determined the slope of the line of best fit. The slope is the oxygen consumption rate in milligrams per liter per minute (APHA, 2005).

3.9.10 Capillary Suction Time (CST) Test

CST test can determine dewatering characteristics of a given sludge rapidly and easily in a simple, inexpensive, and easy way. High CST value is usually an indicator of poor sludge dewaterability (EPA, 1987).

CST test was used for the evaluation of the dewatering performances of both disintegrated sludge samples 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 CST analyzer can be seen in Figure 3.9.



Figure 3.9 View of capillary suction time analyzer

A sample of sludge is placed in the sample container. The timer activated when water reaches the first probe. After the water reaches the second probe, the timer deactivates. The time interval between timer activation and deactivation gives us the capillary suction time as a measurement of sludge dewaterability (Erden and Filibeli, 2010).

3.9.11 Specific Resistance to Filtration (SRF) (Buchner Funnel) Test

SRF is widely used parameter in order to compare filtration characteristics of different types of sludge and determine the optimum conditioning chemical requirements for a specific sludge. The lower specific resistance values demonstrated the better dewatering characteristic of sludge. SRF value of sludge is determined using Buchner Funnel Test equipment consists of a graduated cylinder as shown in Figure 3.10.

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 (Erden and Filibeli, 2010).



Figure 3.10 Buchner Funnel Apparatus

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.

$$r = (2PA^2b) / \mu w \quad (\text{Eq.12})$$

Where,

r = specific resistance (m/kg),

P = pressure of filtration (N/m²),

A = area of filter (m²),

b = slope of time/volume vs. volume curve (sec/m²),

μ = viscosity of filtrate (N (sec)/m²), and

w = weight of dry solids / volume of filtrate (kg/m³).

In this thesis, SRF test was applied sludges from control and modified runs (Ozone and OSA systems) for evaluation of dewatering characteristics. Viscosities of filtrate samples were also measured using Brookfield RVDV III Rheometer for calculation of SRF (r) value.

3.9.12 Particle Size Analysis

Particle size distributions were monitored using a Malvern Mastersizer 2000QM analyzer shown in Figure 3.11.



Figure 3.11 View of Malvern Mastersizer 2000QM particle size analyze

CHAPTER FOUR

RESULTS & DISCUSSION

4.1 Results of Optimization Study in the Activated Sludge Process

Box-Behnken Statistical Design Program was used in order to determine the optimum operational conditions in the activated sludge processes. The experiments were chosen using variable parameters and the obtained efficiencies from these experiments were based on a mathematical model. HRT, SRT and initial COD concentration were chosen as variable parameters for the activated sludge process (HRT: 5-25 h, SRT: 5-30 d and COD_i: 300-500 mg/L).

17 experiments shown in Table 4.1 were carried out in two different activated sludge process, simultaneously. The results of the experiments obtained after the steady-state conditions. COD concentrations of influent and effluent were measured three times a week for each process.

Table 4.1 Experimental data points suggested by Box-Behnken statistical design program

	Factor 1	Factor 2	Factor 3
	A:Initial COD	B:HRT	C:SRT
Run	mg/L	hour	day
1	300.00	5.00	17.50
2	400.00	5.00	5.00
3	300.00	15.00	30.00
4	300.00	25.00	17.50
5	400.00	15.00	17.50
6	500.00	15.00	5.00
7	400.00	15.00	17.50
8	400.00	15.00	17.50
9	400.00	15.00	17.50
10	400.00	25.00	5.00
11	400.00	15.00	17.50
12	400.00	5.00	30.00
13	400.00	25.00	30.00
14	500.00	25.00	17.50
15	500.00	5.00	17.50
16	500.00	15.00	30.00
17	300.00	15.00	5.00

The response function coefficients were determined using experimental data for each independent variable. The analysis of variance (ANOVA) program was used for the determination of most suitable response function and correlation of the experimental data. The results of the ANOVA test for COD removal are presented in Table 4.2. The quadratic model provided the best fit to the experimental data with the lowest standard deviation, the highest correlation coefficient (0.95) and the lowest p-value according to ANOVA test.

Table 4.2 ANOVA analysis for COD removal efficiency

Source	Sum of Squares	d	Mean Square	F Value	p-value Prob > F	
<i>COD removal (%)</i>						
Mean vs Total	1.546E+0	1	1.546E+0			
Linear vs Mean	199.95	3	66.65	8.55	0.0021	
2FI vs Linear	11.75	3	3.92	0.44	0.7313	
<u>Quadratic vs 2FI</u>	<u>76.70</u>	<u>3</u>	<u>25.57</u>	<u>13.89</u>	<u>0.0025</u>	<u>Suggeste</u>
Cubic vs Quadratic	11.86	3	3.95	15.41	0.0116	Aliased
Residual	1.03	4	0.26			
Total	1.549E+0	1	9111.14			
<i>Lack of Fit Tests</i>						
Linear	100.31	9	11.15	43.45	0.0012	
2FI	88.56	6	14.76	57.54	0.0008	
<u>Quadratic</u>	<u>11.86</u>	<u>3</u>	<u>3.95</u>	<u>15.41</u>	<u>0.0116</u>	<u>Suggeste</u>
Cubic	0.000	0				Aliased
Pure Error	1.03	4	0.26			
<i>Model Summary Statistics</i>						
	<i>Standard Deviation</i>		R^2	$Adj.R^2$	$Press$	
Linear	2.79		0.6636	0.586	190.10	
2FI	2.99		0.7026	0.524	368.74	
<u>Quadratic</u>	<u>1.36</u>		<u>0.9572</u>	<u>0.902</u>	<u>191.36</u>	<u>Suggeste</u>
Cubic	0.51		0.9966	0.986	+	Aliased

The estimated coefficients of the response functions are given in Table 4.3. The predicted values of the response functions and experimental data are given in Table 4.4. Using the equation obtained from the Box-Behnken, the results of the variable range could be predicted.

Table 4.3 Response function coefficient for COD removal efficiency (%)

Coefficients	Value
b_0	107.1719
b_1	-0.09977
b_2	-0.2229
b_3	1.335136
b_{12}	0.001678
b_{13}	-0.00025
b_{23}	0.00132
b_{11}	7.5E-05
b_{22}	-0.0118
b_{33}	-0.02565

Table 4.4 Experimental and predicted COD removal efficiency (%)

Run	<i>Exp.COD (%) COD Removal</i>	<i>Prd.COD (%)</i>
1	100	99.42
2	87.5	86.77875
3	100	100.8713
4	100	98.4075
5	96.92	97.448
6	89	88.12875
7	96.88	97.448
8	97.7	97.448
9	97.92	97.448
10	88.5	88.79125
11	97.82	97.448
12	95.69	95.39875
13	97.35	98.07125
14	97.39	97.97
15	90.68	92.2725
16	97.76	92.2725
17	90	96.45875

Response function predictions were in good agreement with the experimental data. When the initial COD concentration was kept 300 mg/L, the hydraulic retention time versus solid retention time were observed. The optimum value can be read from the Figure 4.1. When initial COD concentration, HRT and SRT were 300 mg/L, 25 h and 25 d, respectively, COD removal efficiency was taken the highest value. The predicted COD removal efficiency was found as 99 % using the equation. For this reason, 25 h for hydraulic retention time, 25 d for solid retention time and 300 mg/L

for initial COD concentration could be chosen as the optimum values for operational parameters.

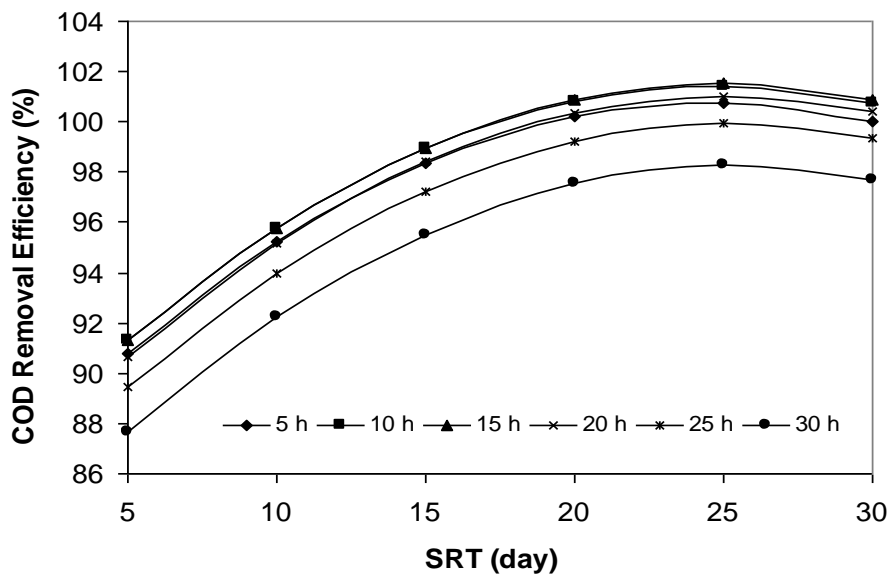


Figure 4.1 COD removal efficiencies versus SRT at different HRTs ($COD_i=300$ mg/L)

The same results could be obtained using the Figure 4.2 depicted COD removal efficiencies versus HRT for different SRT values at 300 mg/L of COD_i .

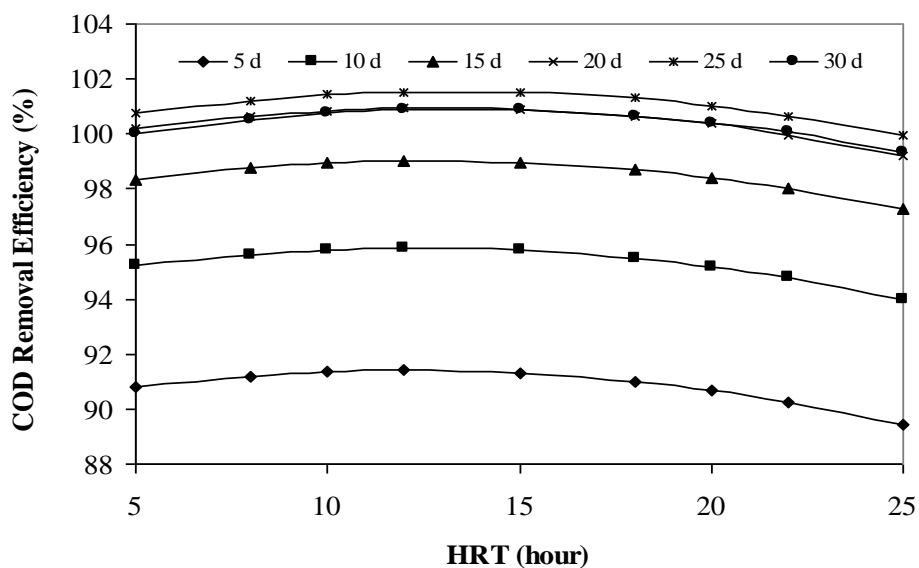


Figure 4.2 COD removal efficiencies versus HRT at different SRTs ($COD_i=300$ mg/L)

While the COD_i was 400 mg/L, the changes of HRT and SRT were illustrated in Figure 4.3 and Figure 4.4. In case of, COD_i : 400 mg/L, HRT: 20 h and SRT: 25 d; the COD removal efficiency was the highest. The predicted COD removal efficiency was found as 98.8 % using the equation. Therefore, 20 h for HRT and 25 d for SRT and 400 mg/L for COD_i concentration could be chosen as the optimum values for operational parameters.

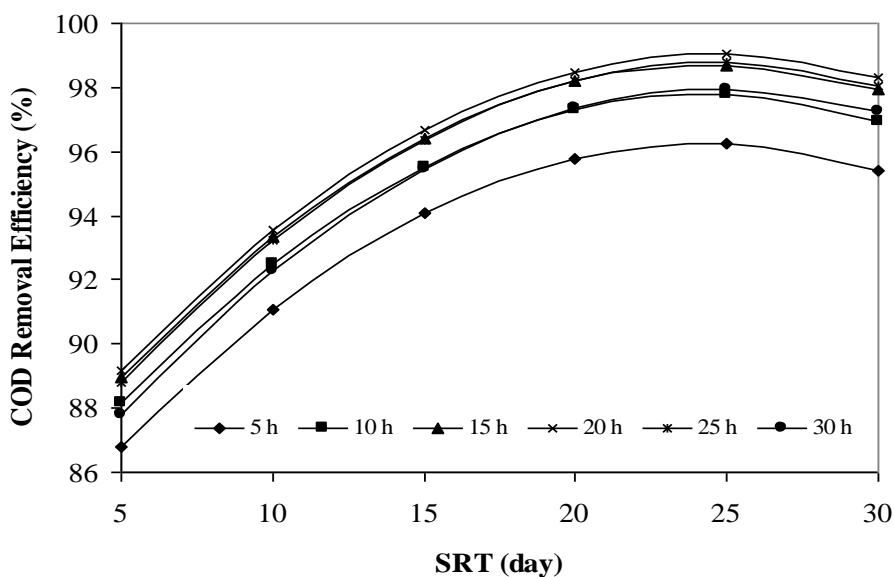


Figure 4.3 COD removal efficiencies versus SRT at different HRTs ($COD_i=400$ mg/L)

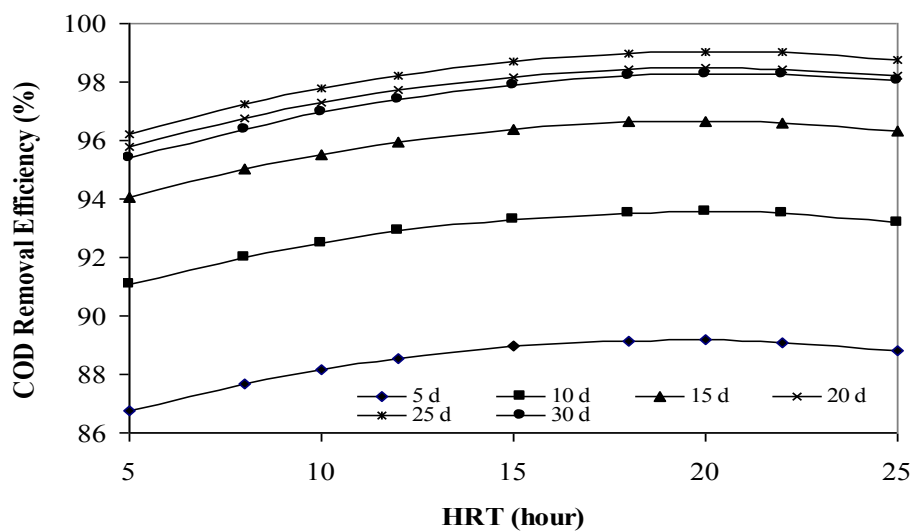


Figure 4.4 COD removal efficiencies versus HRT at different SRTs ($COD_i=400$ mg/L)

While the COD_{ini} is 500 mg/L, COD removal efficiencies versus HRT and SRT are illustrated in Figure 4.5 and Figure 4.6 and the COD_i is 500 mg/L. In case of, COD_i : 500 mg/L, HRT: 25 h and SRT: 25 d; the COD removal efficiency was the highest. The predicted COD removal efficiency was found as 99.1 % using the equation. Therefore, 20 h for HRT, 25 d for SRT and 500 mg/L for COD_i concentration could be chosen as the optimum values for operational parameters

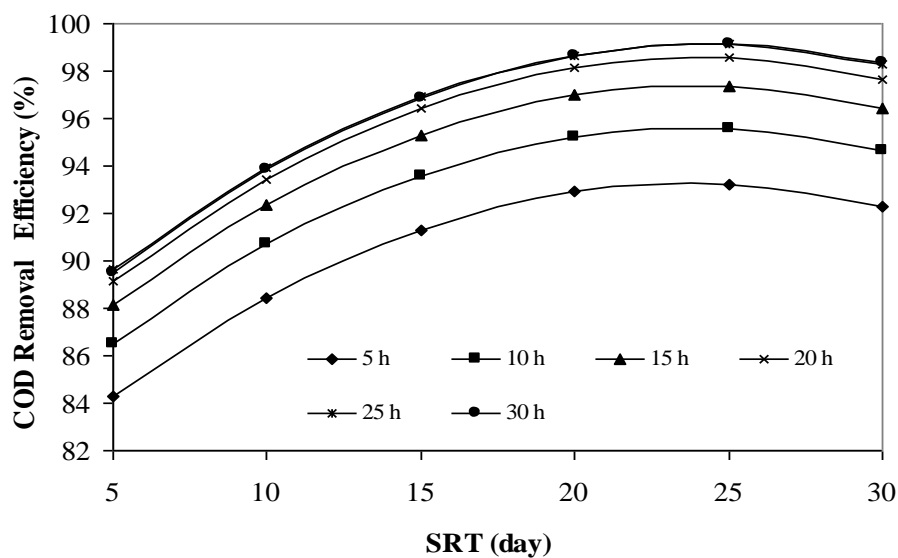


Figure 4.5 COD removal efficiencies versus SRT at different HRTs ($COD_i=500$ mg/L)

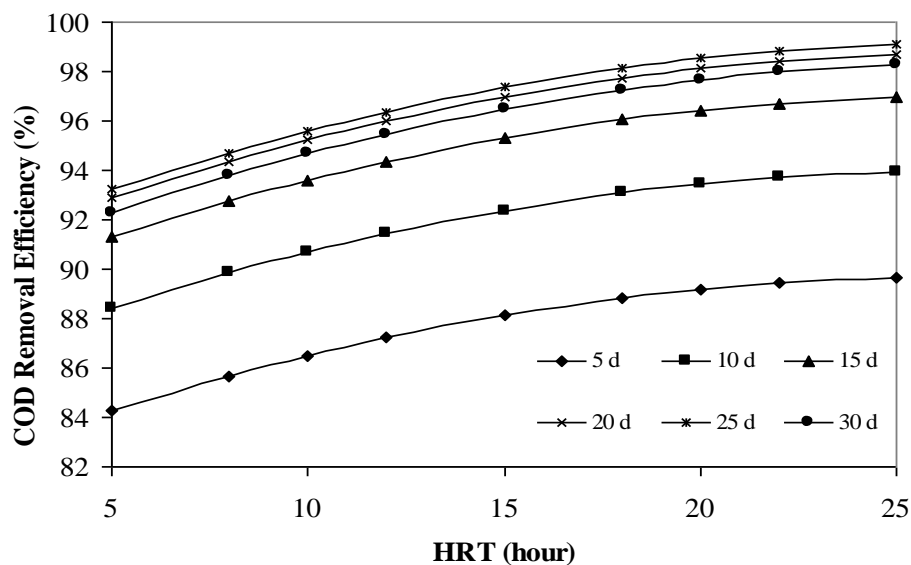


Figure 4.6 COD removal efficiencies versus HRT at different SRTs ($COD_i=500$ mg/L)

Consequently, three different initial COD concentrations were studied and 400 mg/L was chosen as the best representative value of initial COD concentration for domestic wastewater. HRT and SRT were chosen 25 h and 25 d as an optimum values, respectively. According to the experimental results, 20 h HRT could be chosen but there was no significantly difference between 20 and 25 h for the COD removal efficiency. When HRT was chosen as 25 h, the flow of the system was lower than the 20 h of HRT.. Because of the lower synthetic wastewater demand, 25 h was determined as an optimum value for HRT.

4.2 Continuous Operation until Steady State Conditions

In this section, the results of operation for two activated sludge processes were presented. The systems were observed in terms of pH, T, DO, MLSS/MLVSS, COD removal efficiency etc. during 45 days.

4.2.1 pH

pH monitoring is used to control nitrification system where suitable range should be from 6 to 9 even though optimal range is much narrower being from 7.5 to 8 (Metcalf & Eddy, 2004).

The changes of pH of aeration tanks were depicted in Figure 4.7. pH values were similar. For Reactor 1, pH was varied in range of 7.06-8.28, while pH was ranged 7-7.89 for Reactor 2. It is a good idea to check the pH of the influent as well every day and after its preparation. The pH changes considerably when it stored in a fridge for a longer time.

4.2.2 Temperature

The right temperature is thus an important factor in wastewater treatment because it affects chemical reactions. In biological treatment processes, like activated sludge, the temperature should be in range from 25 to 35 °C because aerobic digestion and nitrification work best in that range ((Metcalf & Eddy, 2004). The changes of

temperature of the aeration tanks during stabilization period are depicted in Figure 4.8. In this period, the temperature was ranged between 21-26 °C.

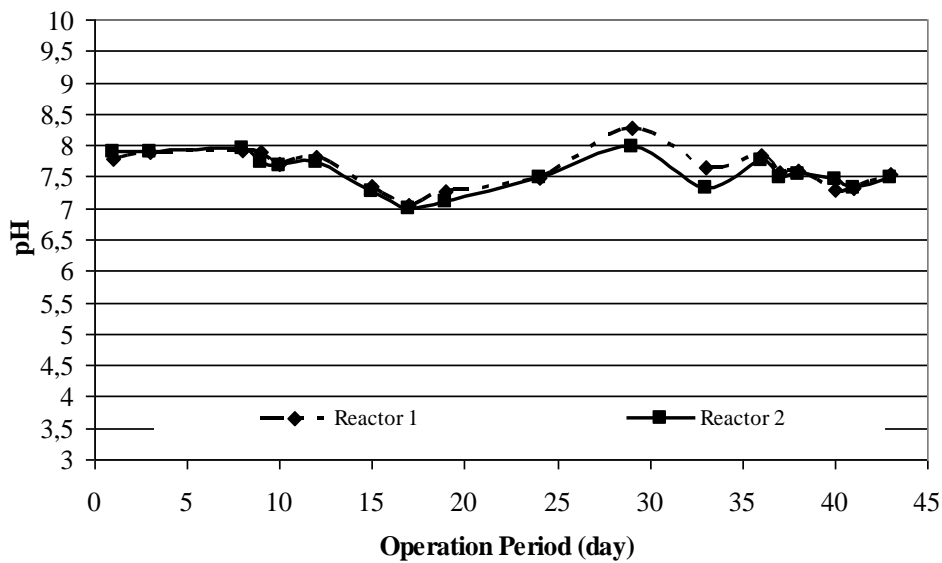


Figure 4.7 pH changes of aeration tanks

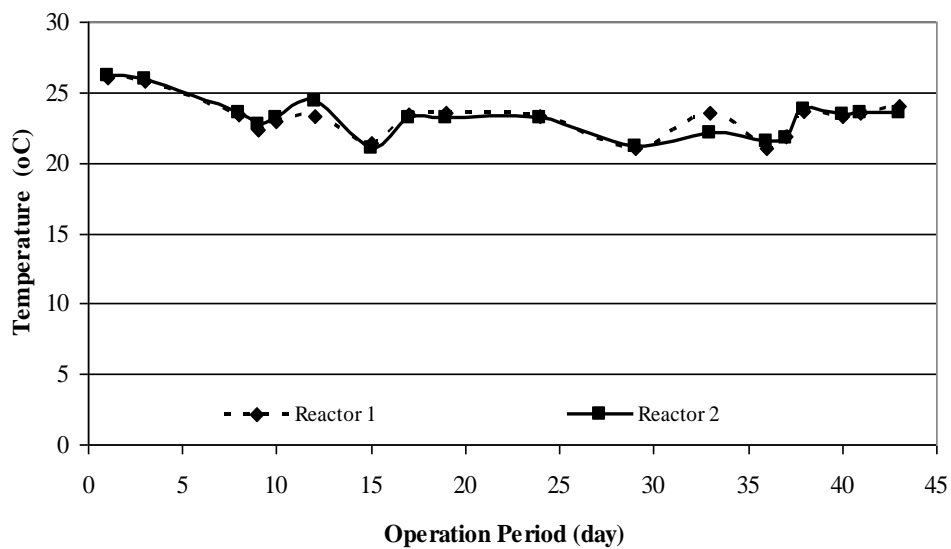


Figure 4.8 Temperature changes of aeration tanks

4.2.3 Dissolved Oxygen (DO)

Being aerobic biological treatment oxygen plays a major part since the microorganisms present in the wastewater need it to be able to do this job. It also helps to eliminate the generation of bad odors. The amount of DO depends on temperature since biochemical reactions increase with the increment of the temperature (Metcalf & Eddy, 2004).

As seen in Figure 4.9, at the beginning of the operation period, the DO concentration values were higher than the other days due to the aeration flow. The aeration rate was decreased gradually and the concentration was kept above 2.5 mg/L during the operation.

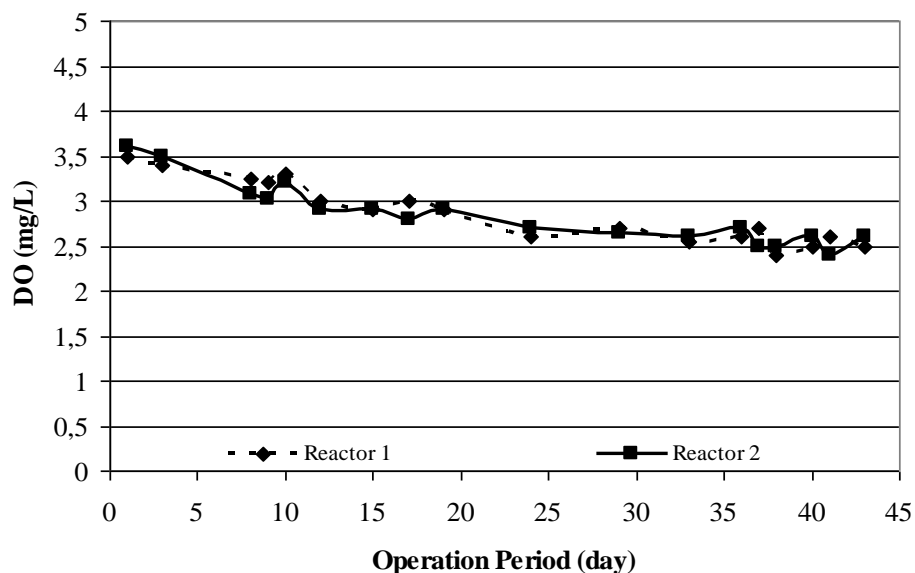


Figure 4.9 DO changes of aeration tanks

4.2.4 Oxidation-Reduction Potential (ORP)

Generally, ORP has been used as the monitoring and controlling parameter in many wastewater treatment plants, especially in chemical treatment and biological treatment units. For example, as the denitrification process was carried out at anoxic condition, ORP value could be used as the set-point to lead the operator to

understand how much time was needed to reach the optimal denitrification condition (Chang et al, 2002).

For both of the reactors, the ORP level was closed. Less than 100 mV was not observed. It can be seen from the Figure 4.10 that generally, the ORP level was around 150 mV.

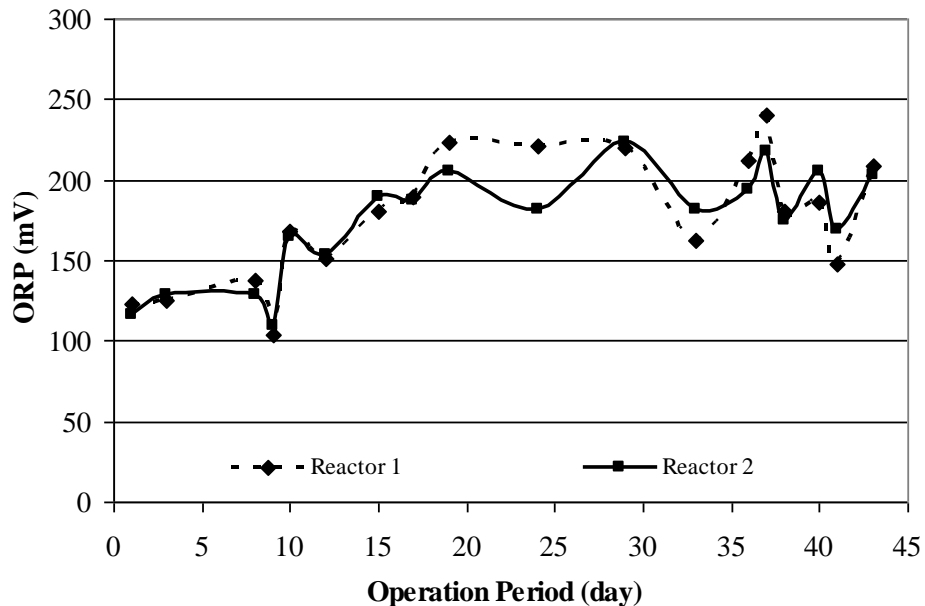


Figure 4.10 ORP changes of aeration tanks

4.2.5 Conductivity

Conductivity is a measure of the ability of an aqueous solution to carry electric current. This ability depends on the presence of ions, on their total concentration, mobility and valence and temperature of measurement. Molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly (APHA, 2005). From Figure 4.11, it can be realized easily that the conductivity values were similar in the activated sludge process as range of 800-1000 $\mu\text{S}/\text{cm}$. After the 10th days of the operation period, the systems were reached steady state conditions in terms of conductivity.

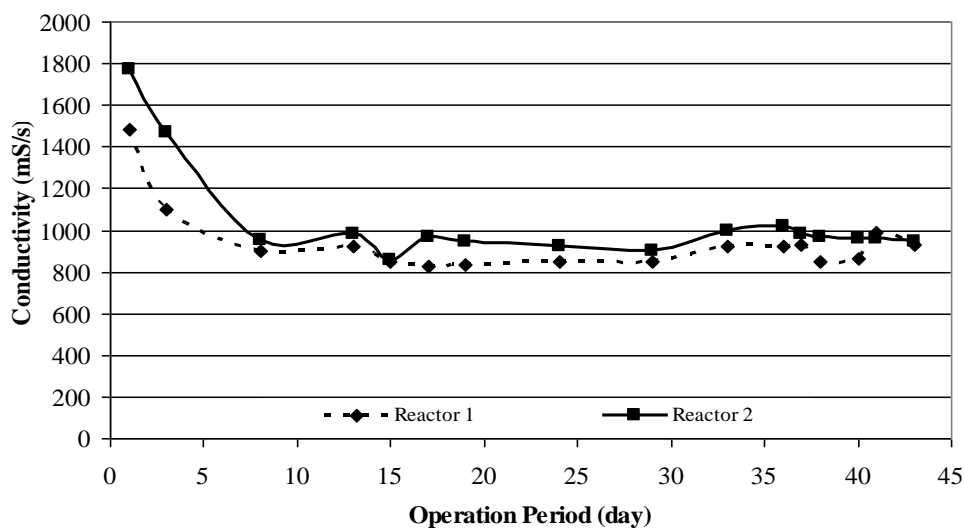


Figure 4.11 Conductivity changes of aeration tanks

4.2.6 Removal of Chemical Oxygen Demand (COD)

After the fifteenth days of the operation period, the COD removal efficiencies were reached about 80 % – 90 %. The last 10th days of the period, the consistent could be seen between the activated sludge processes in terms of COD removal as shown in Figure 4.12.. The highest COD removal efficiency and its sustainability were mean that the steady state was achieved.

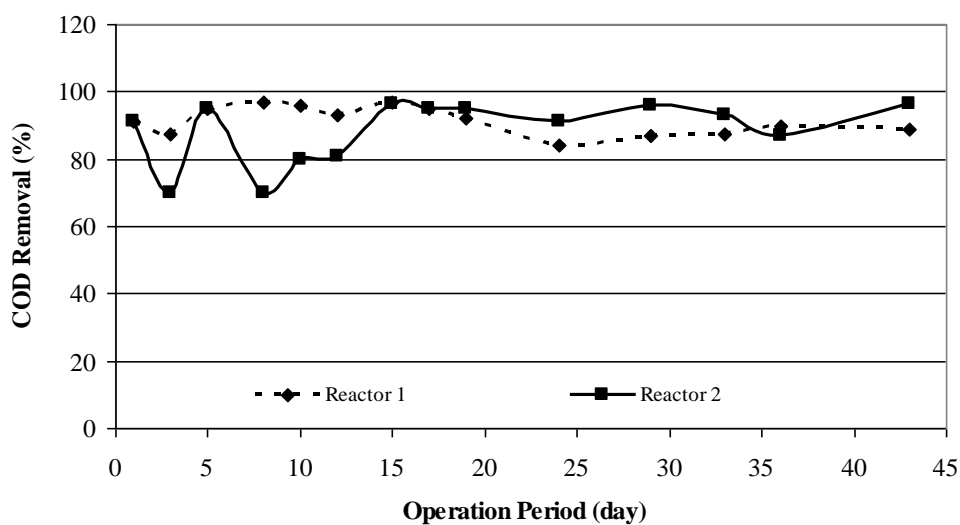


Figure 4.12 COD removal efficiencies of activated sludge processes

4.2.7 $\text{NH}_4\text{-N}$ Removal

The decrease of the ammonium concentration of the influent and the increase of the nitrate concentration of the effluent were pointed out that the nitrification was occurred in the systems. Especially for the last days of the operation, the removal of ammonium nitrogen was reached high efficiency (>90 %) (Figure 4.13).

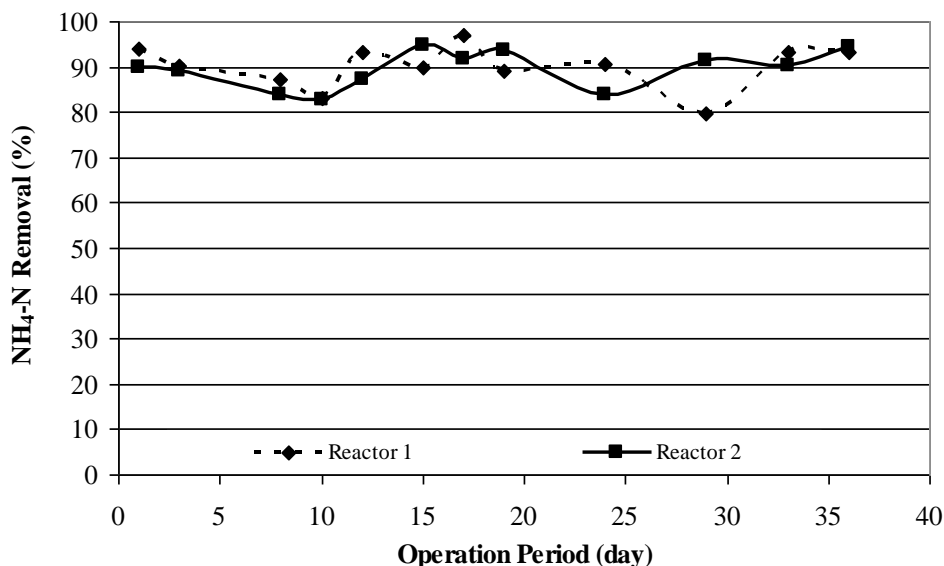


Figure 4.13 $\text{NH}_4\text{-N}$ removal changes of aeration tanks

4.2.8 MLVSS/MLSS

Other methods must be used if an accurate estimation of microbial activity is required (e.g. biochemical assessment); although for routine operational control the MLSS is sufficient. The normal MLSS range is 1500-3500 mg/L for conventional activated sludge units, rising to 8000mg/L for high-rate systems. The MLSS concentration is controlled by altering the sludge wastage rate. In theory the higher the MLSS concentration in the aeration tank, then the greater the efficiency of the process as there is a greater biomass to utilize the available substrate. However, in practice, high operating values of MLSS are limited by the availability of oxygen in the aeration tank and the ability of the sedimentation unit to separate and recycle activated sludge.

One of the important parameters observed during the operation period was MLSS/MLVSS which indicate that the presences of the microorganisms for the removal of carboneous and nitrogen. MLVSS/MLSS was nearly stable during the operation period (Figure 4.14). It means that the sufficient concentration of MLSS/MLVSS was maintained for the high removal efficiency both COD and nitrogen. The average MLVSS/MLSS was 0.85 for reactor 1 and 0.84 for reactor 2.

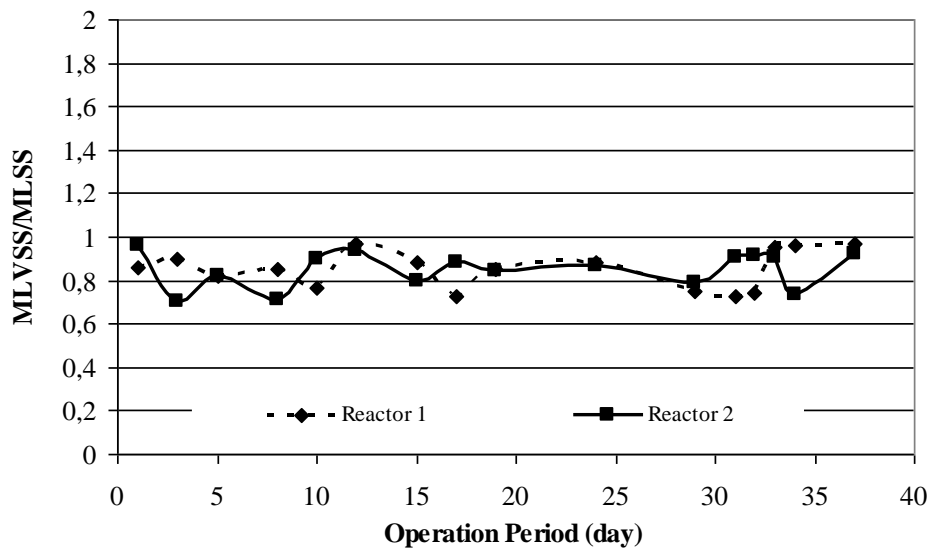


Figure 4.14. MLVSS/MLSS changes of aeration tanks

4.2.9 $PO_4\text{-P}$ Concentration of Influent and Effluent

$PO_4\text{-P}$ was an observed parameter in the influent and effluent of the processes but no removal was expected. The $PO_4\text{-P}$ concentration of the influent was ranged 3.53-5 mg/L due to the C/NP=100/5/1 ratio (Figure 4.15). The $PO_4\text{-P}$ concentration of the effluent was ranged 4.13-5.3 mg/L (Figure 4.16).

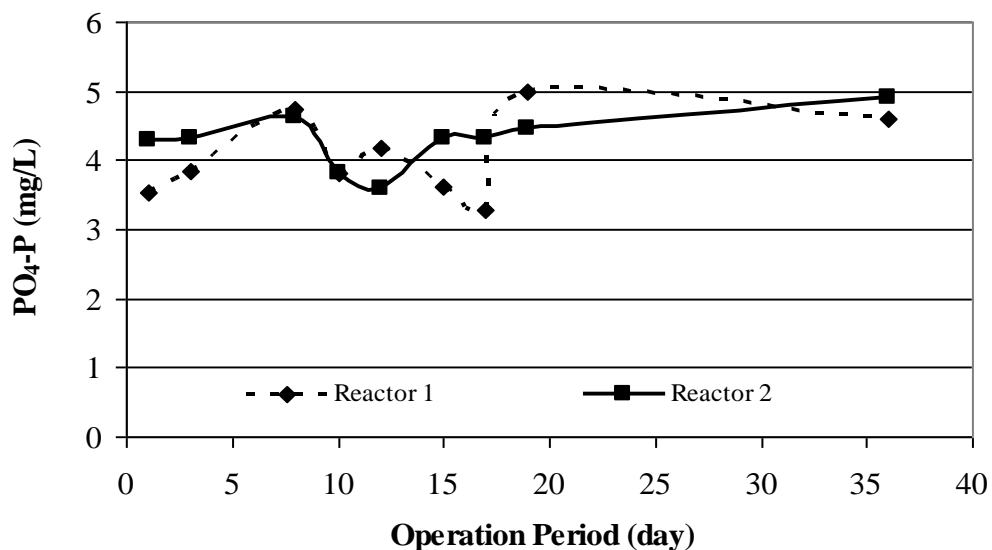


Figure 4.15 PO₄-P contents of influent

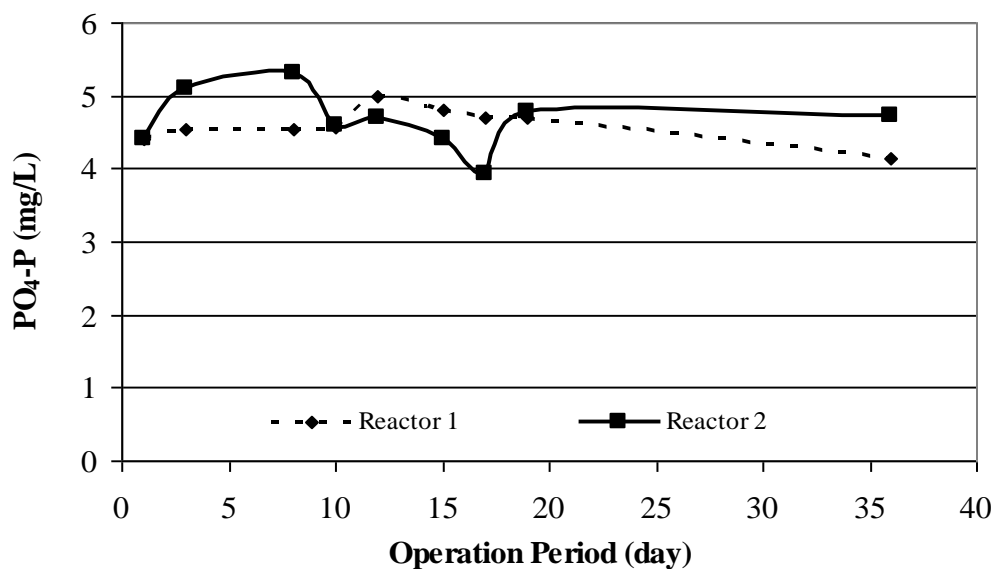


Figure 4.16 PO₄-P contents of effluent

4.2.10 NO₃-N Concentration of Effluent

NO₃ concentration of Reactor 1 was 4.3 mg/L as a minimum value and 27.9 mg/L as a maximum value of the operation period. For Reactor 2, the lowest value was

4.36 mg/L and the highest value was 30 mg/L. After the 30th days of the period, the systems became stable in terms of the NO₃ concentration of the effluent for both reactors (Figure 4.17).

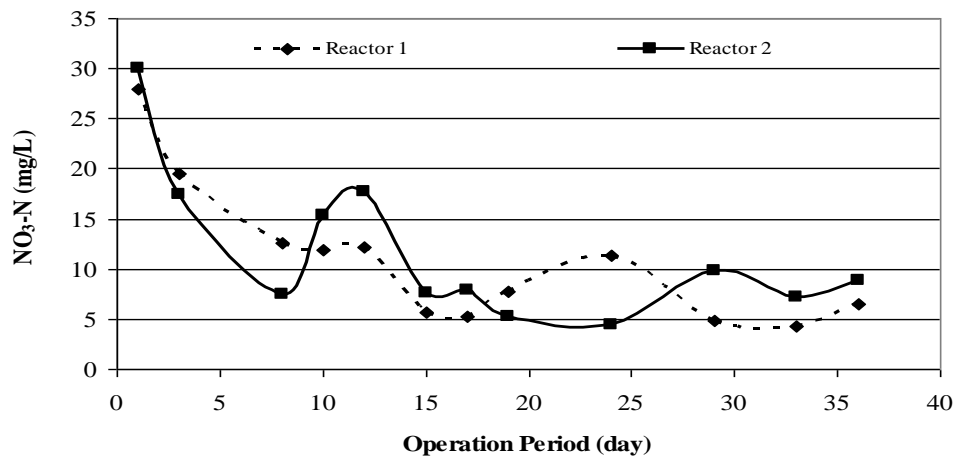


Figure 4.17 NO₃ concentrations of the effluent

4.2.11 NO₂-N Concentration of Effluent

It can be seen from the Figure 4.18, during the operational period, low values were measured for NO₂-N concentration. The concentration of NO₂-N was around 1 mg/L for both reactors.

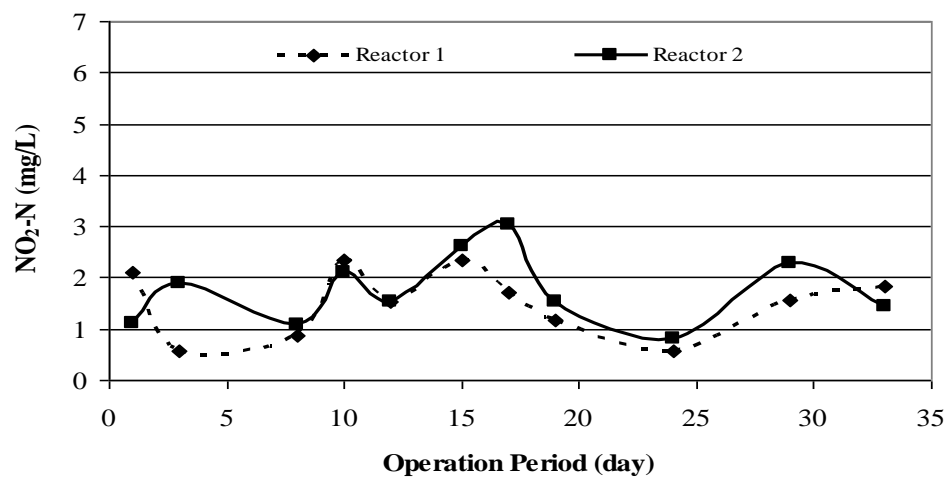


Figure 4.18 NO₂-N concentrations of effluent

4.2.12 Capillary Suction Time (CST)

Dewaterability characteristics of activated sludge of the systems represented by CST were similar (Figure 4.19). The average value of CST was 11.8 and 12 s for Reactor 1 and 2, respectively.

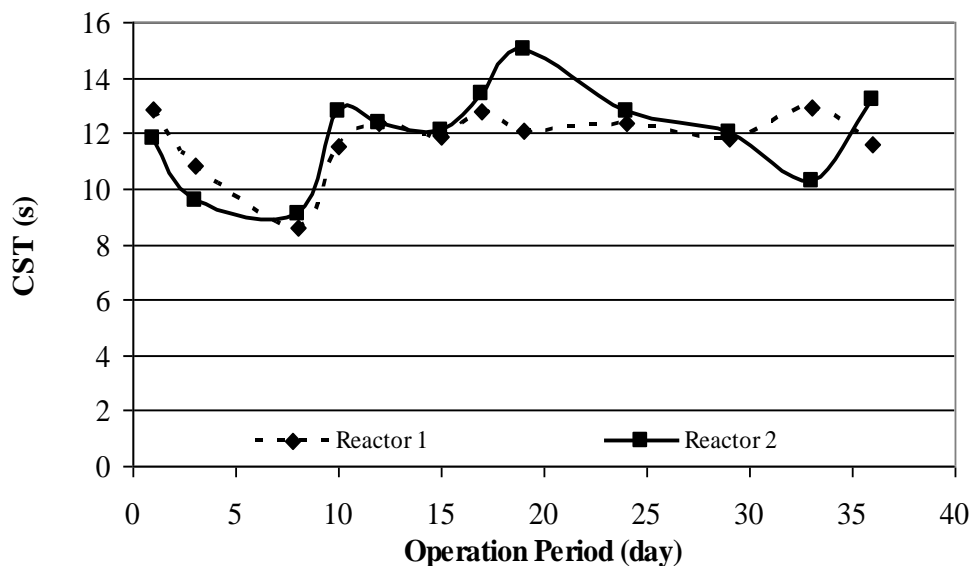


Figure 4.19 Change of CST

4.2.13 Particle Size Distribution

The particle size distributions of the systems were depicted in Figure 4.20 and 4.21. The particle size was close in Reactor 1 but in Reactor 2, the size of the particle was changed during operational period.

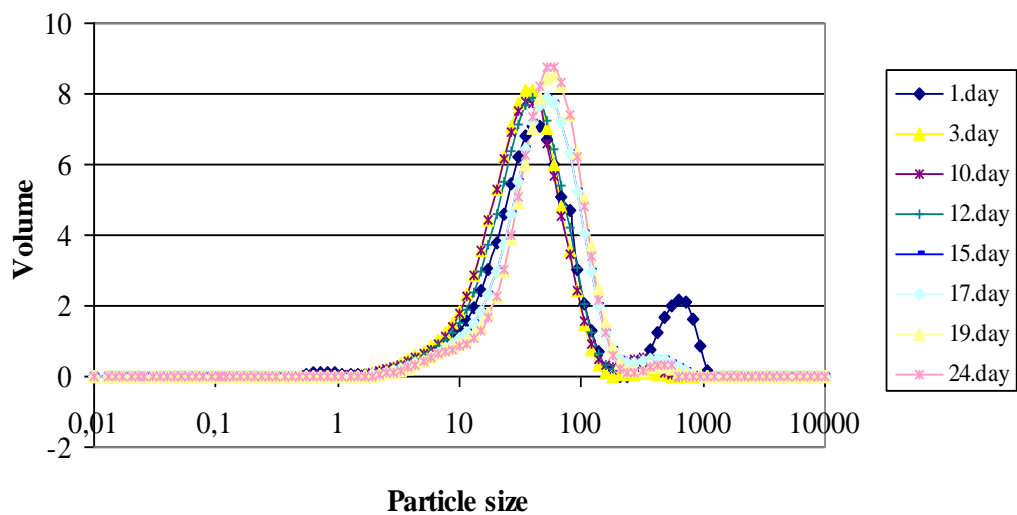


Figure 4.20 Particle size distribution for Reactor 1

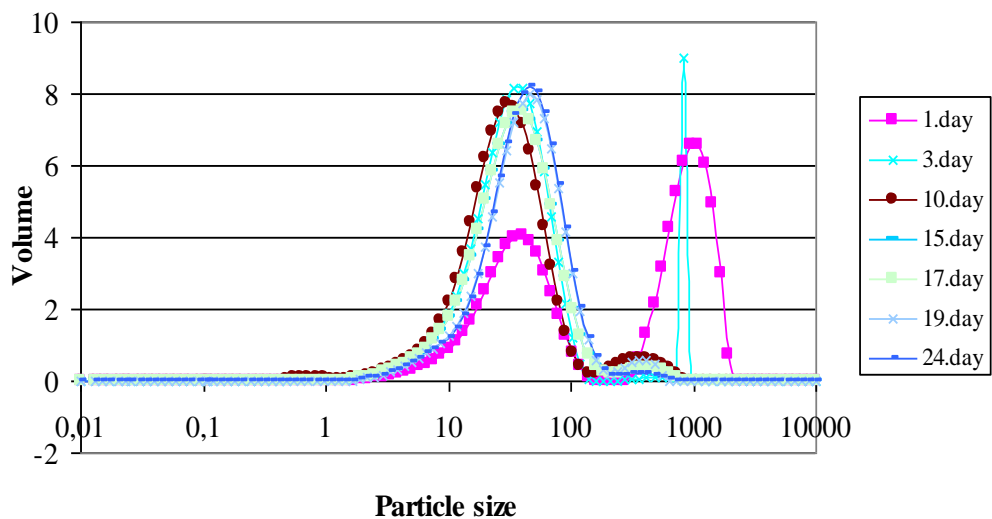


Figure 4.21 Particle size distribution for Reactor 2

4.3 Optimization of Ozone Dose

The sludge ozonation experiments were conducted for seven different ozone doses ranged between 0.007-0.06 gO_3/gTS . 400 mL sludge sample volume was used for

each experiment. This volume was corresponded to $0.1Q_R$ of return activated sludge flow rate per day. After each ozonation study, the sludge and supernatant were analyzed in order to investigate the effect of ozonation on DD related to total and soluble COD concentrations.

4.3.1 Soluble COD (SCOD) and Disintegration Degree

The most important parameter in evaluating the performance of sludge ozonation is the efficiency of sludge solubilization (Chu et al., 2009a). In order to evaluate the disintegration performance, DD parameter developed by Zhang et al. (2009) was used (Eq. 3). The transporting of organic matter contents of the sludge to the liquid phase is the main target of the disintegration. The solubilization of organic matters can be achieved with the ozone oxidation applied for disintegration of sludge.

It was found that approximately 60 % of the soluble COD generated due to the ozonation was in a biodegradable form at the early stage of ozonation while the remaining soluble organic matter was refractory (Saktaywin et al., 2005). In addition to this, generally, the reported efficiency of sludge solubilization was 30-60 % using ozone oxidation (Chu et al., 2009a). In this study, agreement with Saktaywin et al. (2005) and Chu et al. (2009a), DD of biological sludge increased significantly with increasing of ozone doses. The DD was obtained 56.2 % at an ozone dose of 0.05 g O_3 /g TS using ozone oxidation as shown in Figure 4.22. The higher ozone dose application resulted in slightly improvement of sludge solubilization. This might be attributed to the complex ozonation process. In mixed liquor, like activated sludge, it has been reported that ozone may first react with the soluble fraction of the activated sludge and then attack the particulate fraction (Cesbron et al., 2003). Ozone is also utilized to oxidize the biodegradable products and consequently ozone is not consumed to transform the remaining refractory organic matter (Chu et al., 2009a). Appropriate ozone dose must be chosen to achieve a balance between sludge reduction efficiency and cost. However, the cost analysis could not carried out in this study; but according to the literature it can be easily said that the ozone cost must be consider for ozonation and the ozone usage must be limited with the sufficient sludge reduction efficiency. The higher ozone doses cause increasing of the energy

consumption and consequently, cost of ozonation process. Because, optimal ozone dose for return activated sludge disintegration was determined as dose of 0.05 g O₃/g TS agreement with Zhang et al., (2009). The higher doses improved disintegration degree, slightly.

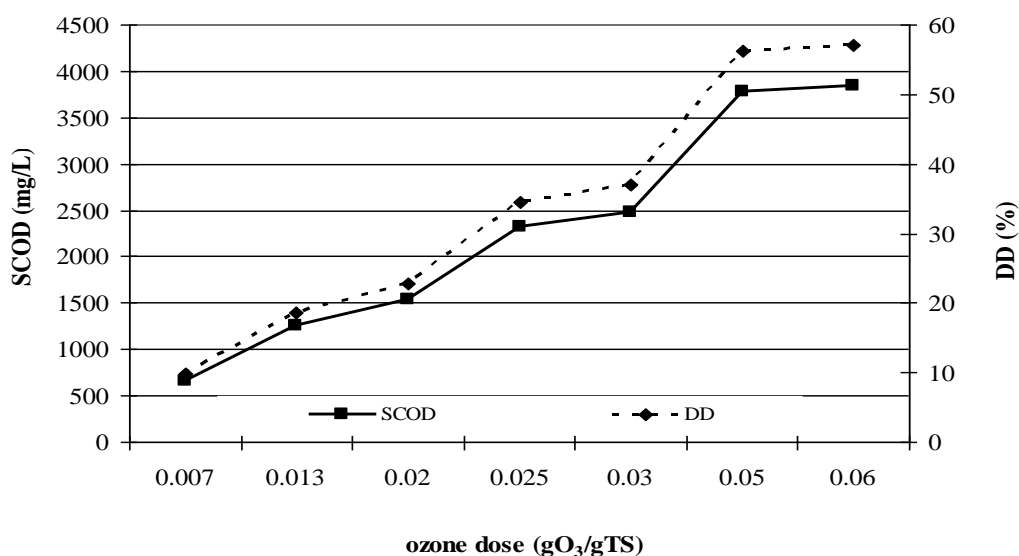


Figure 4.22 Changes in SCOD and DD with different ozone doses

4.3.2 Effect of Ozonation on Sludge Reduction

Ozone lysis releases the sludge organics into the surrounding water and reduces the solid content of sludge leading to the sludge TS and VS reduction. The decreasing of TS and VS indicates the importance of ozone oxidation in sludge destruction and solubilization.

Zhang et al. (2009) reported that when the ozone dose was 0.05 gO₃/gTS, the reaction time was 105 min, TS and VS decreased by 1621 mg/L, and 1219 mg/L; the remaining TS and VS were 1679 mg/L and 1451 mg/L; the corresponding reduction ratio was 49.1 % and 45.7 %, respectively.

The ozonation of sludge leads to a decrease in the ratio of VSS/SS and pH value. The ratio of VSS/TSS decreased from 78 % in raw sludge to 73 % in ozonated sludge with a dose of 0.16 gO₃/gTSS (Bougrier et al., 2006) and pH decreased from

6.2 to 3 at an ozone dose of 0.5 gO₃/gTS (Deleris et al., 2002). In this thesis, pH values were decreased from 7.27 to 5.58 at an ozone dose of 0.05 gO₃/gTS.

TSS and VSS contents of the sludge were decreased with the increasing of the ozone dose as shown in Figure 4.23. The TSS and VSS contents of the sludge were significantly changed up to dose. At ozone dose of 0.05 gO₃/gTS, TSS and VSS reduction of sludge was 77.78 % and 71.59 %, respectively. At an ozone dose of 0.06 gO₃/gTS, TSS and VSS reduction were similar to the result of 0.05 gO₃/gTS ozone doses with 77.78 % and 72.73 % reduction capacity.

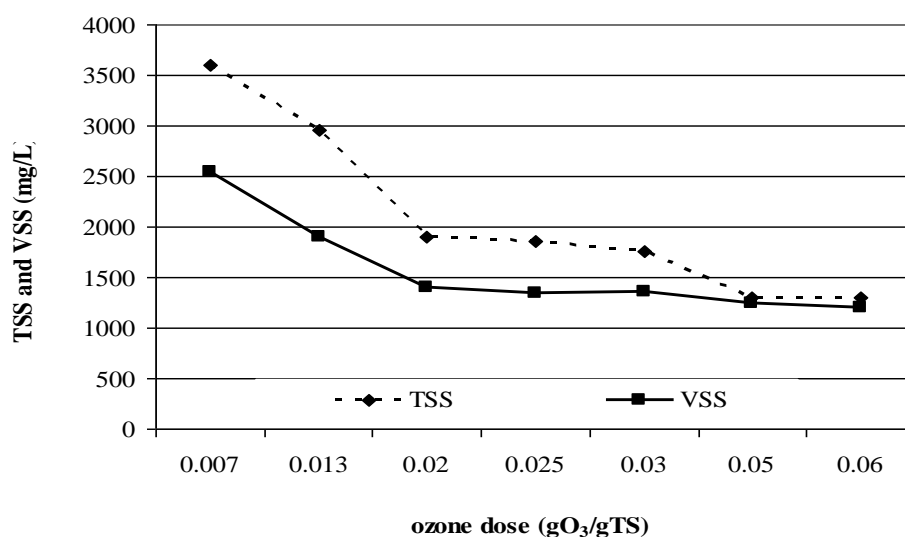


Figure 4.23 VSS and TSS contents of ozonated sludge with different ozone doses

4.3.3 Effect of Ozonation on Supernatant

The production of soluble N forms can be used as an indicator of ozonation efficiency. During ozonation, soluble nitrogen, phosphorus and COD concentrations increase. Organic nitrogenous and phosphorus are the major contributors to the increase in soluble nitrogen and phosphorus concentrations (Chu et al., 2008; Dogruel et al., 2007). N solubilization during sludge ozonation was found to be proportional to the COD solubilization

Sludge supernatant characteristics were affected by ozone oxidation in this study. The variations of TN and TP were depicted in Figure 4.24. During the course of ozonation, there were significant rises both TN and TP. When the ozone dose was 0.05 gO₃/gTS, TN and TP increased by 144 mg/L and 24.2 mg/L compared to raw sludge. The maximum TN concentration was achieved as 155 mg/L at ozone dose of 0.06 gO₃/gTS. TP increased significantly higher than 0.02 gO₃/gTS up to ozone dose of 0.03 gO₃/gTS. Above this dose, TP concentration was almost stagnated.

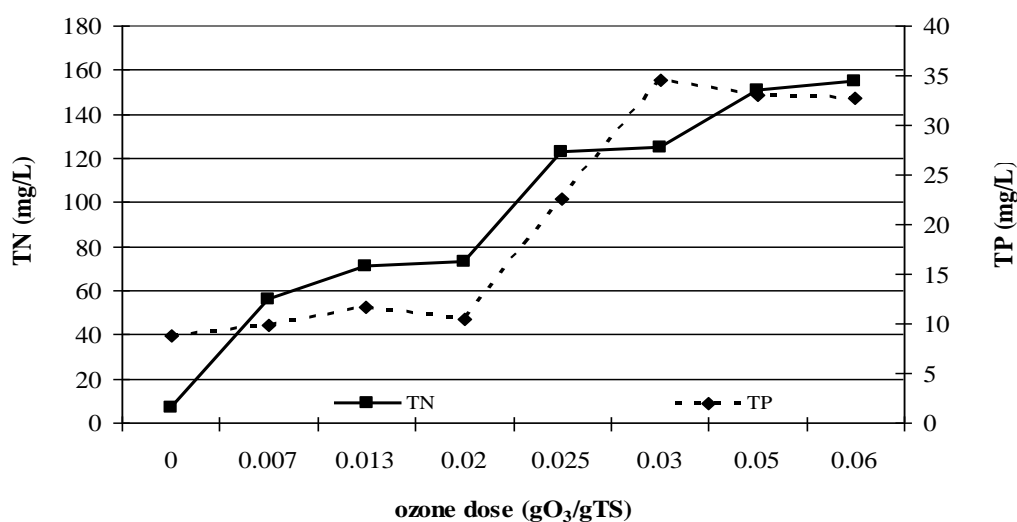


Figure 4.24 Changes of TN and TP with different ozone doses

4.3.4 Effect of Ozonation on Sludge Characteristics

Proteins are an important compound in excess sludge. At an ozone dose of 0.06-0.16 gO₃/gTSS, the fraction of protein-N in the supernatant of the ozonated sludge was 17-27 % of total N (Chu et al., 2008). Following ozonation, the characteristics of the sludge were greatly changed. The changes in protein contents of the sludge were decreased after the ozonation due to the cell lysis as shown in Figure 4.25.

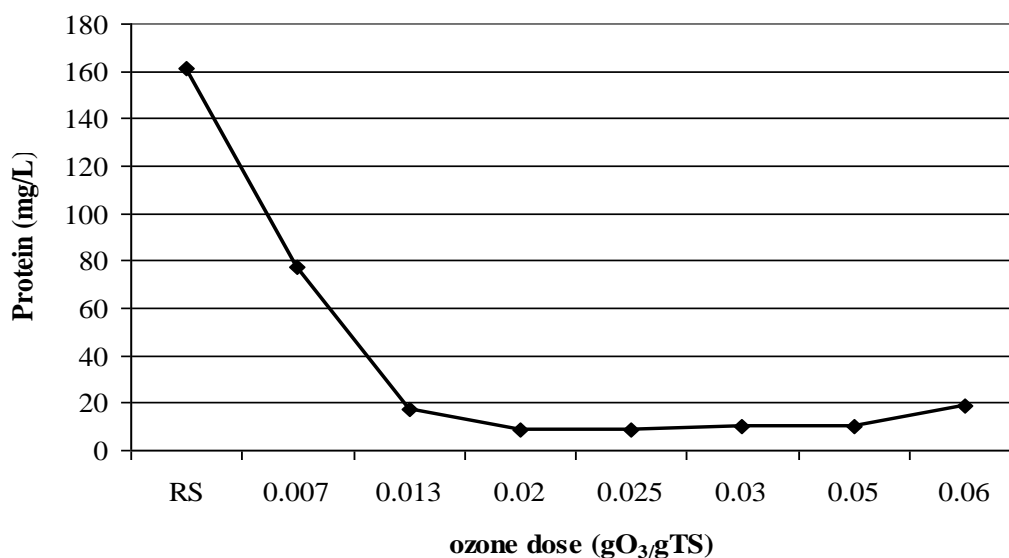


Figure 4.25 Changes of protein contents of sludge after ozonation process

The protein content of the sludge was decreased rapidly up to ozone dose of 0.013 gO₃/gTS. The ozonation was continued with higher ozone doses but the significantly decrease in protein contents of the sludge was not observed.

Protein released by cell lysis has a negative effect on sludge dewatering due to their surface charge. Researches showed that ozonated sludge allows low dewatering and filterability compared to raw activated sludge (Chu et al., 2009a). A strong increase in the CST value from 152 s to 382 s after ozonation with a dose of 0.1 gO₃/gTSS has been reported (Bougrier et al., 2006).

In this optimization study of the thesis, CST values were increased with increasing of the ozone dose. It can be realized from the Figure 4.26 that CST value of return sludge was increased from 15 s to 713 s after ozonation with an ozone dose of 0.05 gO₃/gTS. When the ozonation continued with an ozone dose of 0.06 gO₃/gTS, CST value increased to 1041 s.

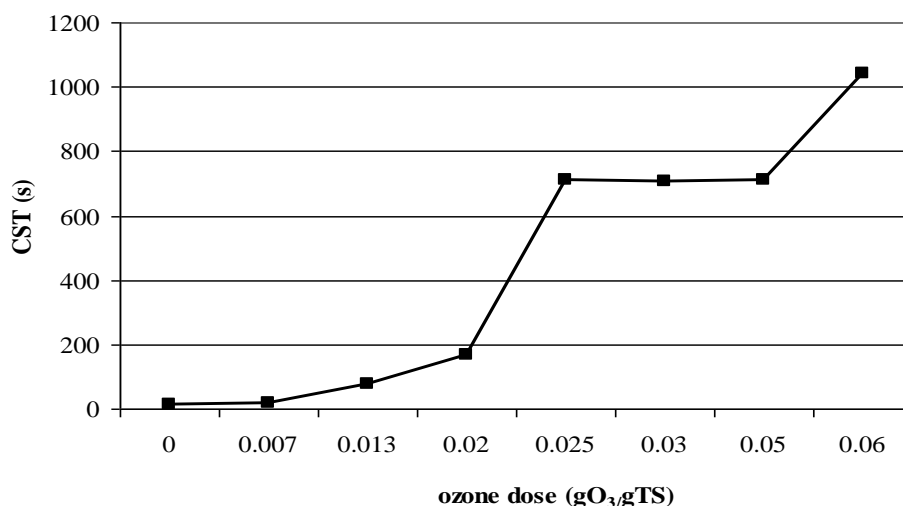


Figure 4.26 Changes of CST with different ozone doses

Moreover, the unsettled micro-particles may have an adverse effect on sludge filtration lead into more compact filtration layer with reduced permeation of liquids (Chu et al., 2009a). The filtration of sludge is related to the ozone dose. SRF value rapidly increased at ozone dose up to 0.2 gO₃/gTS and then decreased dramatically at a dose of 0.5 gO₃/gTS (Deleris et al., 2002).

In this thesis, SRF values rapidly increased at ozone dose up to 0.02 gO₃/gTS and then decreased at a dose of 0.05 gO₃/gTS with a little difference between the results of the Deleris et al. (2009) (Figure 4.27). However, the significantly decrease of SRF after a specific value was observed in this study similar to study by Deleris et al. (2009).

Sludge settling properties especially represented by SVI were changed after ozonation process as shown in Figure 4.28. SVI was decreased dramatically with a low ozone dose of 0.007 gO₃/gTS and the decrease of SVI proceeded to an ozone dose of 0.03 gO₃/gTS. It was attributed to sludge disintegration resulted in increasing of fine particles.

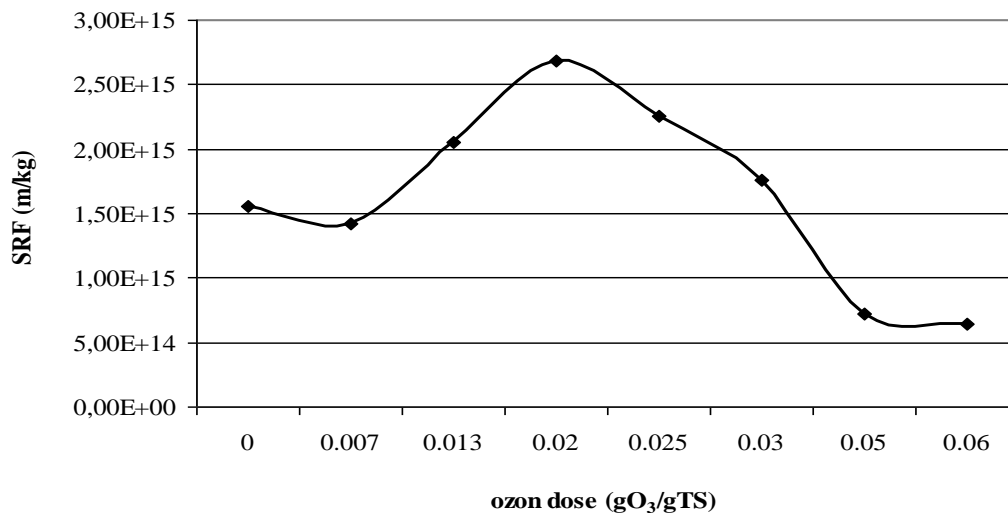


Figure 4.27 Changes of SRF with different ozone doses

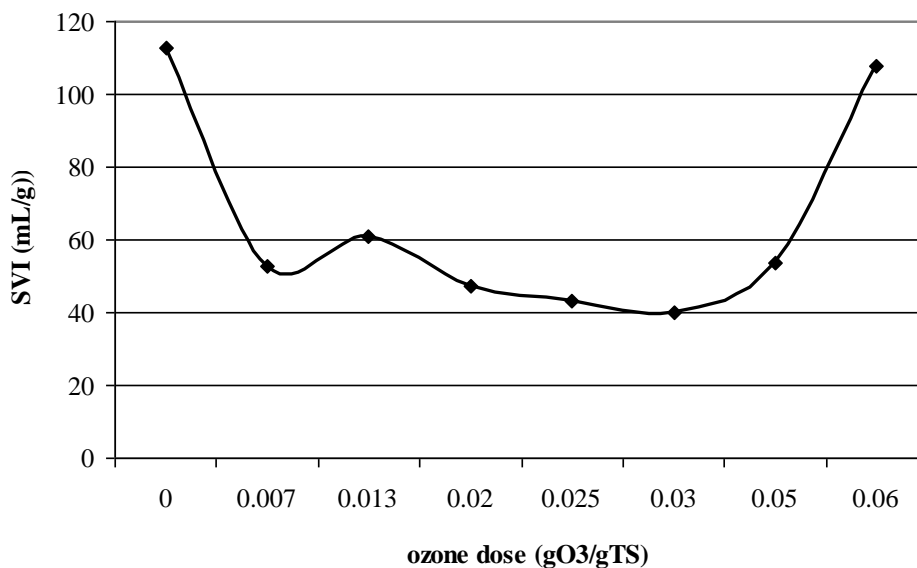


Figure 4.28 Changes of SVI with different ozone doses

Sludge disintegration produces smaller flocs and a turbid supernatant (Bohler and Siegrist, 2004). According the results, when the ozonation process was applied with the higher ozone dose of 0.03 gO₃/gTS, SVI was increased rapidly because of the

dominant fine particles. Turbid supernatant was observed for ozonated sludge particularly at a high ozone dose of 0.06 gO₃/gTS as shown in Figure 4.29.

Ozone oxidation provides reduction of particle size especially at high ozone doses compared to raw sludge. The reduction of particle size with ozonation can be attributed to destruction of floc structure within the sludge and disruption of microorganisms resulted in cell lysis. The disruption of microorganism must be supported with other analyses addition to particle size analysis because of the similarity of disrupted cells walls and original cells (Muller et al., 2004).

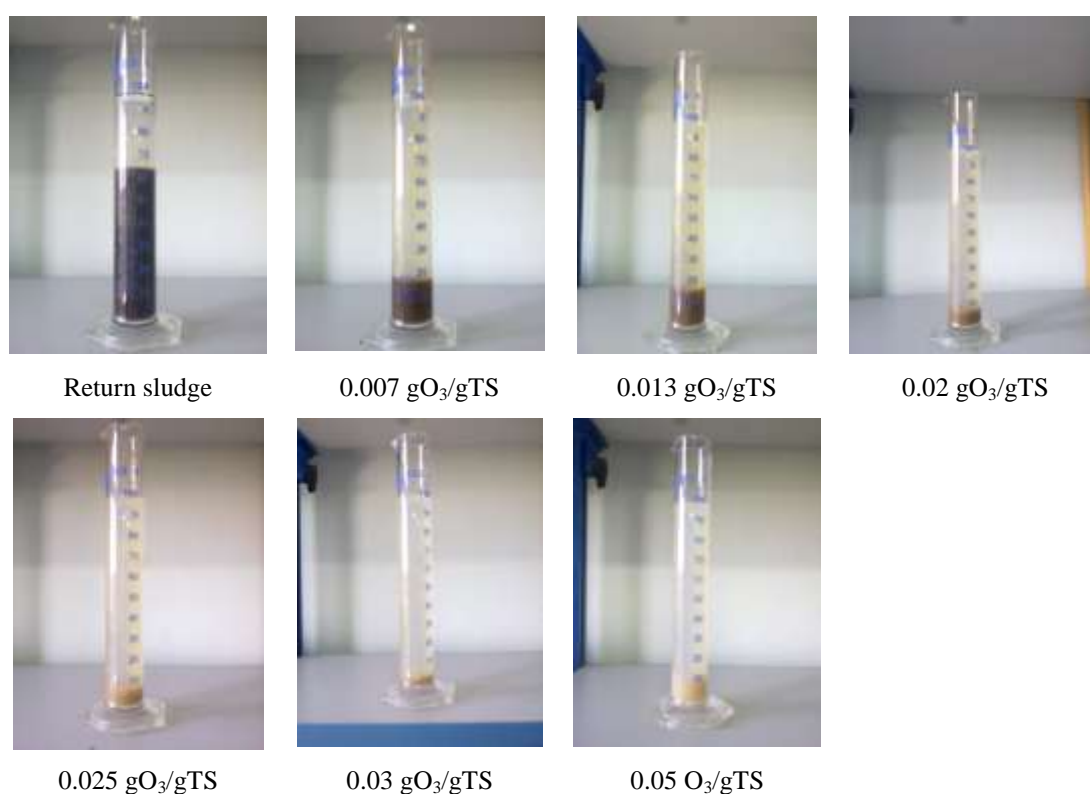


Figure 4.29 The settling properties for each ozonated sludge

The particle size distributions for different ozone dose were given in Table 4.5. d(0.1), d(0.5) and d(0.9) indicate 10, 50 and 90 % of particles (in volume) presented the values lower or equal to d(0.1), d(0.5) and d(0.9), respectively. Ozone oxidation resulted in reduced particle size especially for high ozone dose. Surface weighted mean decreased by 32.647 μm corresponding to decrease of 84 % at ozone dose of

0.05 gO₃/gTS compared to raw return activated sludge. The changes of particle size and deterioration of floc structure can be seen in Figure 4.30.

Table 4.5 Particle size changes for different ozone dose

Ozone dose (gO ₃ /gTS)	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	38.929	74.397	22.71	60.297	128.879
0.007	34.296	69.325	18.657	51.875	121.924
0.013	29.996	71.148	16.969	49.798	127.263
0.02	25.013	48.359	12.837	43.541	92.001
0.025	12.295	39.832	9.091	33.076	81.472
0.03	11.198	49.163	7.418	29.353	102.940
0.05	7.282	33.846	3.104	22.219	85.457
0.06	6.364	40.165	2.376	18.873	123.243

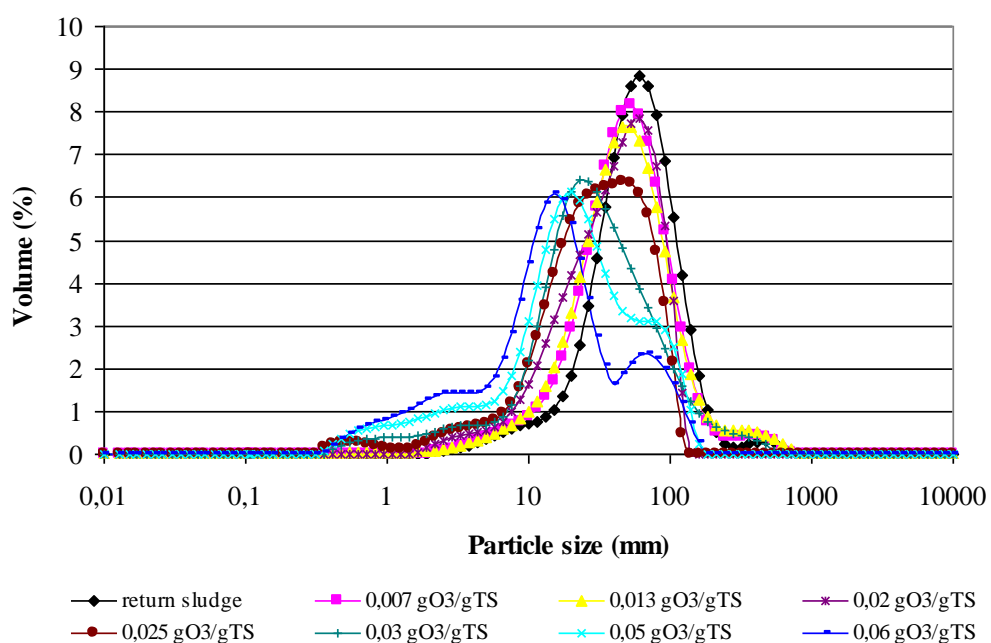


Figure 4.30 Variation of particle size distribution for different ozone doses.

4.4 Ozonation with 10 % of Return Activated Sludge

The effectiveness of partial ozonation of return activated sludge was investigated for the minimization of excess sludge production using ozonation coupled with activated sludge process. 10 % flowrate of return activated sludge of the system ($0.1 Q_R$) was ozonated during a month with dose of $0.05 \text{ gO}_3/\text{gTS}$. The performance of the ozonation system was evaluated considering sludge reduction and dewatering capacity compared to control run (without ozonation). Furthermore, dewaterability, filterability and settling properties of the ozonated sludge were analyzed in terms of CST; SRF and SVI, respectively.

4.4.1 Effects of Ozonation on Sludge Reduction

The ozonation period was limited with a month. The comparison of sludge reduction in terms of MLSS between ozone and control run were depicted in Figure 4.31.

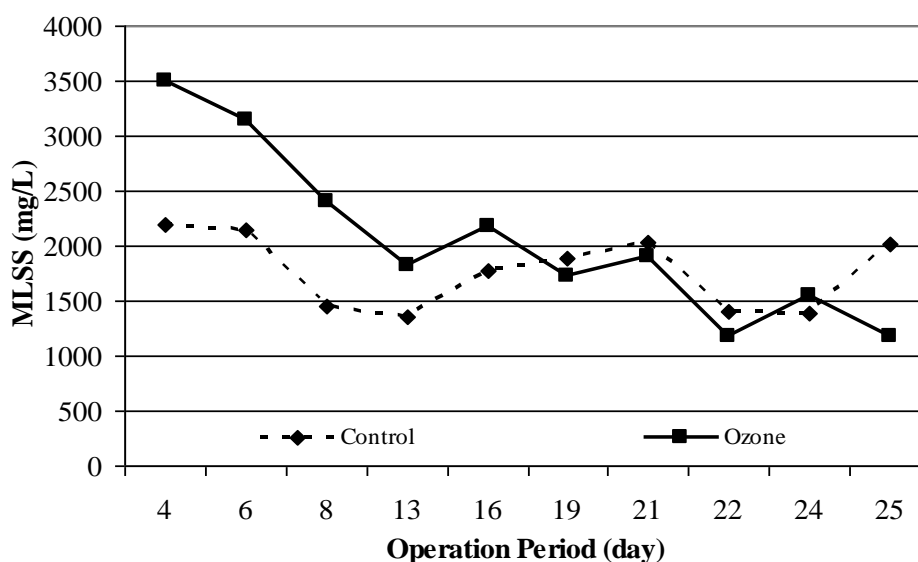


Figure 4.31 Variation of MLSS for control and ozone run

Ozone run achieved 66 % MLSS reduction for ozonated sludge. Similarly, Yan et al., (2009a) reported that the results showed 73.5 % of MLSS reduction with a batch ozonation of 300 mL of the excess sludge that was discharged from the reactor at a

dose of 0.15 gO₃/gMLSS. In order to investigate the effect of sludge ozonation on reduction of excess sludge production, the amounts of MLVSS in the reactors were also measured. It can be seen from Figure 4.32 that circulation of ozonated return activated sludge resulted in decrease of MLVSS. After 6th day of the study, the MLVSS concentrations were varied from 1060 to 1330 mg/L. These results indicated that MLVSS concentration was kept stable after 6th day in ozone run.

Furthermore, control run showed fluctuation in results. The average values of MLVSS/MLSS were 0.70 and 0.64 for control and ozone run, respectively. The higher value for MLVSS/MLSS in control reactor could be attributed to the slight accumulation of inorganic suspended solids in ozone reactor when compared with control reactor during the introduction of the ozonated sludge. These findings showed that the changes of MLVSS/MLSS in this study are significant. Yan et al., (2009a) found 0.90 and 0.88 of average MLVSS/MLSS for control run and ozone run, respectively.

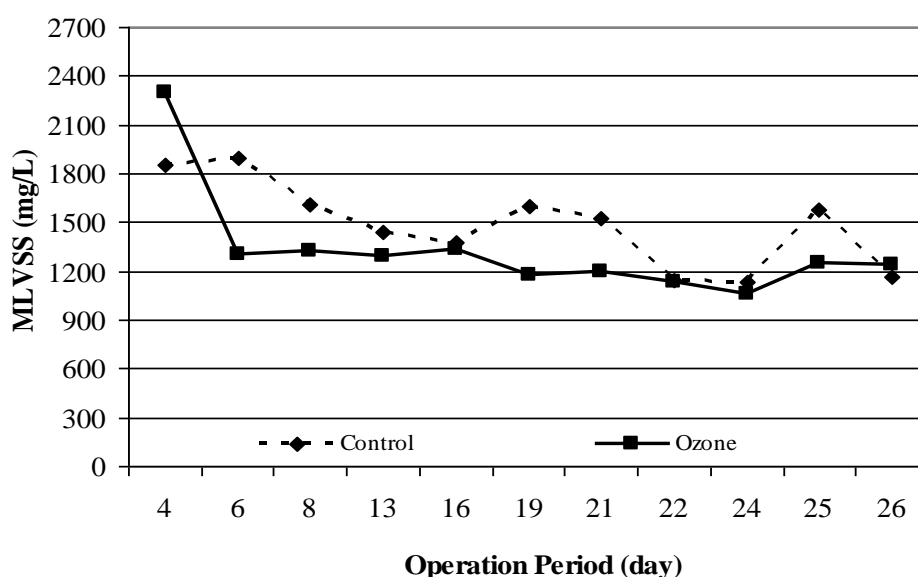


Figure 4.32 Variation of MLVSS for control and ozone run

It could be seen that from Figure 4.33, the sludge yield decreased with the increase in the amount of ozonated sludge. Y_{obs} values of ozone run were reduced from 0.44 mgMLVSS/mgCOD_{removed} to 0.25 mgMLVSS/mgCOD_{removed} during the

operation period. So, 43 % Y_{obs} reduction could be achieved in ozone run during the operation period. At the end of the operation, the 56 % of Y_{obs} reduction was observed in ozonated system compared to control system while average Y_{obs} value of control system was 0.53 mgMLVSS/mgCOD_{removed}.

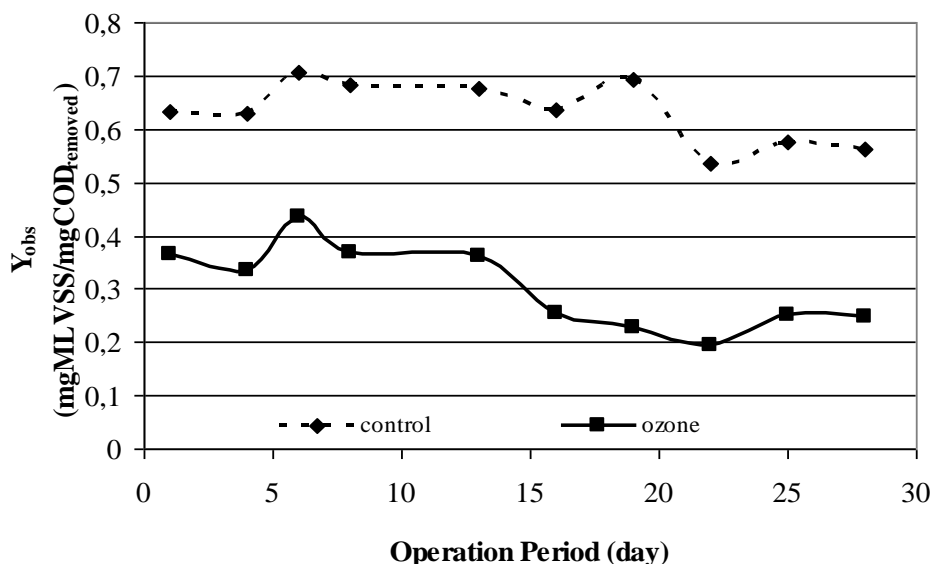


Figure 4.33 Variation of Y_{obs} for control and ozone run

When we compared the Y_{obs} results of this study with the previous studies, it can be said that the reduction efficiency was as good as study by Egemen et al., (1999). They investigated two continuous flow lab-scale activated sludge systems fed with synthetic wastewater, operating at SRT of around 5 d and run in parallel: one as control system and one integrated with ozonation. The Y_{obs} of the ozonated system averaged 0.11 gTSS/g soluble COD_{removed}, with respect to a value of 0.29 g TSS/g soluble COD_{removed}, measured in the control system. These values for Y_{obs} are lower than the values obtained from this study. It can be attributed to the different operational conditions. Moreover, the exact ozone dosage was also not indicated. There is a little difference between the results of the yield reduction of these studies. Egemen et al., (1999), observed a yield reduction of 62 % in their study.

4.4.2 Effects of Ozonated Sludge on Effluent Quality

The influence of sludge ozonation has been drawn significant attention in biological treatment plants. COD removal efficiencies for ozone and control run were depicted Figure 4.34.

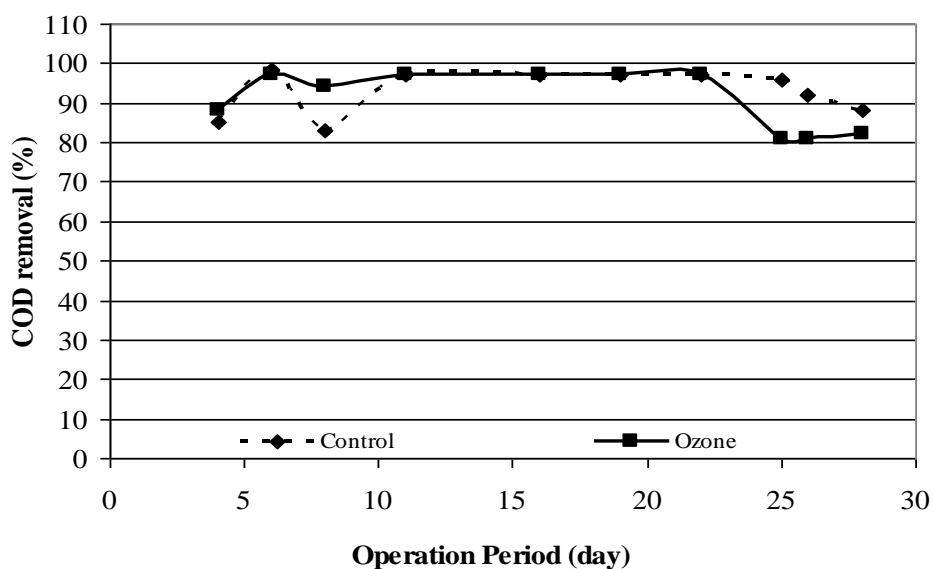


Figure 4.34 Variation of COD removal efficiency for control and ozone run

In ozone run, the COD removal efficiency decreased slightly. After 25th day of the operation COD removal efficiency ranged 88-96 % in control run. COD removal efficiency became stable around 81 % in ozone run. It can be said that, the ozonation process can change the COD removal efficiency of the activated sludge. It seemed that the treatment performance was weakened due to the activated sludge ozonation whereas considering the additional organics introduced into systems by ozonation. The increase in COD concentration of effluent might be attributed to an increase in inert SCOD in the effluent because of released inert dissolved and colloidal COD during long-term operation (Chu et al., 2009a). It was reported that there was slight increase in TOC concentration after ozonation (Yasui and Shibata, 1994; Yasui et al. 1996). Deleris et al, (2002) reported that there was a 5 % decrease of COD removal in ozonation system. Chiovala et al., (2007) and Sakai et al., (1997) explained the increase of COD concentration of effluent with the production of non-biodegradable

COD fraction during ozonation. Yan et al., (2009a) observed no increase in the effluent COD concentration. Bohler and Siegrist (2004) were also found that there was an increase in COD concentration of effluent similar to present study. The effects of ozonation on nitrogenous compounds were also evaluated by determining the increase of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$. The $\text{NH}_4\text{-N}$ removals of the systems were varied from 89 to 94 % and 87 to 96 % for control and ozone run, respectively. For the last days of the operation, the average $\text{NH}_4\text{-N}$ removal efficiency were 90 % and 88 % for control and ozone run as depicted in Figure 4.35

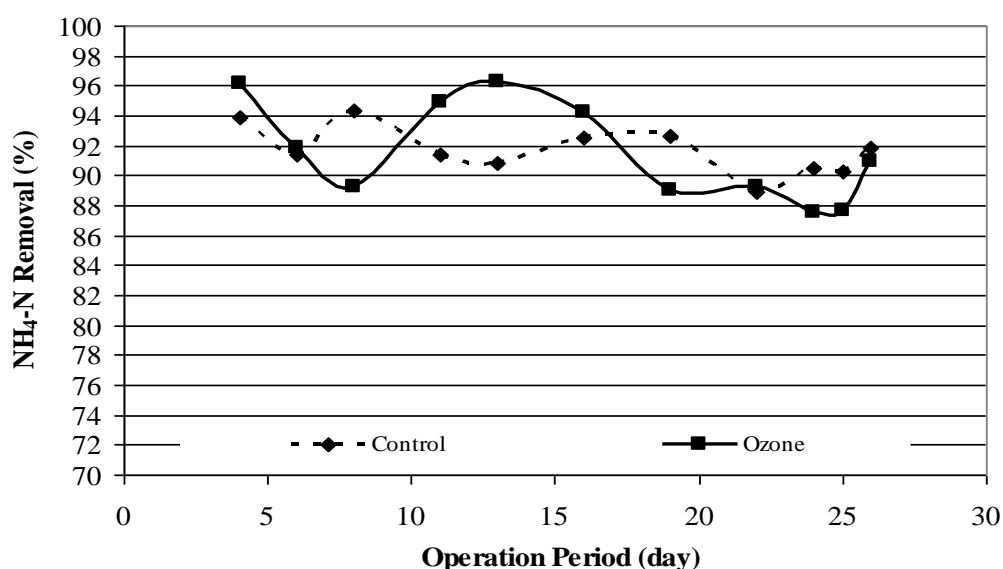


Figure 4.35 Variation of $\text{NH}_4\text{-N}$ removal efficiency for control and ozone run

The deterioration of the nitrification rate caused by ozonation is due to the direct influence of ozone on nitrifiers and floc structure, but it may also be influenced by the higher soluble COD released during ozonation. The results of the present study indicated that there was a slight decrease in $\text{NH}_4\text{-N}$ treatment capacity of ozonated systems. Conversely, Yan et al., (2009a) reported that the TN concentration of effluent of ozonated systems was almost unaffected. 50 % of nitrogen was removed in ozonated systems with the same efficiency for control run. The lack of obvious differences in TN removal was attributed to 12 h of settling time and $\text{DO}=0$ mg/L in settling tank lead to denitrification (Yan et al., 2009a). The comparison of effluent $\text{NO}_3\text{-N}$ concentrations between ozone and control run were depicted in Figure 4.36.

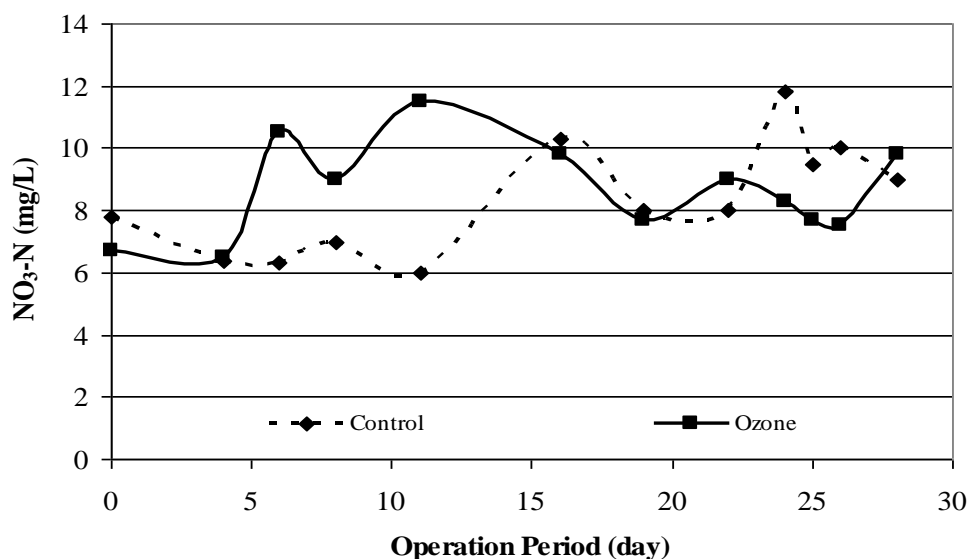


Figure 4.36 $\text{NO}_3\text{-N}$ concentration of effluent for control and ozone run

One of the main factors limiting denitrification is the availability of a carbon source in the influent wastewater. If the ozonated sludge is recycled to a pre-denitrification stage, the soluble biodegradable COD generated by ozonation can be used to improve denitrification capacity. Conversely, ozonation may reduce the population of denitrifiers and could decrease the rate of denitrification. Dytczak et al., (2007) indicated that denitrification was enhanced rather than inhibited by ozonation. In fact, an increase in denitrification rate (measured as Nitrite+Nitrate Utilization Rate) was observed for increasing ozone dosages. Effluent $\text{NO}_3\text{-N}$ concentrations of the control run were low for the beginning of the operation period then increased but for ozone run, $\text{NO}_3\text{-N}$ concentrations of the effluent were higher than control run in the first half of the operation period. In the first half of the operation, ozonation affect the $\text{NO}_3\text{-N}$ concentrations of the effluent, significantly. It can be attributed to the increased nitrogen loading after the recirculation of ozonated sludge (Chiovala et al., 2007 and Sakai et al., 1997). The comparison of $\text{PO}_4\text{-P}$ concentration of effluent between ozone and control run was depicted in Figure 4.37.

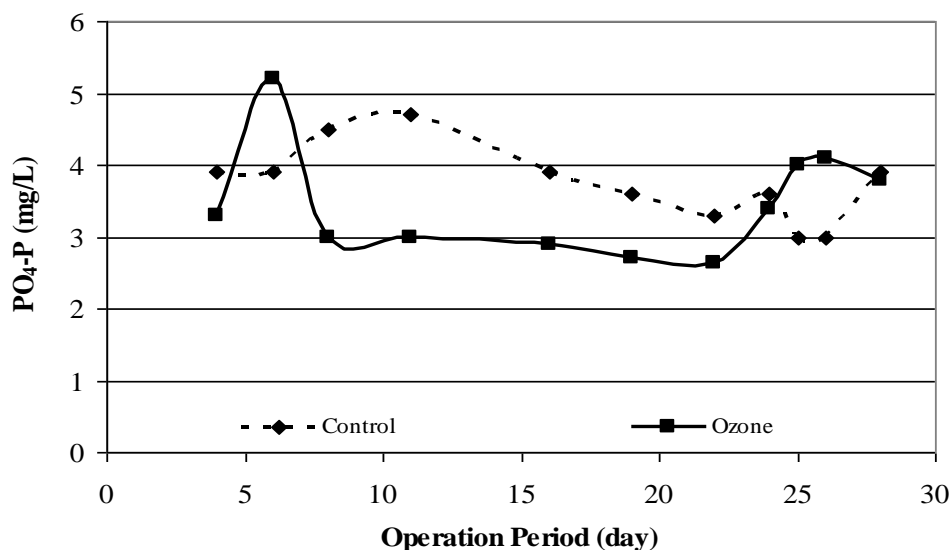


Figure 4.37 PO₄-P concentration of effluent for control and ozone run

The effluent PO₄-P concentrations of the control run were higher than ozone run until the end of the operation period. Only at the last days of the operation the PO₄-P concentrations of the ozonated system were higher than the control run. It can be concluded that the PO₄-P concentration of the effluent is higher than the control run in case of long-term operation of ozone run. According to Sakai et al., (1997) the low phosphorus removal in ozone treatment can be related to discharge of phosphorus released by ozonation due to the reduced sludge. Conversely, Yan et al., (2009a) reported that the average TP in the effluent of ozonated reactor was nearly 30 % greater than that of the effluent of control run.

4.4.3 Changes of Total Nitrogen and Total Phosphorus Concentrations

The TN concentration of the systems was main indicator parameter for the effects of ozonation because of cell lysis. Cell lysis resulted in higher total nitrogen concentration in the aeration tanks of ozone run. The release of cell contents maintained the extra substrate for aeration tanks. 60 mg/L of TN concentration was not exceeded for both systems. The variations of TN concentrations of aeration tanks were depicted in Figure 4.38.

TN concentrations of ozone run compared to control run related to the increased nitrogen loading after the recirculation of ozonated sludge (Chiovala et al., 2007 and Sakai et al., 1997).

Figure 4.38 approved the increase of TN in aeration tank of activated sludge systems coupled with ozonation.

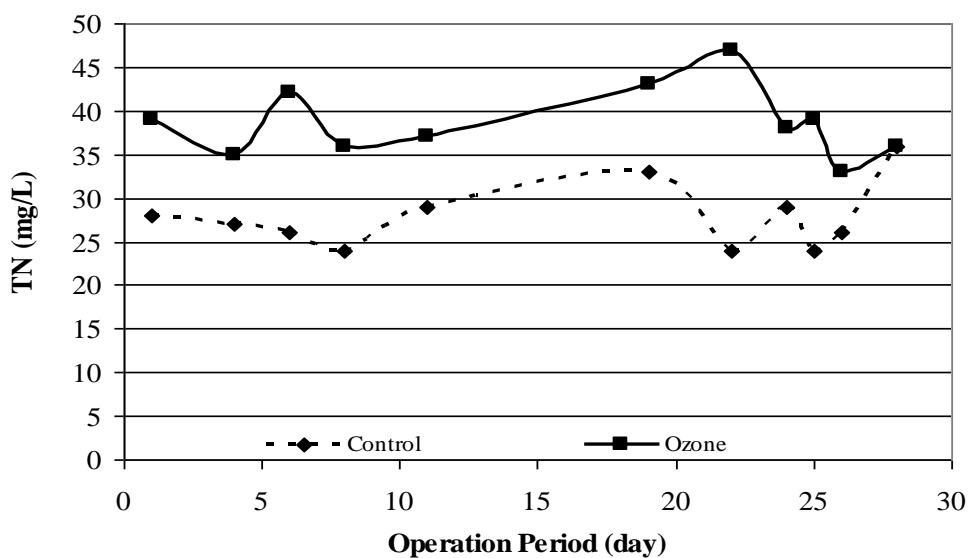


Figure 4.38 Variation of TN for control and ozone run

The comparison of TP concentrations of aeration tanks of were depicted in Figure 4.39. It can be seen that from the Figure 4.39, TP concentration of ozone run were close to control one. TP concentrations were varied from 2.5 to 5 mg/L for both systems.

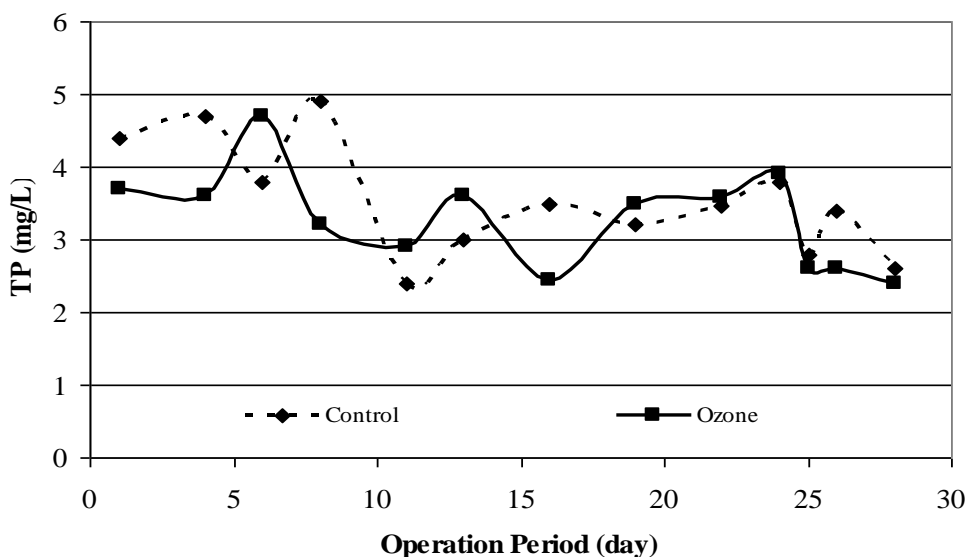


Figure 4.39 Variation of TP for control and ozone run

4.4.4 Changes of Sludge Settling and Dewatering Properties

SVI was used as a standard parameter for expressing sludge settleability. SVI was analyzed for determination of dewatering potential by simple settlement. SVI values were evaluated as an indicator good settling properties of sludge. SVI values of the control run were always higher than the ozonated system agreement with Wolff and Hurren (2006). Average SVI values were 105 and 84 mL/gMLSS for the ozone and control run, respectively as shown in Figure 4.40.

The average sludge volume index (SVI) values of control and ozone reactors during a month operation were 105 and 84 mL/gMLSS, respectively, which indicates that the settling capability of the activated sludge in ozone reactor was slightly better than that of the control reactor.

According to Wolff and Hurren (2006), the floc becomes rounder and more compact, which also improves settling properties, and SVI decreases. Deleris et al., (2002) reported that partial ozonation the return sludge with doses of 0.016-0.080 gO₃/gTSS reduced the SVI from 59 mL/gTSS to 43 mL/gTSS.

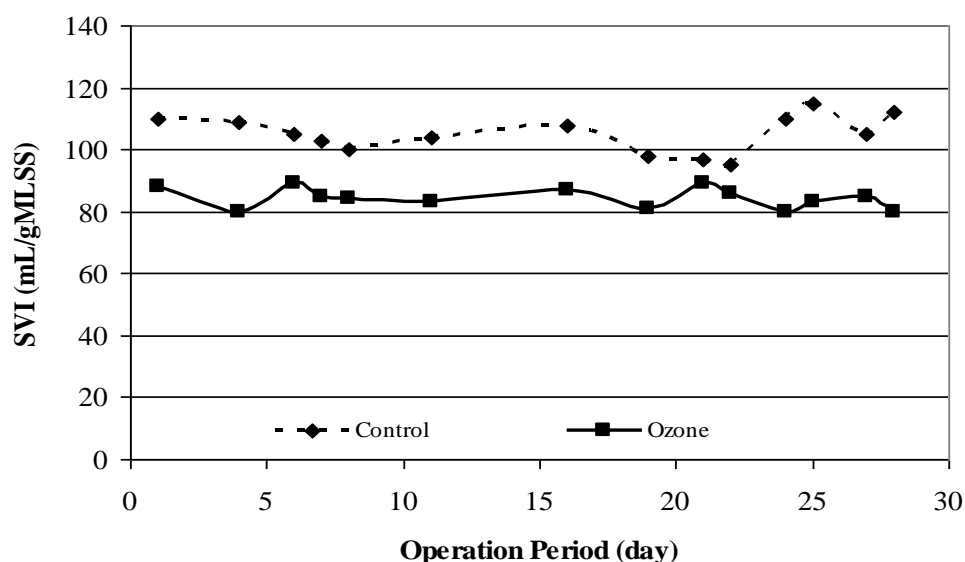


Figure 4.40 Variation of SVI for control and ozone run

CST is a quick and simple method to evaluate the filterability of sludge. This method neglects the shear effect on sludge, and it cannot determine dewaterability differences between dewatering processes, but gives an approach dewatering capacity of sludge. CST was also analyzed for determination of dewatering capacity of return activated sludge and ozonated sludge in this study. The ozonation effects on dewaterability capacity were observed after ozonation. The unsettled micro-particles may have been negative effect on sludge filtration. Bougrier et al., (2006) reported that CST values increased from 151 s to 382 s after ozonation with an ozone dose of 0.1 gO₃/gTS. The optimization study carried out prior to present study showed that 0.05 gO₃/gTS increased CST value from 169 s (at a dose of 0.025 gO₃/gTSS) to 713 s. However, long-term operation of ozonation coupled with activated sludge system had higher CST value than the control run during the operation period with slight difference. CST values were varied from 11 to 14 s for both systems. The variety of CST values for activated sludge processes were depicted in Figure 4.41.

SRF can be used for the evaluation of the mechanical dewatering unit performance. SRF values for ozone run were higher than the control run. In this continuous operation, the filterability of ozonated sludge was badly affected with an insignificant difference. The variety of the SRF values can be seen in Figure 4.42.

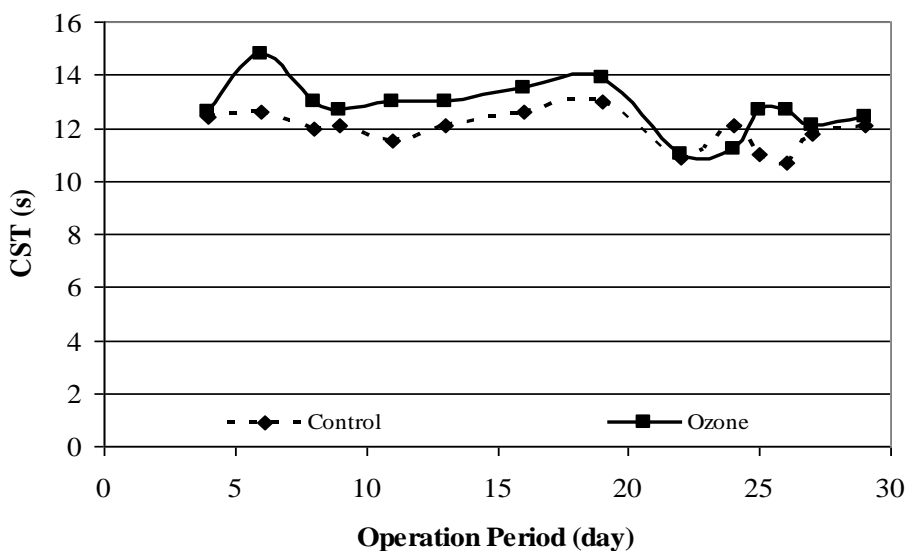


Figure 4.41 Variation of CST for control and ozone run

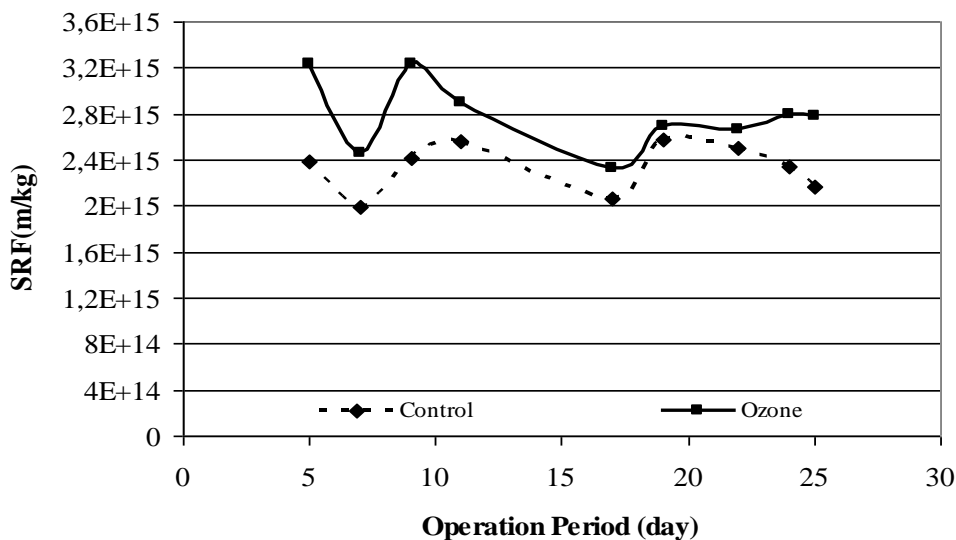


Figure 4.42 Variation of SRF for control and ozone run

4.5 Ozonation with 0.2 of Return Activated Sludge

After the ozonation with 0.1 of return activated sludge, 800 mL corresponded to 0.2 Q_R of return activated sludge was subjected to batch ozonation with optimum ozone dose during a month. The other unmodified system was served as a control run and operated in parallel with the same conditions without ozonation. There was

no excess sludge wastage from ozone run during the experimental period. The control run was performed under the same conditions in parallel. The results of control and ozone systems were evaluated considering sludge reduction. Furthermore, sludge properties of ozonated sludge were investigated.

4.5.1 Effects of Ozonated Sludge on Sludge Reduction

It was confirmed that the biodegradability of the sludge was improved after ozonation. The effect of sludge ozonation on the minimization of excess sludge production was studied with the measurement of MLSS and MLVSS concentration of aeration tanks. The ratio of VSS/TSS decreased from 78 % in raw sludge to 73 % in ozonated sludge with a dose of 0.16 gO₃/ T (Bougrier et al., 2006). Results of the present study showed that the MLSS was reduced by 71 % at an ozone dose of 0.05 gO₃/gTS at the end of the operation compared to the beginning of the operation. While the ozone dose was kept as high 0.05 gO₃/gTS per day, no excess sludge was wasted. The changes of MLSS and MLVSS concentrations of the aeration tank were depicted in Figure 4.43 and Figure 4.44, respectively.

It can be seen from Fig. 4.43 and 4.44 that MLSS and MLVSS were always decreasing during ozonation. It can be deduced that the decrease of MLSS was mainly due to the decrease of MLVSS, because the decreased MLVSS accounted for main part of the lost MLSS.

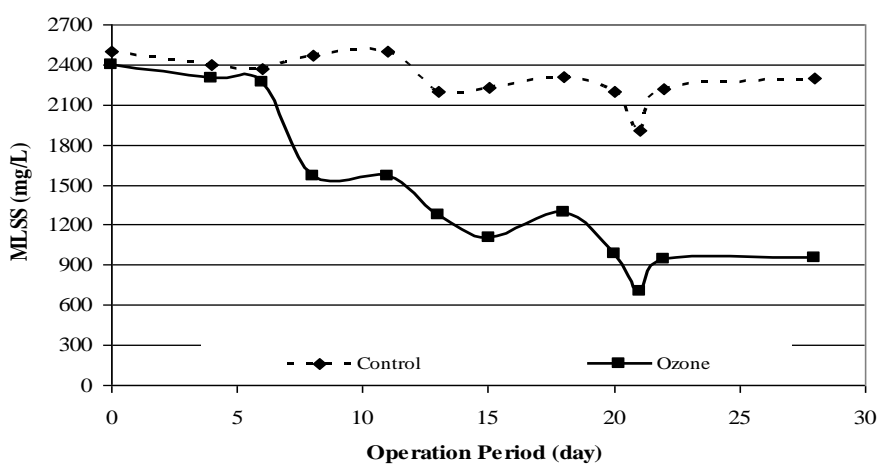


Figure 4.43 MLSS variation of aeration tanks for control and ozone run

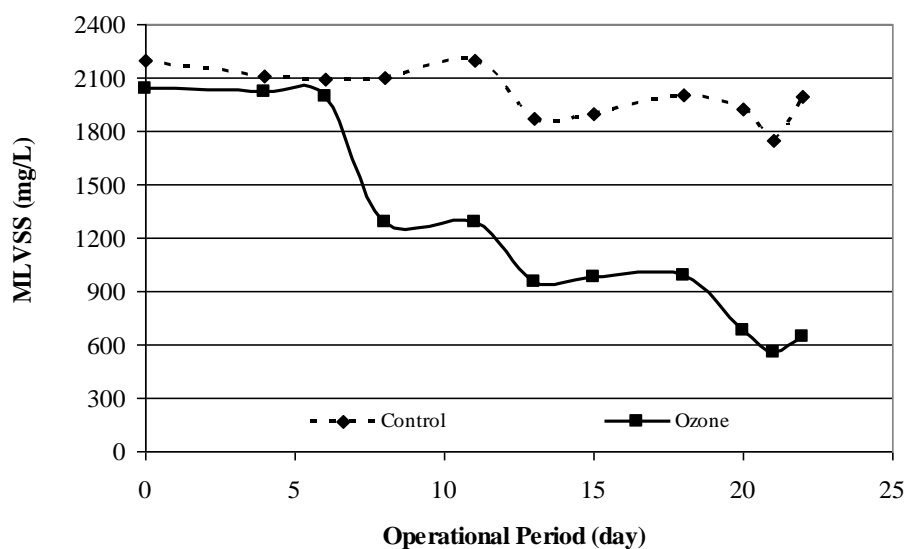


Figure 4.44 MLVSS variation of aeration tanks for control and ozone run

71 % of MLSS reduction was achieved in ozonated system at the end of the operation period compared to the beginning of operation period. Similarly, Demir and Filibeli (2011) reported that the results showed 66 % of MLSS reduction with an ozonation of 400 mL of the return sludge corresponded to $0.1 Q_R$ that was discharged from the reactor at a dose of $0.05 \text{ gO}_3/\text{gMLSS}$. It was concluded from the results of previous study by Demir and Filibeli (2011) and present study that when the volume of ozonated sludge increased, the MLSS reduction was also increased due to the cell lysis.

It can be seen from Figure 4.44 that MLVSS was decreased with the circulation of ozonated sludge. The values of MLVSS/MLSS increased from 0.84 and 0.75 for ozone reactor during the operation period. The average value of MLVSS/MLSS for control run was 0.87.

Y_{obs} values of the reactors can be seen in Figure 4.45. Y_{obs} values of ozone run were reduced from $0.45 \text{ mgMLVSS}/\text{mgCOD}_{\text{removed}}$ to $0.12 \text{ mgMLVSS}/\text{mgCOD}_{\text{removed}}$ during the operation period. So, 73 % Y_{obs} reduction could be achieved in ozone run during the operation period. At the end of the operation, the

62 % of Y_{obs} reduction was observed in ozonated system compared to control system while average Y_{obs} value of control system was 0.53 mgMLVSS/mgCOD_{removed}.

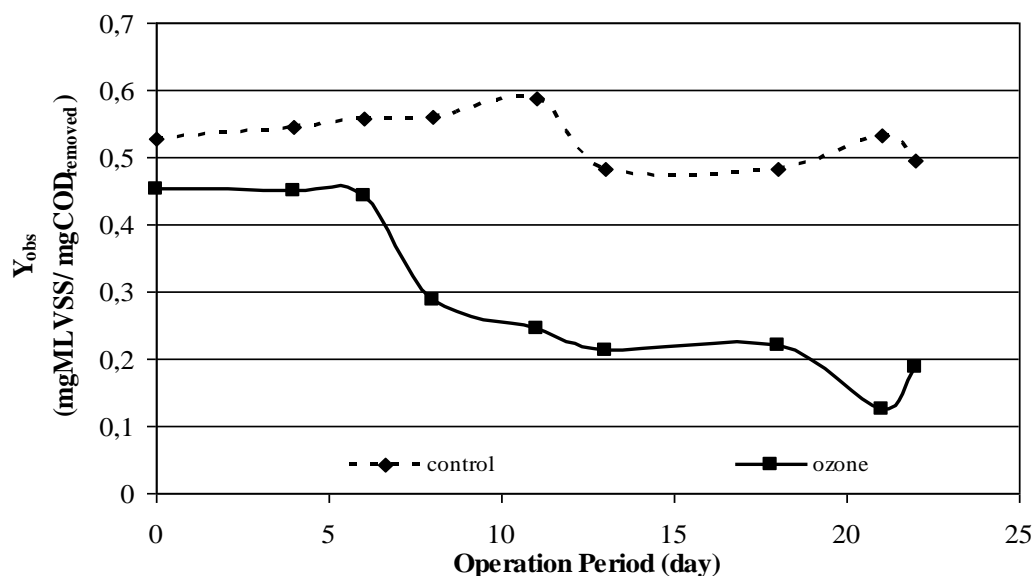


Figure 4.45 Variation of Y_{obs} for control and ozone run

4.5.2 Effects of Ozonated Sludge on Water Quality

The influence of sludge ozonation on effluent quality in the biological treatment process is very important for the application of ozone for the sludge reduction. It was reported that ozonation of the returned activated sludge had no significant negative impact on the final effluent quality (Dytczak et al., 2006; Sakai et al., 1997). Beside this, because of ozonation, inert dissolved and colloidal COD is released into the solution, and leads to an increase in inert SCOD of the effluent during long-term operation (Kamiya and Hirotsuji, 1998; Lee et al., 2005; Sakai et al., 1997; Yasui et al., 1996). In addition to this, because previously conducted studies used different activated sludge reactors and different types of wastewater, comparison of COD and TN treatment abilities after feeding with the ozonated sludge is difficult (Yan et al., 2009b). In this study, the water treatment performance of two activated sludge process is shown in Figure 4.46 in terms of COD removal efficiency. The effluent COD concentrations were always at satisfactory level for both activated sludge processes.

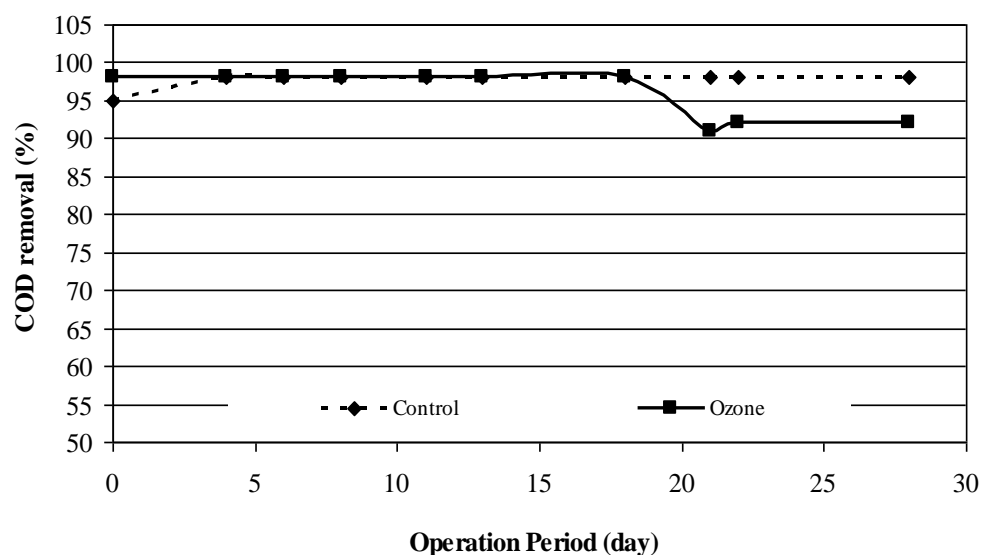


Figure 4.46 Variation of COD removal efficiency

After ozonation, the COD removal efficiency of ozone reactor was slightly decreased after 20th day of operation period. Kamiya and Hirotsuji (1998) also reported that SS and SCOD in the effluent were always satisfactory at a level in a pilot-scale activated sludge system coupled with sludge ozonation for 112 days of operation without excess sludge wasting. From the literature, it can be concluded that the ozonation can change COD removal capacity and slightly increase of COD can be seen in the effluent (Yasui and Shibata, 1994). However, Lee et al., (2005) and Sakai et al., (1997) reported that no obvious increase observed in the effluent COD and BOD, respectively (Huysmans et al., 2001). The differences between the results can be attributed to the using of different wastewater, different type of reactor and operational conditions. The results of present study proved Lee et al., (2005) and Sakai et al., (1997) that there was no significantly increase in effluent COD, in other words, COD removal efficiency was not significantly decreased after ozonation as shown in Figure 4.46. The result of the study by Yan et al., (2009b) indicated that the COD treatment capacity of ozonated reactor was almost completely unaffected by feeding with ozone-treated sludge.

Ozonation did not affect the nitrification capacity. The ammonium removal efficiency of the ozone and the control run were similar during 50 days of operation

(Yan et al., 2009a). The study by Dytczak et al., (2006) showed that although additional ammonia released from recycled sludge after ozonation was approximately 5.9 % more in an SBR, the ammonium in the effluent was always below the detection limit of 0.3 mg/L (Wolff and Hurren, 2006). Nitrite was not detected, indicating complete nitrification. It can be seen from the Figure 4.47 similarly, in this study, the ammonium removal efficiency was not significantly affected by ozonation. The removal efficiencies of $\text{NH}_4\text{-N}$ were ranged between 85 to 93 % for both reactors. It can be easily realized from the Figure 4.48, as a result of high level of nitrification capacity, the effluent $\text{NO}_3\text{-N}$ concentration in ozone run was higher than control run.

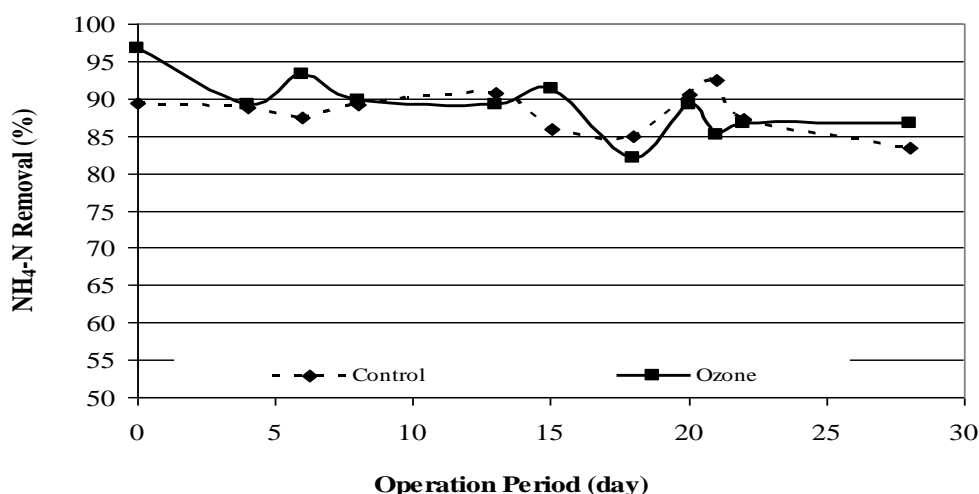


Figure 4.47 Variation of $\text{NH}_4\text{-N}$ removal efficiency

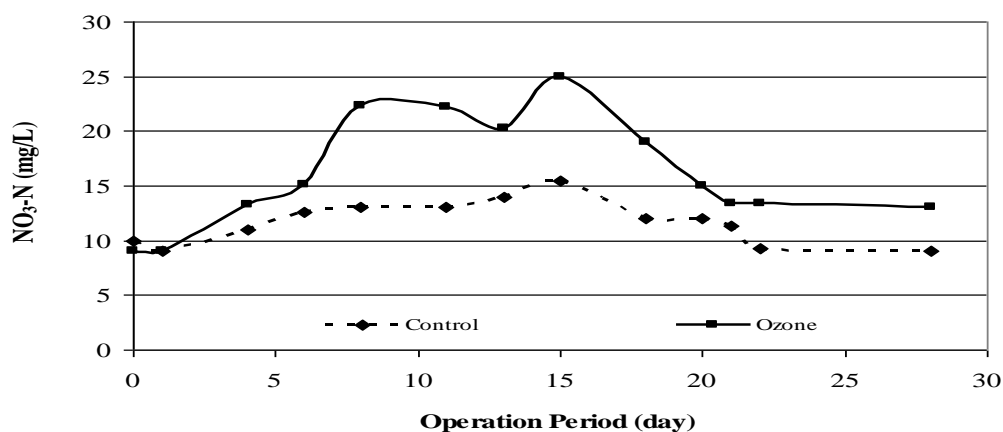


Figure 4.48 Variation of $\text{NO}_3\text{-N}$ concentration of effluent

When the ozonated sludge was recirculated to the bioreactor, the nitrogen loading increased and the TN effluent concentrations were slightly higher compared to the control run (Sakai et al., 1997). It was confirmed in this study with the higher TN concentration in ozone run during operation period compared to control run as presented in Figure 4.49. Moreover, according to Yan et al., (2009b) the average effluent of the control and ozone reactors was nearly the same. The lack of obvious differences in the TN removal was attributed to settling time in settling tank and 0 mg/ of DO value in the settling tank.

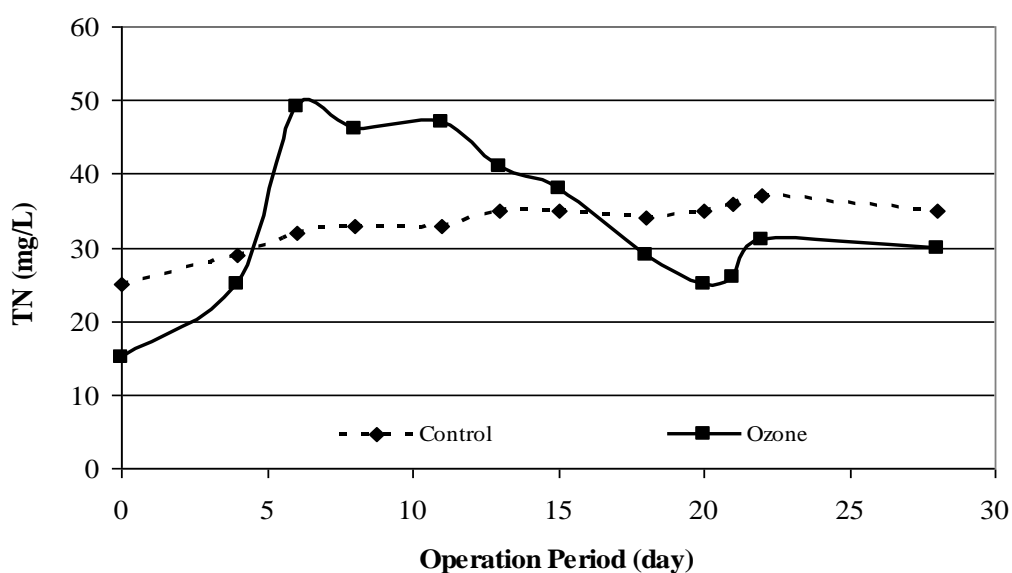


Figure 4.49 Variation of TN concentrations of aeration tanks

Effluent $\text{PO}_4\text{-P}$ concentration (Figure 4.50) and TP concentration of aeration tank in ozonated reactor (Figure 4.51) were increased gradually during the operation period and were always higher than control run due to the cell lysis. Most of the phosphorus released by sludge ozonation was discharged as part of the soluble component in the effluent due to the reduced sludge discharge. The average $\text{PO}_4\text{-P}$ values in the effluent of ozone and control reactors were 5.3 and 8 mg/L. The slightly higher $\text{PO}_4\text{-P}$ concentration was observed in ozone reactor since phosphorus could not be withdrawn with the excess sludge in ozone reactor, other methods such as chemical precipitation should be combined for phosphorus removal (Yan et al., 2009b; Zhou et al., 2008)

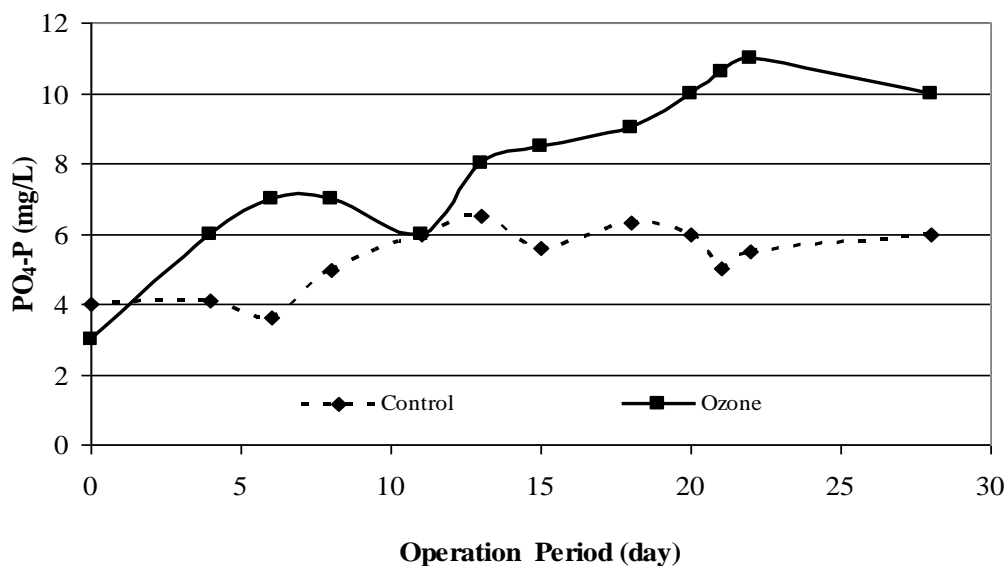


Figure 4.50 Variation of PO₄-P concentration of effluent

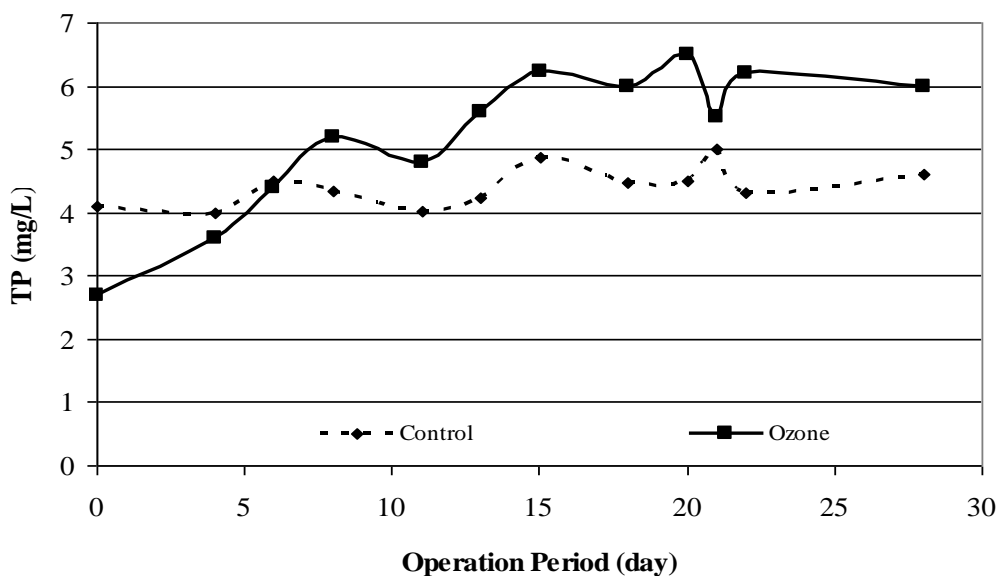


Figure 4.51 Variation of TP concentration of aeration tanks

4.5.3 Sludge Settling Properties and Dewatering Characteristics

The settling properties of the sludge can also be improved by ozonation (Caravelli et al., 2006; Deleris et al., 2002; Kamiya and Hirotsuji, 1998; Weemaes et al., 2000). Improves of sludge settling can be achieved by the recirculation of the ozonated sludge to aeration tank (Bohler and Siegrist, 2004). It can be attributed to rounder

and more compact shape of floc after ozonation (Wolff and Hurren, 2006). An improvement in the settling properties of the sludge was reported by several researchers (Deleris et al., 2002; Kamiya and Hirotsuji, Paul and Debellefontaine, 2007; Vergine et al., 2007; Weemaes et al., 2000). Sludge volume index (SVI) can be used to evaluate the sludge settleability. In this study, the SVI reduced from about 110 mL/mgMLSS to 82 mL/mgMLSS by the partial ozonation of the returned sludge with doses of 0.05 g O₃/g TS. It can be seen from Figure 4.52, SVI values of ozone run was lower than control run during the operation period. It can be said that sludge settling properties can be improved for long-term operation by ozonation. It was concluded from previous studies that dewatering and filterability of ozonated sludge was low compared with raw activated sludge due to the negative effect of surface charge of proteins released by cell lysis. Moreover, the micro-particles may have also a negative effect on sludge filtration. The capillary suction time (CST) value increases from 151 s to 382 s after ozonation with a dose of 0.1 g O₃/g TSS (Bougrier et al., 2006). In this study, lower dewatering capacity represented by higher CST values as illustrated in Figure 4.53. was monitored in ozone run. However, the CST value difference between ozone and control run can be negligible. It can be concluded from these results that in continuous operation, the dewatering capacity of ozone run was not significantly affected.

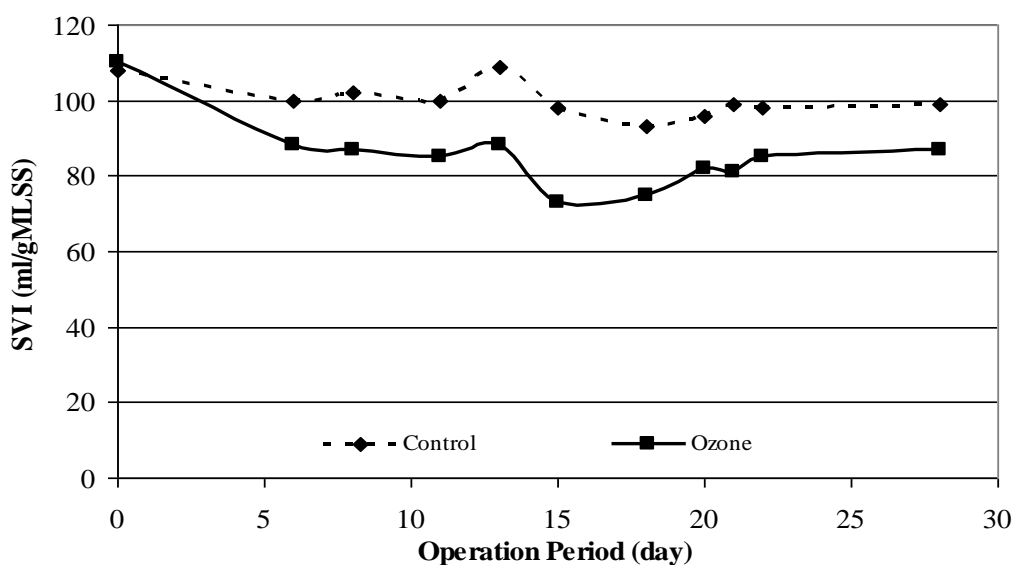


Figure 4.52 Changes of SVI

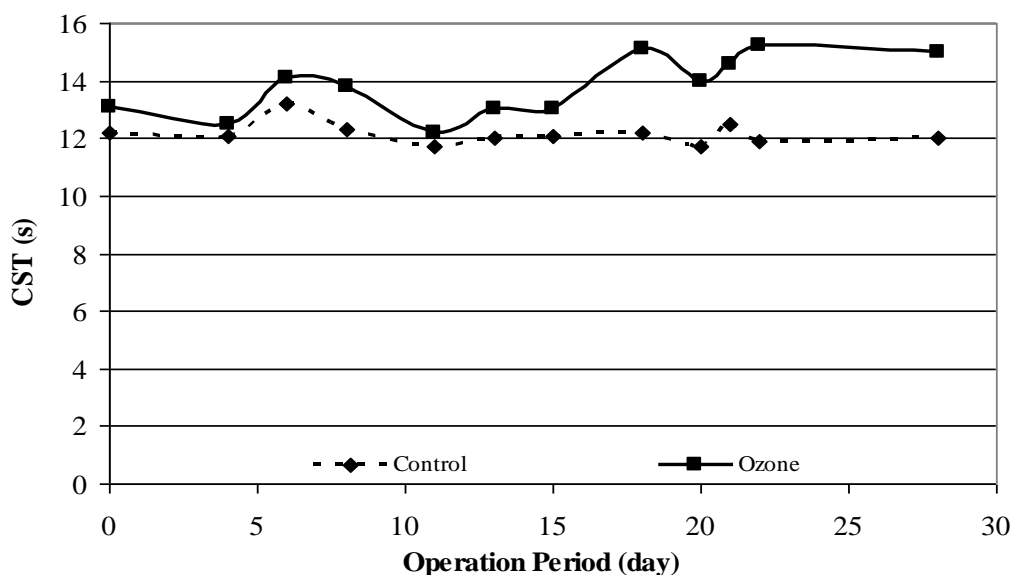


Figure 4.53 Changes of CST

In present study, SRF values in ozone run were always higher than control run (Figure 4.54) in continuous operation. In the batch optimization study of ozone dose, SRF values of ozonated sludge were increased gradually. After the application of $0.02 \text{ gO}_3/\text{gTS}$, these values were decreased dramatically. In this continuous operation, the filterability of sludge was not significantly affected by ozonation. There was little difference between ozone and control run according to the SRF values.

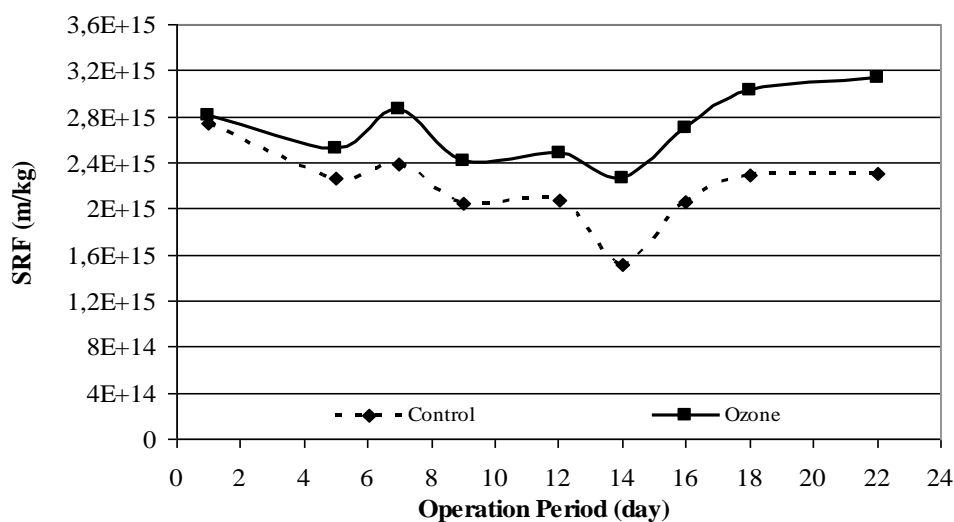


Figure 4.54 Changes of SRF

Particle size and density are critical parameters for settling of activated sludge. In addition, floc stability is important since weak flocs can disintegrate in the treatment plant due to shear forces, which leads to increased numbers of small flocs or dispersed bacteria in the effluent (Wilén et al., 2008). Particle size can be changed by ozonation. Lower ozone doses have not significantly effect on particle size (Zhang et al., 2009). Bougrier et al., (2006) reported that the medium diameter of particles before and after ozonation (0.16 g O₃/g TS) was 36.3 μm and 32.6 μm, respectively. Zhao et al. (2007) reported that the media diameter of sludge particles reduced from 6 μm to 4μm at an ozone dose of 0.04 g O₃/g TSS. Sludge destruction by ozonation leads to an increase of small particles at higher ozone doses. Sludge disintegration results in smaller flocs and a turbid supernatant. The changes of particle size distribution after ozonation are depicted in Figure 4.55 and Fig 4.56. It can be realized from the figures, the ozonation changed the particle size. It is attributed to sludge disruption by ozonation resulted in smaller flocs formation.

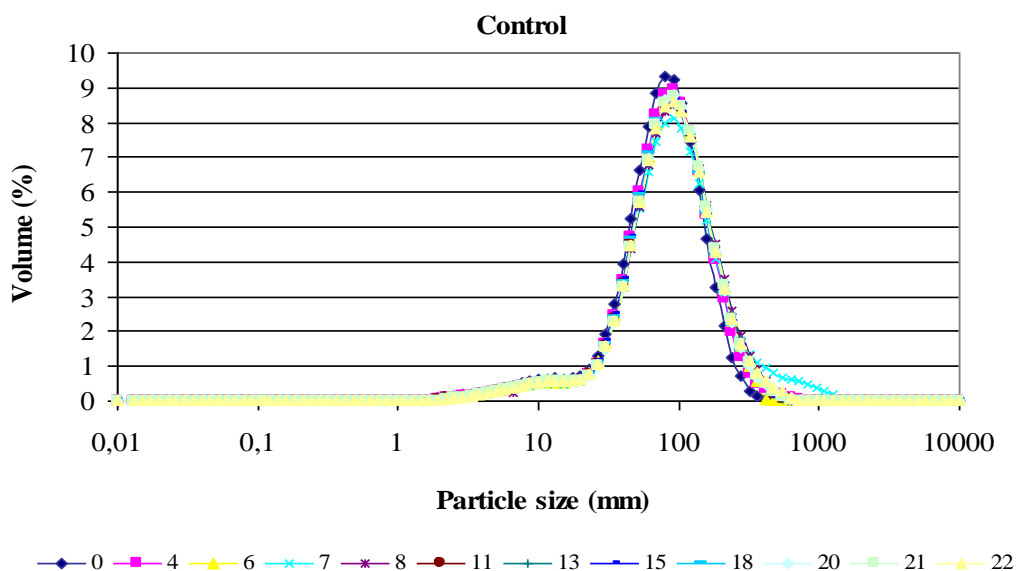


Figure 4.55 Changes of particle size for control run

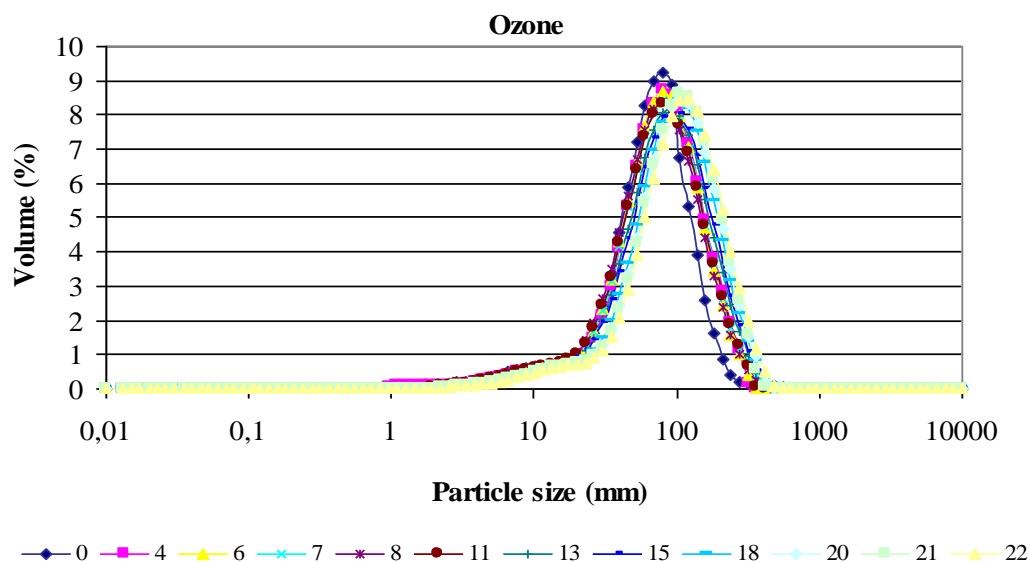


Figure 4.56 Changes of particle size for ozone run

4.6 Continuous Operation of OSA Process

4.6.1 Comparison of OSA and Control System in terms of Sludge Production

Compared with the control run, Y_{obs} in OSA system is clearly reduced at low ORP level as can be seen in Figure 4.57.

In OSA system, Y_{obs} was decreased from 0.52 to 0.2 mgMLSS/mgCOD_{removed} during operation period. 62 % reduction efficiency was obtained in yield production in OSA system during the operation. In control system, the average Y_{obs} value was 0.52 mgMLSS/mgCOD_{removed}. OSA system was also achieved 58 % reduction efficiency of Y_{obs} compared to control run at the end of the operation. It can be concluded that a low ORP level in anaerobic tank promotes the excess sludge reduction. The first study applying the OSA process to evaluate the reduction of excess sludge was carried out by Chudoba et al. (1992). At lab-scale and using synthetic wastewater, the sludge production of a conventional activated sludge system was compared to that of the OSA process. In the case of the OSA process, the anaerobic reactor was maintained at ORP of -250 mV. The observed sludge yield in

the activated sludge system was $0.37 \text{ kgTSS/kgCOD}_{\text{removed}}$, while in the OSA process was $0.22 \text{ kgTSS/kgCOD}_{\text{removed}}$ (reduction of 40 %)

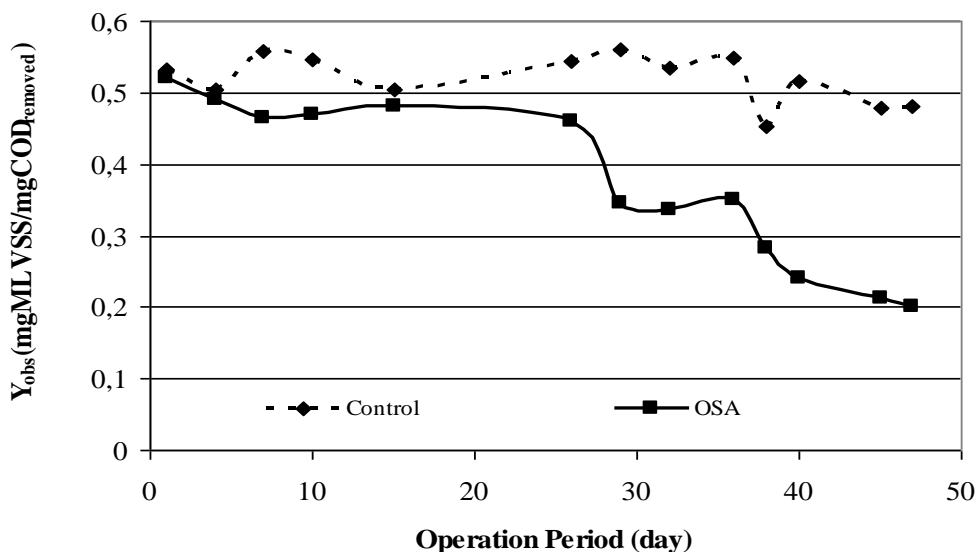


Figure 4.57 Changes of Y_{obs} for OSA and control run

The impact of the 16-h anaerobic exposure on the MLSS can be seen in Figure 4.58. It is determined that the MLSS concentration was reduced by 37 % in the sludge from the OSA system during the treatment. This means that a low ORP and no external food source may promote the sludge reduction since such an environment may impose stress upon the microbes.

The impact of the anaerobic exposure on the MLVSS can also be seen in Figure 4.59. It is determined that the MLVSS concentration was reduced by 41 % in the sludge from the OSA system during the treatment.

The excess sludge production rate of the OSA system at the ORP level of -250 mV in its anaerobic tank was less with respect to that at the ORP level of $+100$ – $+150 \text{ mV}$. Therefore, it can be concluded that the OSA system can reduce excess sludge effectively and the ORP level in the anaerobic tank may be one of the keys to achieving an effective reduction in excess sludge.

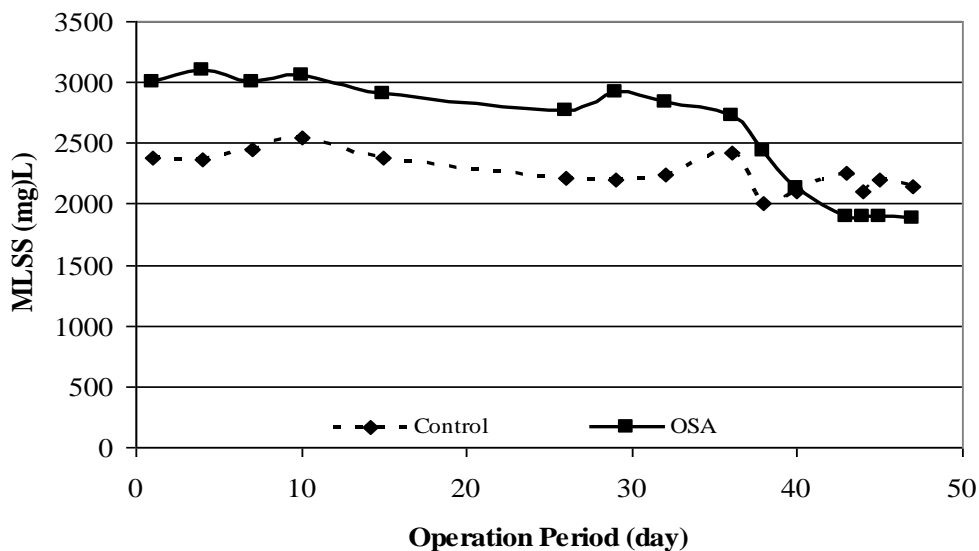


Figure 4.58 Changes of MLSS for OSA and control run

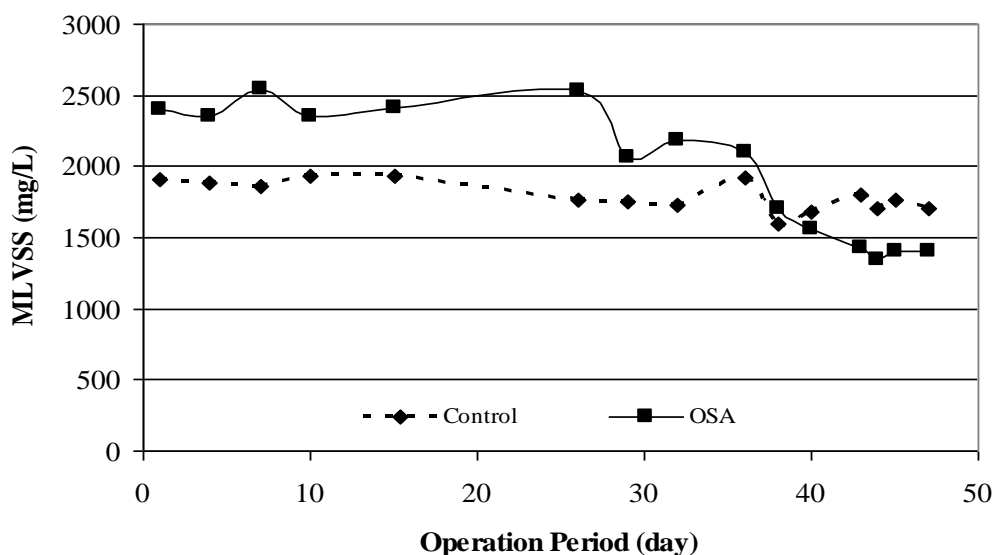


Figure 4.59. Changes of MLVSS for OSA and control run

4.6.2 Comparison of OSA and Control System in terms of Effluent Quality

Figure 4.60 summarizes the COD removal of the systems. It was found that COD concentrations in the effluent in the OSA system were lower than that in the effluent of the reference system due to the additional substrates from the anaerobic tank. The results indicated that when compared with the control reactor, the reactor that was

fed with sludge from anaerobic tank showed good removal of COD without formation of any excess sludge. The high removal efficiencies in OSA systems mean that the insertion of the anaerobic tank actually improves the COD removal under the same influent COD concentration. An explanation is that when sludge is exposed in a low ORP environment in the anaerobic tank, the sludge may be “starved” under a “stressful condition which in turn increases its substrate removal ability in the following aerobic environment with the presence of adequate food in aeration tank to which the anoxically treated sludge returns (Chen et al., 2001; Saby et al., 2003).

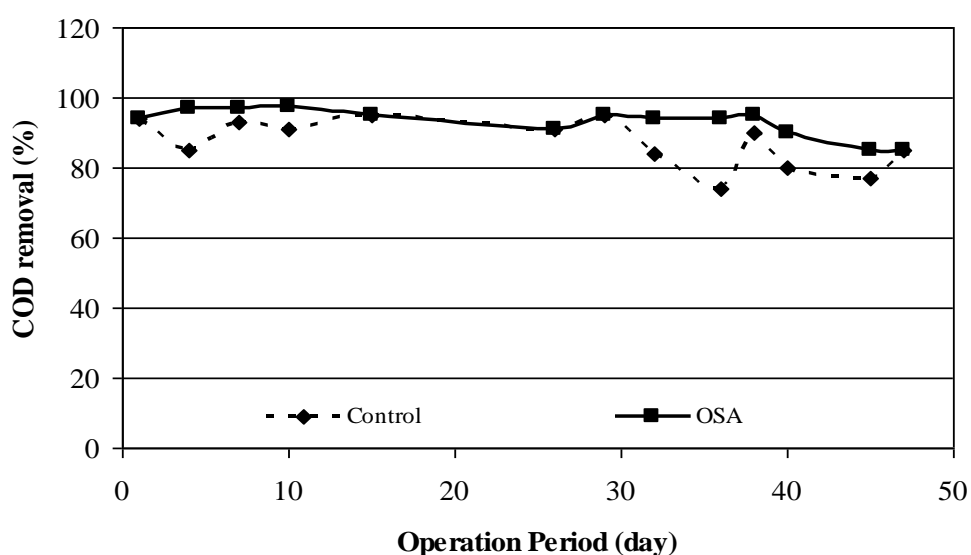


Figure 4.60 Changes of COD removal efficiencies (%) for OSA and control run

The $\text{NH}_4\text{-N}$ removal efficiency was lower compared to control run during the operation period due to denitrification. Figure 4.61 is demonstrated the $\text{NH}_4\text{-N}$ removal capacity of OSA and control systems. In control system, the removal of $\text{NH}_4\text{-N}$ increased and reached 96 %. On the other hand, in OSA system, the removal of $\text{NH}_4\text{-N}$ decreased from 87 % to 76 % due to the effect of denitrification. However, in long-term operation, it can be said that both systems showed similar removal efficiencies for $\text{NH}_4\text{-N}$.

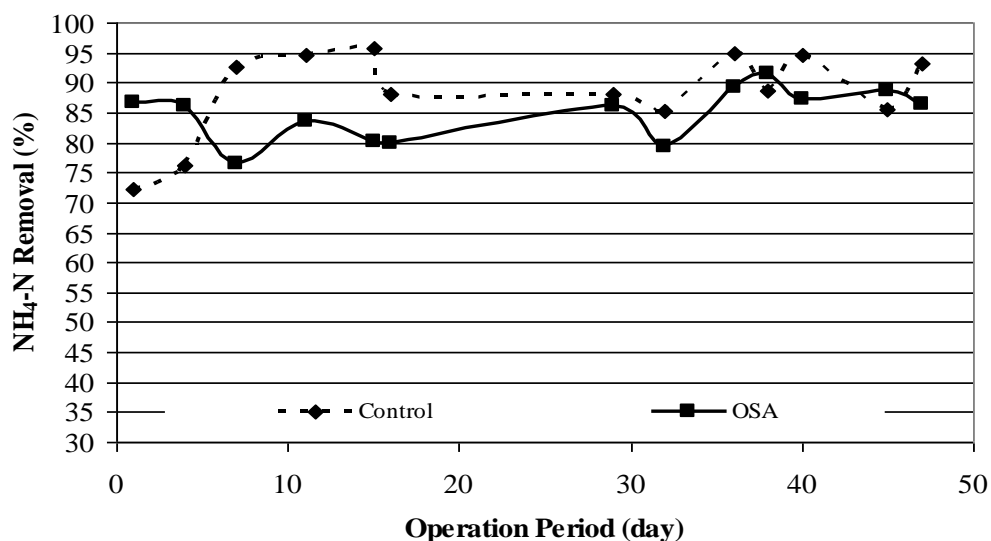


Figure 4.61 Changes of NH₄-N removal efficiencies (%) for OSA and control run

In Figure 4.62, in OSA system the NO₃-N concentration of effluent decreased significantly and this decrease of NO₃-N concentration of effluent in OSA system can be attributed to the denitrification (Saby et al., 2003).

The phosphorus release after the anaerobic conditions was proved with increasing of PO₄-P concentration of effluent in OSA system as shown in Figure 4.63. The PO₄-P concentration of effluent in OSA system was increased from 4 mg/L to 6.8 mg/L due to addition of sludge kept under -250 mV ORP level with no external food.

The presence of the anaerobic reactor also affects the release of phosphorus and in particular, a higher increase of PO₄ concentration in the treated effluent from the wastewater treatment units was observed for lower ORP values

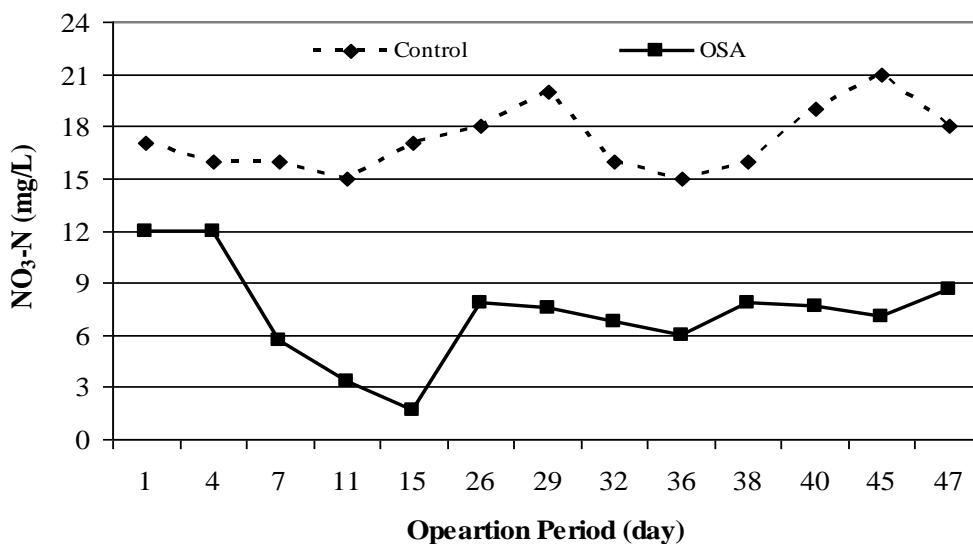


Figure 4.62 Changes of NO₃-N concentration of effluent for OSA and control run

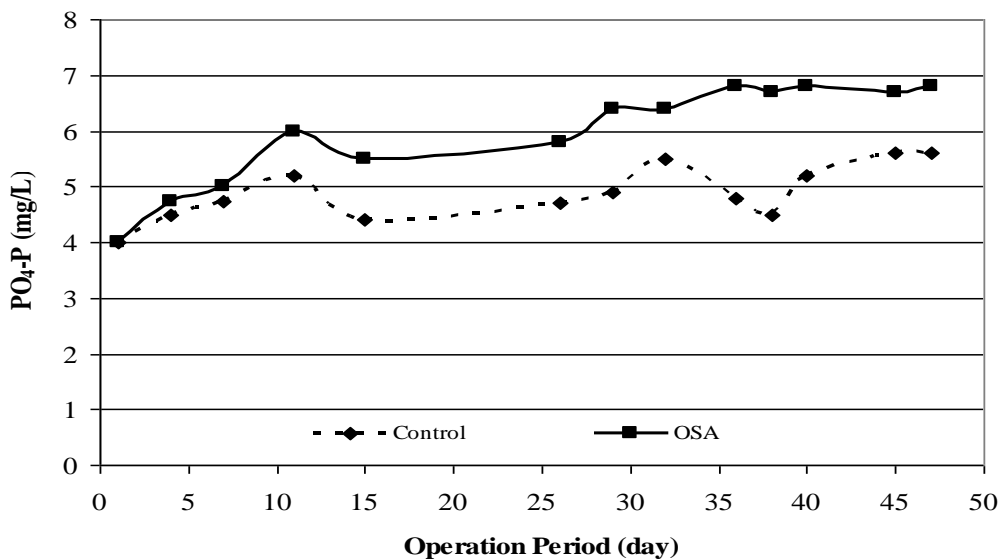


Figure 4.63 Changes of PO₄-P concentration of effluent for OSA and control run

4.6.3 Effects of Anaerobic Zone of OSA on TN and TP Concentrations

The TP concentration of aeration tank in OSA system was gradually increased from 3 mg/L 8.6 mg/L due to release of phosphorus in anaerobic tank as seen in Figure 4.64.

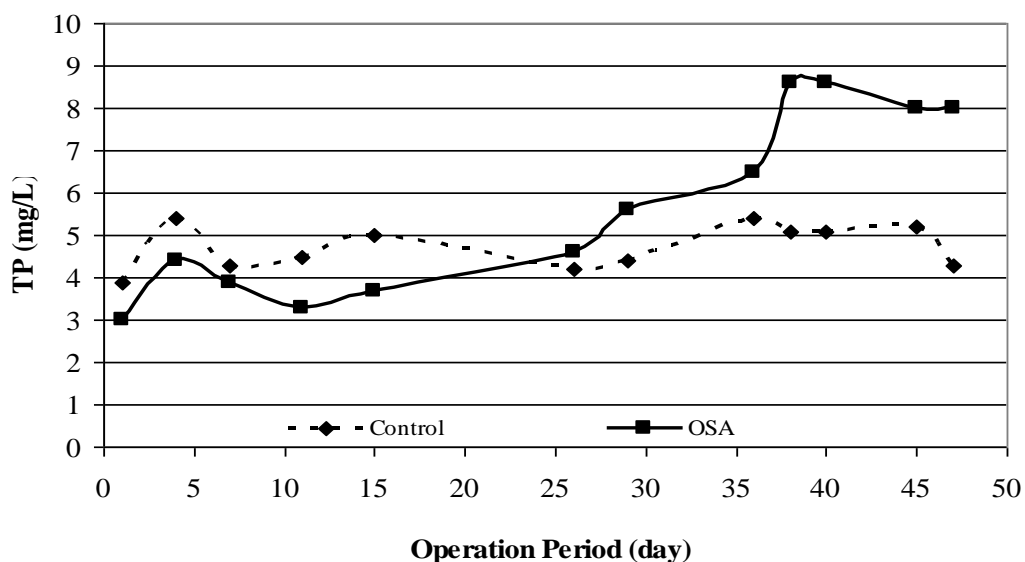


Figure 4.64 Changes of TP concentration of aeration tank for OSA and control run

TN concentration of OSA process was higher than that control reactor as shown in Figure 4.65 due to the release of cell contents after the anaerobic tank.

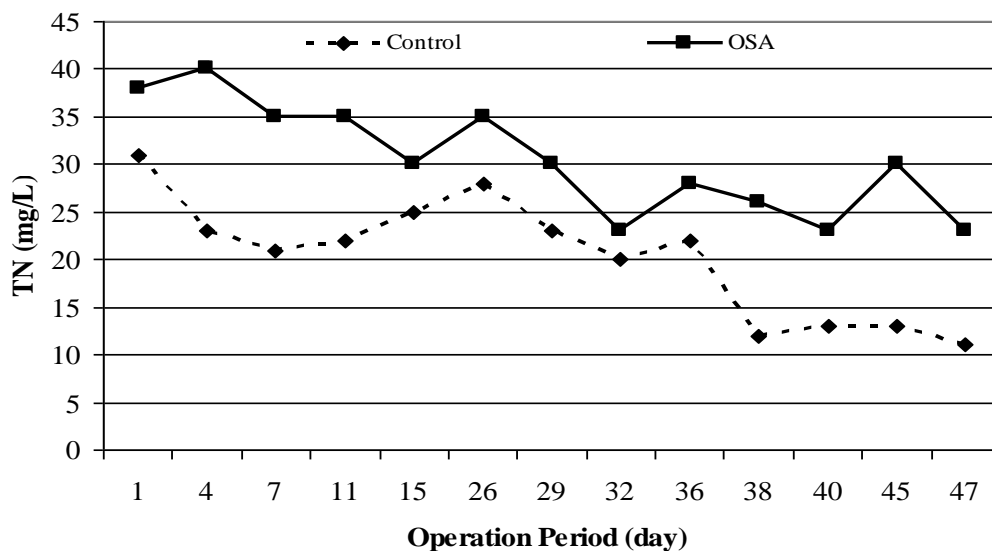


Figure 4.65 Changes of TN concentration of aeration tank for OSA and control run

4.6.4 Comparison of OSA and Control System in terms of Sludge Characteristics

The settleability of the OSA system sludge was also found better than that of the control system in terms of SVI as shown in Figure 4.66. Over the entire operation, average SVI values were 94 and 115 for OSA and control systems, respectively.

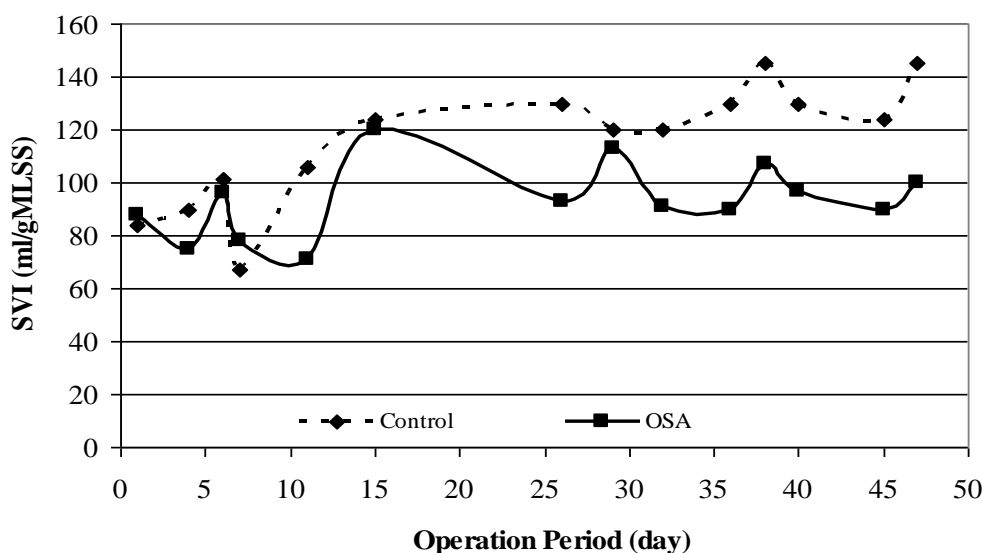


Figure 4.66 Changes of SVI values for OSA and control run

Similar to this study, Saby et al., (2003) suggested an improvement in settleability in OSA sludge with around 100 of SVI value. The maintenance of low SVI was attributed to the low ORP level in the anaerobic tank. It can be revealed that low ORP level was necessary to maintain low SVI values.

In the continuous operation of OSA and control systems, CST parameter was used for evaluation of filtration characteristics of sludge and to see the effect of ORP level in anaerobic tank of OSA system on dewatering characteristics of sludge.

CST variations during the operation period are given in Figure in Figure 4.67. For OSA system, CST values were higher than the control run for the beginning of the operation. With increasing operation time, the CST values were decreased for OSA system. Higher CST values were obtained in control system compared to OSA

system during the long-term operation. It was revealed that the OSA system enhanced the filterability of sludge.

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 low SRF values showed in Figure 4.68 that OSA process improves the filterability characteristics of sludge in long term operation, and it can be applied to biological sludge without deterioration of sludge filterability.

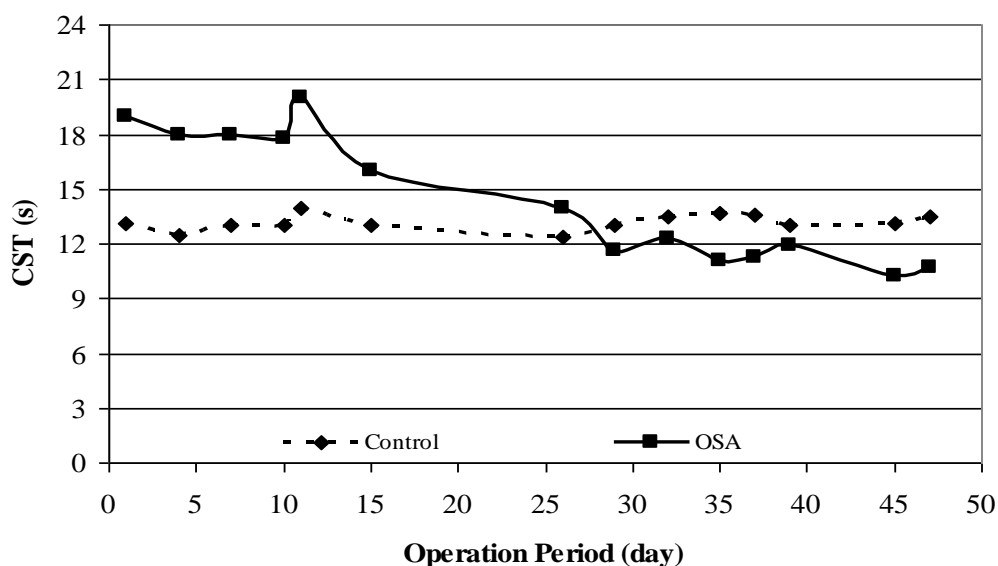


Figure 4.67 Changes of CST values for OSA and control run

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). The particle size distribution for control and OSA system were illustrated in Figure 4.69 and 4.70, respectively.

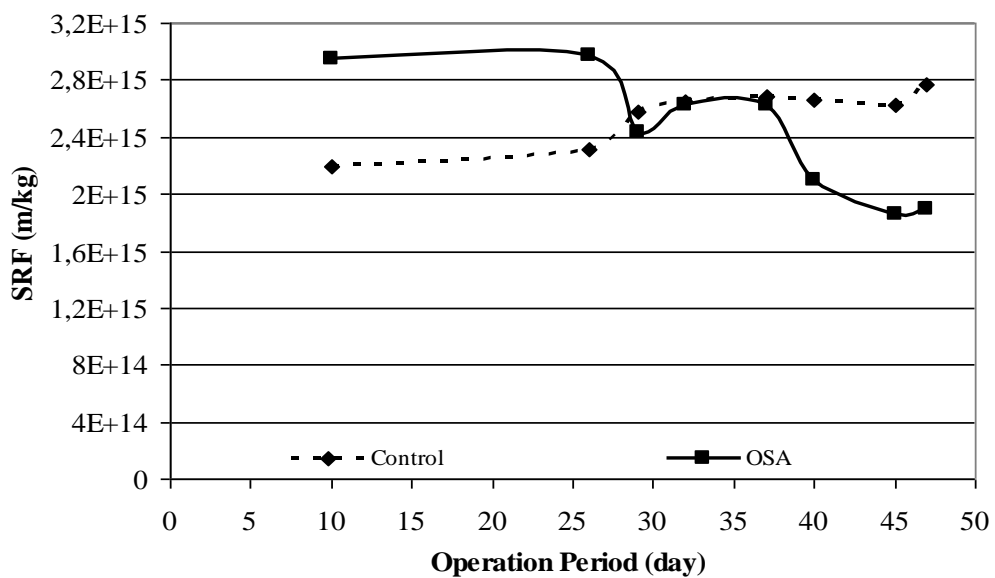


Figure 4.68 Changes of SRF values for OSA and control run

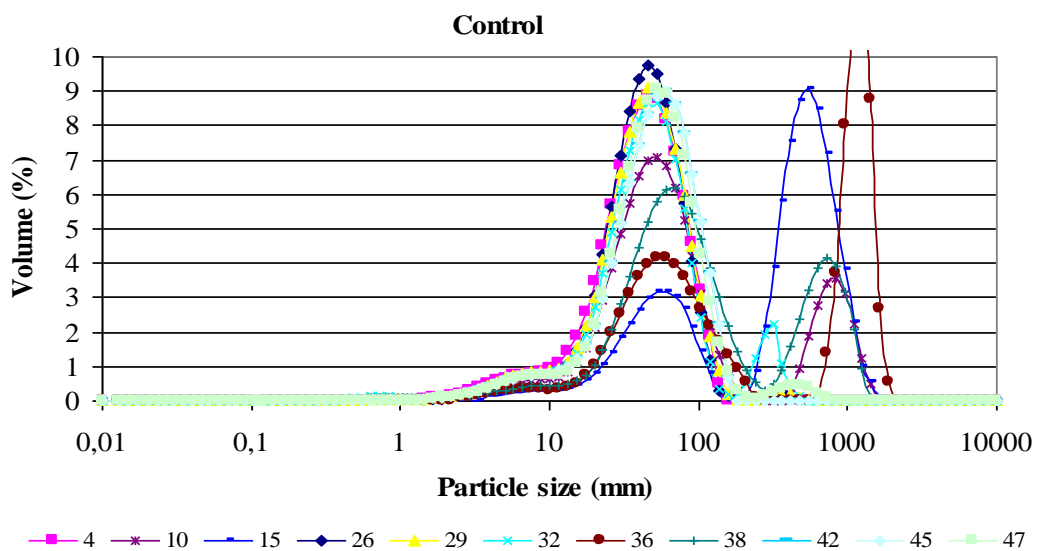


Figure 4.69 Changes of particle size for control system

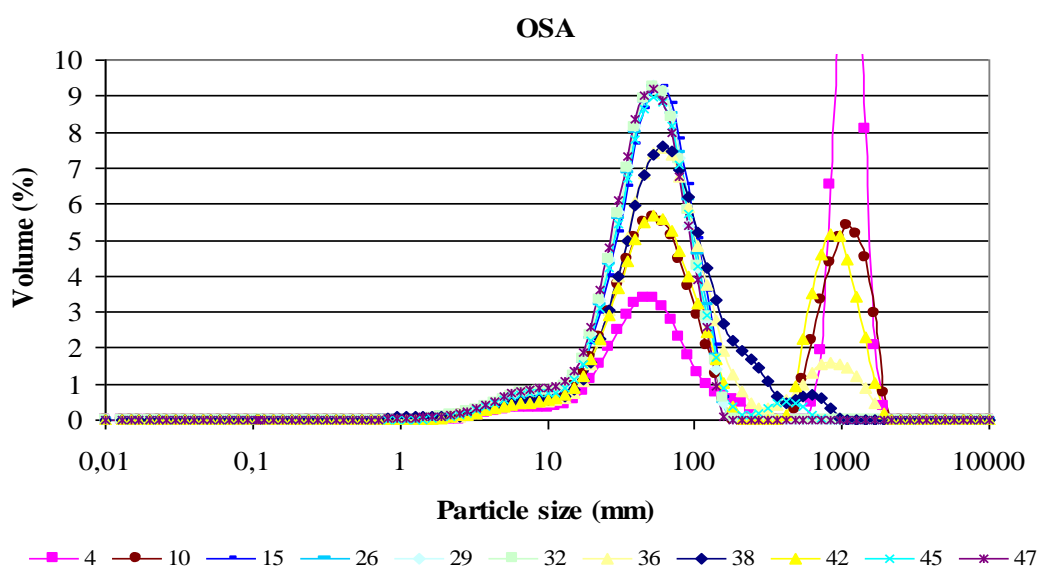


Figure 4.70 The changes of particle size for OSA system

4.6.5 Comparison of OSA and Control System in terms of OUR and SOUR

The profile of OUR is valuable for determining the solubilization of activated sludge. Monitoring of OUR value is an available technique for investigating the performance in aerobic, anoxic and anaerobic. The increase in OUR value leads to the increase in SCOD concentration (Chang et al., 2002). For the beginning of the operation period, in OSA system, OUR values increased due to the COD solubilization. After 15th day of the period, OUR values decreased to 0.15 mg/L.min as shown in Figure 4.71.

SOUR values in OSA system were also increased due to OUR values as illustrated in Figure 4.72. The milligram of oxygen consumed per gram of volatile suspended solids (VSS) per hour was increased after the anaerobic tank under low ORP level during the operational period.

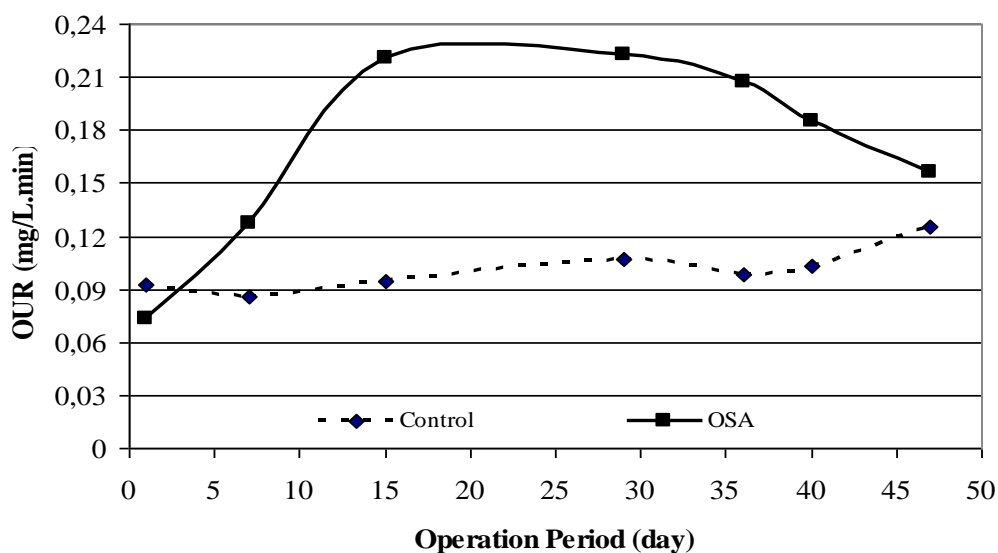


Figure 4.71 Changes of OUR values for OSA and control run

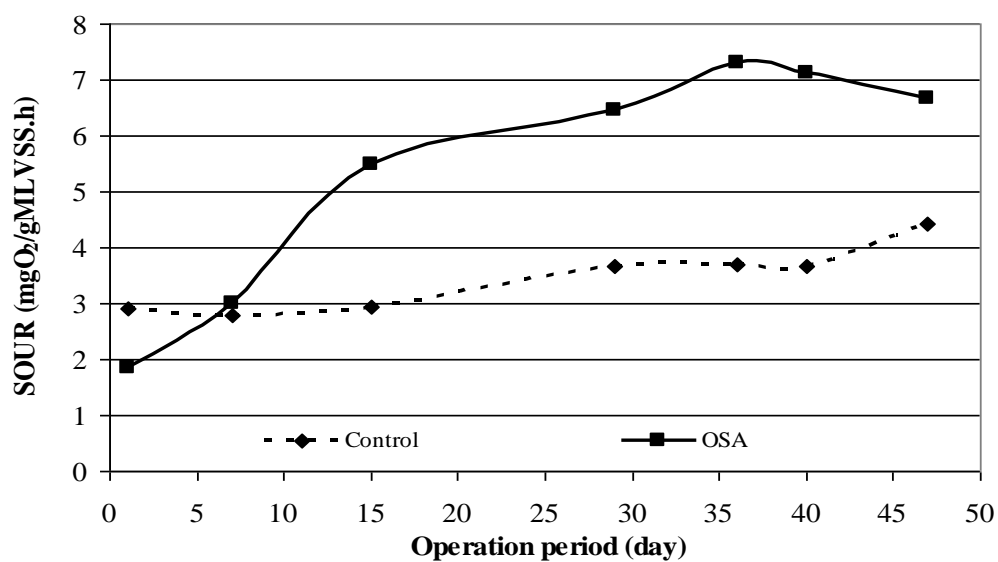


Figure 4.72 Changes of SOUR values for OSA and control run

4.7 Batch Experiments of OSA Systems

4.7.1 Batch Experiment I: Sludge Decay

A possible explanation is that the rate of cell death accelerated when sludge undergoes low ORP values in the anaerobic reactor. In the anaerobic reactor, an

increase of soluble COD was observed. The solubilized COD could be related to cellular death. According to this hypothesis, the anaerobic reactor behaves like a cell lysis reactor and when the sludge returns to the aerobic activated sludge stage, the soluble COD supports cryptic growth, which leads to an overall sludge reduction. The effect of the 18 h-anaerobic conditions on the MLSS concentration demonstrated in Figure 4.73. It can be realized that MLSS concentration was reduced by 19 % in the control run after the anaerobic exposure while 13 % of MLSS reduction observed in the sludge from OSA system during 18 h. Low ORP level and absence of external food may promote the sludge reduction by the stress upon the microorganisms. The stress on the OSA system was lower than control system because microorganisms have already acclimated to the low ORP level.

As shown in Figure 4.74 and 4.75 during the anaerobic exposure, SCOD, $\text{NH}_4\text{-N}$, TN and TP in the supernatant were increased. At the end of the anaerobic treatment, the release cell contents may contribute to the increase of SCOD, $\text{NH}_4\text{-N}$, TN and TP. The concentration of COD and nitrogen components were low because of the anaerobic treatment. The anaerobic treatments of sludge with no food, the hydrolysis and acidogenesis processes were occurred. In the hydrolysis step, organic compounds were hydrolyzed to simple components. Then simple organics were degraded to volatile fatty acids and the sludge decay resulted in excess sludge reduction.

The changes of OUR and SOUR before and after anaerobic treatment were shown in Figure 4.76. These values for control run were lower than OSA system before anaerobic treatment. The 18 h- anaerobic period affected them for both control and OSA systems. The increase of OUR and SOUR may be the indicator of the endogenous metabolism. After anaerobic treatment, the cellular components were oxidized to produce maintenance energy and there was no energy for growth. Therefore, the sludge production was decreased after anaerobic treatment for control and OSA system as demonstrated before by MLSS reduction. It was proved that higher endogenous respiration in the systems might lead to lower sludge production.

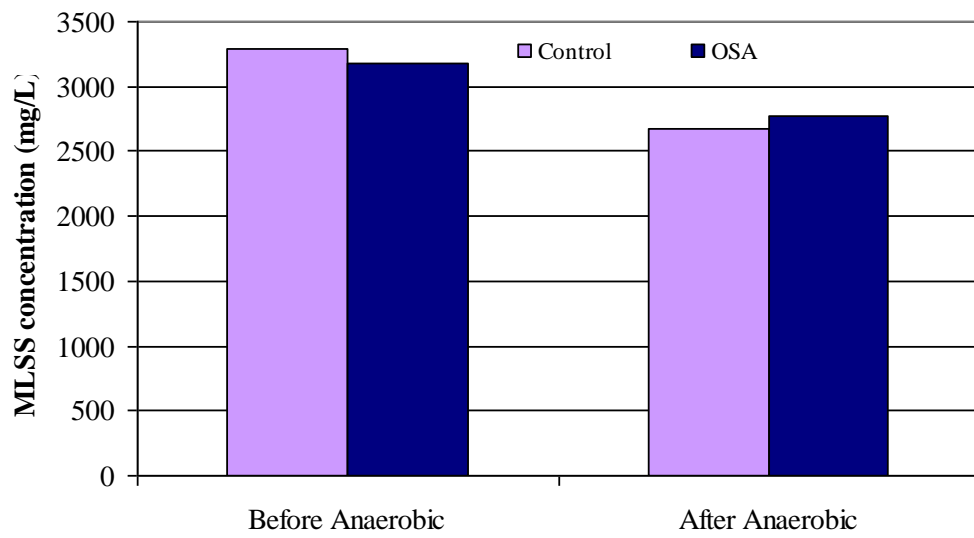


Figure 4.73 MLSS concentrations of control and OSA batch experiment

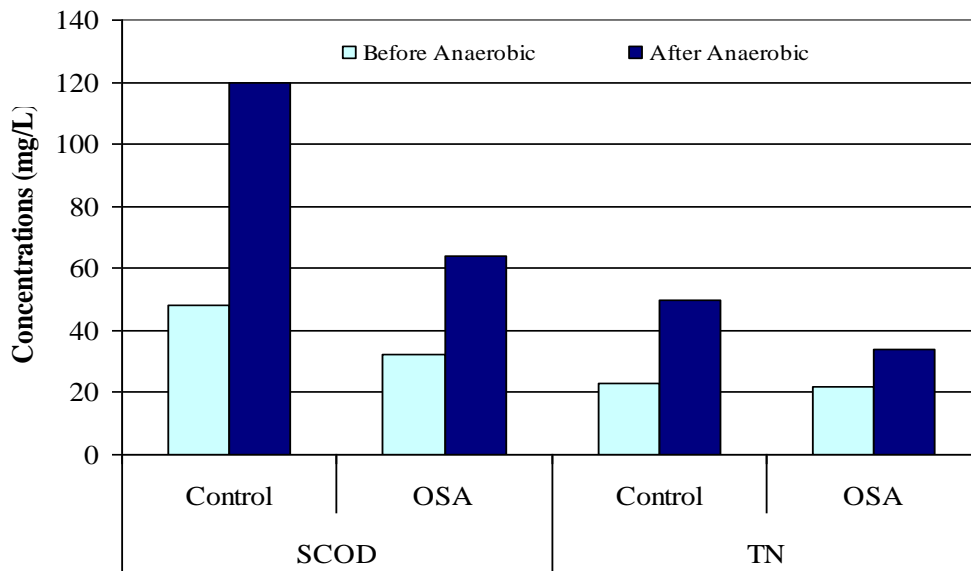


Figure 4.74 SCOD and TN concentrations of control and OSA batch experiment

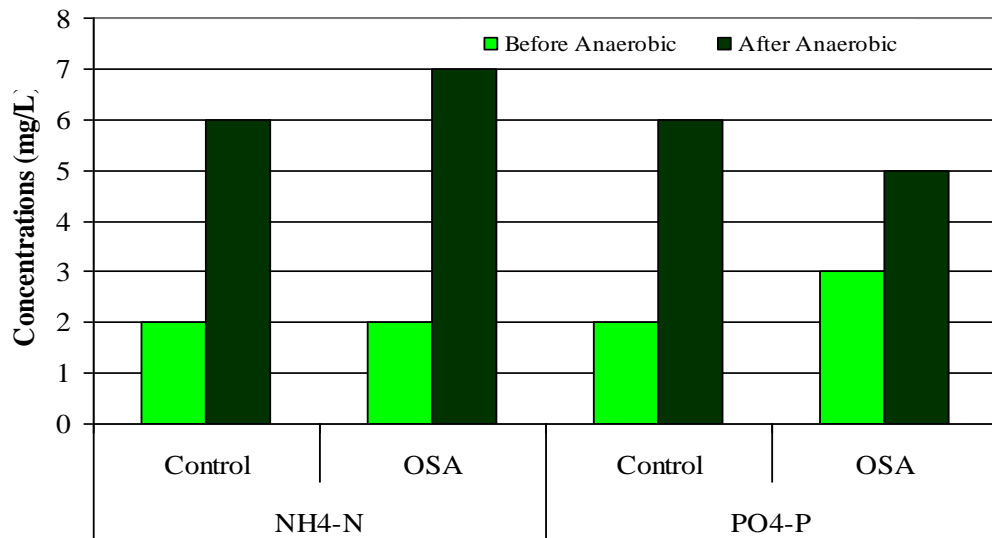


Figure 4.75 $\text{NH}_4\text{-N}$ and TP concentrations of control and OSA batch experiment

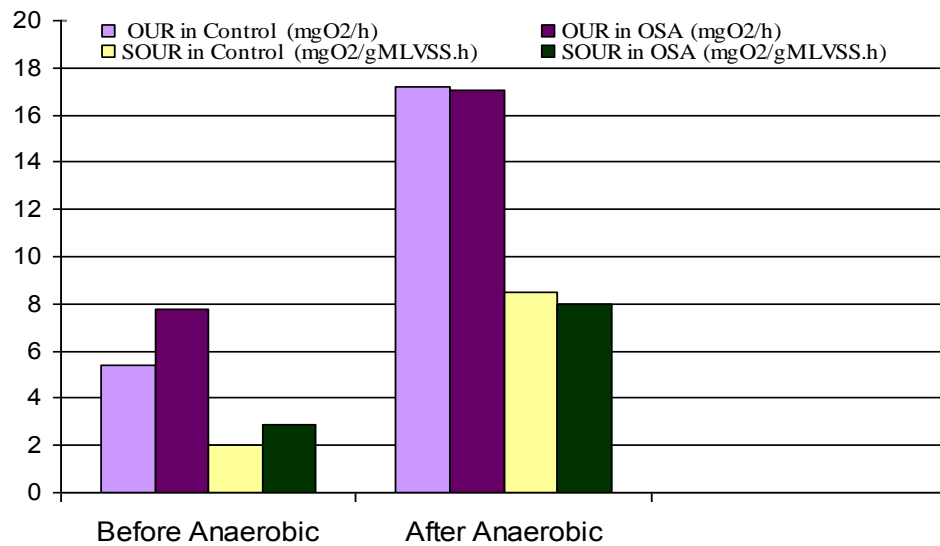


Figure 4.76 Change of OUR and SOUR after anaerobic treatment for control and OSA

Y_{obs} values in the batch OSA and control systems were presented in Table 4.6. The sludge reduction in terms of Y_{obs} caused by sludge decay in OSA batch reactor was 40 % compared to control batch reactor for the 1st batch experiment.

Table 4.6 Yobs for the batch experiment I

Measurements	Control batch reactor	OSA batch reactor
1	0.42	0.25
2	0.39	0.27
3	0.41	0.24
Average	0.41	0.25

4.7.2 Batch Experiment II: Energy Uncoupling

A decrease of ATP content in sludge occurs when the sludge remains in the anaerobic reactor, without external substrate and at low ORP levels. When the sludge returns to the activated sludge stage optimal conditions for the formation of new ATP are stored. The cyclic alternation of ATP content in sludge uncouples catabolism and anabolism, which causes in biomass yield favoring sludge reduction.

Results in the Table 4.7 show that there was an energy uncoupling theory for the sludge reduction in the anaerobic aerobic batch experiment.

Table 4.7 Yobs for the batch experiment II

Measurements	Control batch reactor	OSA batch reactor
1	0.4	0.39
2	0.39	0.38
3	0.41	0.37
Average	0.4	0.38

The sludge reduction in terms of Y_{obs} caused by energy uncoupling in OSA batch reactor was 5 % compared to control batch reactor for the 2nd batch experiment. At first study application, the OSA process to evaluate the reduction of excess sludge was carried out by Chudoba et al., (1992). At lab scale and using synthetic wastewater, the sludge production of a conventional activated sludge system was compared to that of the OSA process. In the case of the OSA process, the anaerobic reactor was maintained at -250 mV ORP similar to this study. The observed sludge yield in the activated sludge was 0.37 kgTSS/kgCOD_{removed}, while in the OSA process was 0.22 kgTSS/kg kgTSS/kgCOD_{removed} (reduction of 40 %). Saby et al., (2003) were also reported that the observed sludge yields in the OSA system were 0.18-0.32 kgTSS/kgCOD_{removed} compared to 0.4 kgTSS/kgCOD_{removed} in the conventional activated sludge process.

CHAPTER FIVE

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusion of Box-Behnken Statistical Design Program

Box-Behnken Statistical Design program was used in order to determine the effects of major operating variables on COD removal and to find the combination of variables resulting in maximum COD removal efficiency. The effects of HRT, SRT and initial COD concentrations were investigated. The experimental range and levels of independent variables were HRT of 25 h, SRT of 5-25 d of SRT and 300-500 mg/L of initial COD concentration. For the levels of each factor for Box-Behnken, 17 experimental points were obtained from the program. In the correlating of the COD removal efficiency with other independent variables, a response surface function was utilized The Software Design Expert (Version 7.0.0 Stat-Ease Inc, Minneapolis, USA was used for the determination of the coefficients and data analysis. The coefficients of the response function were obtained using experimental data. Predicted values of percent COD removal efficiency were determined by the response functions with the obtained coefficients. The correlation coefficients (R^2) between the observed and predicted values were obtained as 0.95. Predicted values were in a good agreement with experimental values. Experimental results demonstrated that SRT is more effective for COD removal. Optimum HRT, SRT and initial COD values for maximum COD removal were determined as 25 h, 25 d and 400 mg/L, respectively.

5.2 Conclusion of Stability of Activated Sludge Systems (Steady State Conditions)

The activated sludge systems were performed under the optimum operational conditions for during 45 days. With the long SRT of 25 d, this operation can be classified as extended aeration process. The extended aeration process is similar to the conventional plug-flow process except that it operates in the endogenous respiration phase of the growth curve, which requires a low organic loading and long aeration time. Because of the long SRTs (20 to 30 d) and HRT about 24 h, aeration

equipment design is controlled by mixing needs and not oxygen demand (Metcalf&Eddy, 2004). When a system operates at a sufficiently long SRT, the excess sludge production is generally reduced. This fact is usually attributed to the lower biomass yield and to concepts such as maintenance energy requirements, endogenous respiration, cell decay and grazing by predators. The observed biomass yield is in fact inversely dependent on the SRT and endogenous respiration in steady state activated sludge process. The sludge production may be reduced by 60 % when SRT is increased from 2 to 18 days. The average observed sludge yield was 0.55 mgMLVSS/mgCOD_{removed}.

Extended aeration systems require long aeration times a low applied organic loads compared to conventional activated sludge processes. Theoretical zero sludge production is not achievable, although, in practice, a significantly lower quantity of excess sludge is produced compared to conventional activated sludge processes. Other benefits were dewatering improvement, lower odor potential and better sludge settleability. In this part of the study, the better filterability of sludge from extended aeration process was proved with low CST value of 12 s.

The system became stable at the end of the one-month considering effluent quality, observed sludge yield and characteristics. The values were varied 7-8.2 and 25-35 °C for pH and temperature. The average values of COD and NH₄-N removal efficiencies of the systems were 89-92 % and 90-94 %, respectively. The NO₃-N and NO₂-N concentrations of the activated sludge process were varied between 5-10 mg/L and 0.8-3 mg/L, respectively. DO concentration was kept at above 2 mg/L for both of the reactors. The ORP level was around 150 mV. Conductivity values were in the range of 800-1000 µS/cm. The MLVSS/MLSS ratio was approximately 0.85.

5.3 Conclusion of Optimum Ozone Dose (Batch Experiments)

The effects of ozonation on sludge properties and supernatant were investigated with seven different ozone doses. The return activated sludge was decomposed effectively by ozonation. The optimum ozone dose was found as 0.05 gO₃/gTS in terms of DD and for this optimum ozone dose, 77.8 % and 71.6 % reduction were

achieved for TSS and VSS, respectively. While TN and TP concentration of supernatant was increasing, protein concentration of ozonated sludge was decreased. Furthermore, CST increased with the increasing of ozone doses but SRF increased to a specific value and then decreased dramatically. The particle size distribution changed significantly with ozone treatment especially at high ozone doses. It can be concluded that the ozonation is an effective method for sludge reduction because of cell lysis and higher ozone doses can achieve little improvement in sludge solubilization.

5.4 Conclusions of Ozonation with 10 % of Return Activated Sludge

The minimization of excess sludge production using modification of activated sludge processes was purposed. Effects of sludge ozonation on reduction of excess sludge production and changes characteristics were evaluated. 66 % MLSS reduction was observed in ozone run with no wasting excess sludge while MLSS was stable in control run. Furthermore, 43 % reduction of Y_{obs} was achieved in ozone reactor during operation period. Y_{obs} reduction in ozone reactor was 56 % compared to control reactor at the end of the operation. The reactor fed with ozonated sludge showed slightly weakened performance for the removal of COD and NH_4-N with satisfactory level. Effluent NO_3-N concentrations of the control run were low for the beginning of the operation period then increased but for ozone run, NO_3-N concentrations of the effluent were higher than control run in the first half of the operation period. It can be attributed to the increased nitrogen loading after the recirculation of ozonated sludge. The effluent PO_4-P concentrations of the control run were higher than the ozonated system. The slightly higher effluent TN concentrations of ozone run compared to control run related to the increased nitrogen loading after the recirculation of ozonated sludge. TP concentration of ozonated system was close to control run. SVI values in ozone reactor were lower than control reactor. SVI values indicated that the settling capability of the activated sludge in ozone reactor was slightly better than that of the control reactor.

Ozone run had higher CST value than the control run during the operation period with slight difference. SRF values of the ozone run were higher than the control run.

CST and SRF values indicated that the filterability sludge was affected by ozonation with an insignificant difference.

5.5 Conclusions of Ozonation with 20 % of Return Activated Sludge

In this part of the study, a comparison between extended aeration activated sludge process and activated sludge process coupled with ozonation system was investigated from the viewpoints of sludge reduction and water treatment capacity. Moreover, changes of sludge characteristics during continuous operation were also considered in this comparison. While 71 % MLSS and 73 % Y_{obs} reduction observed in ozone run during the operation period, 62 % Y_{obs} reduction was obtained in ozone run compared to the control run.

The results of the study, there was no significantly increase in effluent COD, in other words, the COD removal efficiency was not significantly decreased after ozonation. Ozonation did not also affect the nitrification capacity. The ammonium removal efficiency of the ozone and control run were similar. Chemical oxygen demand and NH_4-N removal efficiencies were closed to control run with 92-100 % and 85-96 % in ozone run, respectively. NO_3-N concentration of effluent and total nitrogen of aeration tank in ozone run were higher than control run due to release of cell contents because of cell lysis. Effluent PO_4-P concentration and TP concentration of aeration tank in ozone run were increased gradually during the operation period and were always higher than control run due to the cell lysis as well as nitrogen. SVI values of ozone run was lower than control run during the operation period. It can be said that sludge settling properties can be improved for long-term operation by ozonation. CST and SRF values in ozone run were slightly higher than control run. The filterability of sludge was affected by ozonation but there was a little difference in filterability capacity and dewaterability between ozone and control run in terms of CST and SRF. Ozonation could change particle size and sludge destruction by ozonation led to an increase of small particles at higher ozone doses.

It can be concluded that the ozonation is an effective method for sludge reduction because of cell lysis.

5.6 Conclusions of OSA Process (Continuous Operation)

In this part of the study, during the operation, 62 % of yield reduction efficiency was achieved in OSA system. The average Y_{obs} value was 0.52 mgMLSS/mgCOD_{removed} in control system. 58 % of reduction efficiency of Y_{obs} was also obtained in OSA system compared to control run at the end of the operation. Low ORP level such as – 250 mV in anaerobic tank encourages the excess sludge reduction. MLVSS concentration was reduced by 41 % in the sludge from the OSA system during the treatment. The sludge reduction may be promoted with low ORP and no external food source. The microbes may be imposed stress by these conditions. The result showed that approximately 53 % of Y_{obs} reduction could be achieved with OSA system

The additional substrates from the anaerobic tank resulted in lower COD concentrations in the effluent in the OSA system than that in the effluent of the control system due. When compared with the control run, OSA system showed better COD removal efficiency. When sludge is subjected in a low ORP condition in the anaerobic tank, the sludge induces a stressful condition and the cell contents were released. In the following aerobic conditions with the presence of food in aeration tank, the overall biomass is reduced. In long-term operation, it can be concluded that both systems showed similar removal efficiencies for NH₄-N. However, the NH₄-N removal efficiency was lower compared to control run during the operation period due to denitrification. In OSA system, the NO₃-N concentration of effluent decreased significantly and it can also be attributed to the denitrification.

The phosphorus release after the anaerobic conditions was proved with increasing of PO₄-P concentration in the effluent in OSA system. The PO₄-P concentration of effluent in OSA system was increased due to addition of sludge kept under -250 mV ORP level with no external food. The presence of the anaerobic reactor also affects the release of phosphorus. TP concentration of OSA process was higher than that control reactor due to the release of cell contents after the anaerobic tank.

It can be revealed that low ORP level was necessary to maintain low SVI values. The settleability of the OSA system sludge was also found better than that of the control system in terms of SVI. In the continuous operation of OSA and control systems, CST parameter was used for evaluation of filtration characteristics of sludge and to see the effect of ORP level in anaerobic tank of OSA system on dewatering characteristics of sludge. OSA system enhanced the filterability of sludge. CST values were increased in OSA system for the beginning of the operation. With increasing operation time, the CST values were decreased for OSA system. Higher CST values were obtained in control system compared to OSA system during the long-term operation. The low SRF values showed that OSA process improves the filterability characteristics of sludge, and it can be applied to biological sludge without deterioration of sludge filterability.

The efficiency can be easily determined by monitoring the ORP values. Monitoring of ORP value is an available technique for investigating the performance in aerobic, anoxic and anaerobic system. The increase in ORP value leads to the increase in SCOD concentration. Increase in ORP and SOUR is an indicator of the COD solubilization in OSA system.

5.7 Conclusions of OSA Process (Batch Experiments)

When sludge subjected to low ORP values in the anaerobic reactor, the rate of cell death accelerated. In the anaerobic reactor, an increase of soluble COD was observed. The solubilized COD could be related to cellular death. According to this hypothesis, the anaerobic reactor behaves like a cell lysis reactor and when the sludge returns to the aerobic activated sludge stage, the soluble COD supports cryptic growth, which leads to an overall sludge reduction. MLSS concentration was reduced by 19 % in the control run. 13 % of MLSS reduction observed in the sludge from OSA system during anaerobic period. The reduction in OSA system was lower than control system since the microorganisms in OSA process have already acclimated to the low ORP level.

SCOD, NH₄-N, TN and TP in the supernatant were increased during the anaerobic exposure. The release cell contents at the end of the anaerobic treatment may lead to the increase of SCOD, NH₄-N, TN and TP. The concentration of COD and nitrogen components were low because of the anaerobic treatment. During the anaerobic treatment, the hydrolysis (the transformation of organic compounds to simple organics) and acidogenesis processes were occurred. Then simple components were degraded to volatile fatty acids and the excess sludge reduction was maintained due to the cell lysis.

The changes of OUR and SOUR values for control run were lower than OSA system before anaerobic treatment. The increase of OUR and SOUR may be the indicator of the endogenous metabolism. After anaerobic treatment, the cellular components were oxidized to produce maintenance energy for growth. Therefore, the sludge production was decreased after anaerobic treatment for control and OSA system due to the oxidation of cellular components to produce maintenance energy and there was no energy. It was proved that higher endogenous respiration in the systems might lead to lower sludge production.

In the second batch experiment in order to investigate the uncoupling metabolism, ATP content in sludge decreased when the sludge remained in the anaerobic reactor, without external substrate and at low ORP levels. When the sludge returns to the activated sludge stage optimum conditions for the formation of new ATP are stored. The cyclic alternation of ATP content in sludge uncouples catabolism and anabolism, which causes in biomass yield favoring sludge reduction.

There was an energy uncoupling theory for the sludge reduction in the anaerobic aerobic batch experiment according to the results. The sludge reduction in terms of Y_{obs} caused by energy uncoupling in OSA batch reactor was 5 % compared to control batch reactor for batch experiment.

5.8 Recommendations

The activated sludge processes used in this research were fed with synthetic wastewater. The systems can be operated with real wastewater using different

activated sludge modifications. The other sludge minimization techniques such as microbial predation and metabolic uncouplers can be studied in order to compare the results of this research

Organic loading rate can be used as a variable instead of initial concentration and sludge yield can be used a response instead of COD removal efficiency for Box- Behnken Statistical Design Program.

Experimental studies were carried out in laboratory scale. Pilot and full scale trials should be done for conclusive results. Furthermore, the cost analysis can be investigated in order to determine the feasibility of full-scale ozone application

REFERENCES

- Ahn, K.-H., Lee, J.W., Cha, H.-Y., Song, K.-G., Park, K.Y., Kim, J. & Lee, Y. (2002). Operational strategies for the optimization of a pilot scale activated sludge system minimizing the sludge production with ozone oxidation, *Proc. 2002 IWA World Water Congress*, Melbourne, Australia, e21255a.
- APHA, AWWA, WEF. (2005). *Standard Methods for the Examination of Water and Wastewater*. 21st ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.
- Bohler, M. & Siegrist, H. (2004). Partial ozonation of activated sludge to reduce excess sludge, improve denitrification and control scumming and bulking. *Water Science and Technology*, 49, 41–49.
- Bougrier, C., Albasi, C., Delgene`s, J.P. & Carre`re, H. (2006). Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability. *Chemical Engineering Process*, 45 (8), 711–718.
- Bougrier, C., Carrère, H., & Delgenes, J. P. (2005). Solubilisation of waste-activated sludge by ultrasonic treatment. *Chemical Engineering Journal*, 106, 163-169.
- Caffaz, S., Santianni, D., Cerchiara, M., Lubello, C. & Stecchi, R. (2005). Reduction of excess biological sludge with ozone: experimental investigation in a full-scale plant. In: *IOA 17th World Ozone Congress*, Strasbourg, France.
- Caravelli, A., Giannuzzi, L. & Zaritzky, N. (2006). Effect of ozone on filamentous bulking in a laboratory scale activated sludge reactor using respirometry and INT-dehydrogenase activity. *Journal of Environmental Engineering*, 132 (9), 1001–1010.
- Cesbron, D., Deleris, S., Debellefontaine, H., Roustan, M. & Paul, E. (2003). Study of competition for ozone between soluble and particulate matter during activated

- sludge ozonation, *Chemical Engineering Research & Design*, 81, (A9), 1165–1170.
- Chang, C.-N, Ma, Y.-S & Lo, C.-W (2002). Application of oxidation–reduction potential as a controlling parameter in waste activated sludge hydrolysis. *Chemical Engineering Journal*, 90, 273–281
- Chen, G. H., An, K. J., Saby, S., Brois, E. & Djafer, M. (2003). Possible cause of excess sludge reduction in an oxicsettling anaerobic activated sludge process (OSA process). *Water Research*, 37, 3855-3866.
- Chen, G. H., Yip, W. K., Mo, H. K. & Liu, Y. (2001). Effect of sludge fasting and feasting on growth of activated sludge cultures. *Water Research*, 35 (4), 1029-1037.
- Chen, G.H., Mo, H.K., Saby, S., Yip, W.K & Liu, Y. (2000). Minimization of activated sludge production by chemically stimulated energy spilling. *Water Science Technology*, 42 (12), 189-200.
- Chen, G.H, Saby, S., Djafer, M. & Mo, H.K. (2001). New approaches to minimize excess sludge in activated sludge systems. *Water Science Technology*, 44 (10), 203-208.
- Chen, G.H., Mo, H.K. & Liu, Y. (2002). Utilization of a metabolic uncoupler 3, 3', 4', 5- tetrachlorosalicylanilide (TCS) to reduce sludge growth in activated sludge culture. *Water Research*, 36, 2077–2083.
- Chiavola, A., Naso, M., Rolle, E. & Trombetta, D. (2007). Effect of ozonation on sludge reduction in a SBR plant, *Water Science and Technology*, 56, (9), 157–165.
- Chon, D.-H., Rome, M., Kim, H.-S. & Park, C. (2011a). Investigating the mechanism of sludge reduction in activated sludge with an anaerobic side-stream reactor. *Water Science and Technology*, 63(1), 93-99.

- Chon, D.-H., Rome, M., Kim, H.-S., Park, K.Y. & Park, C. (2011b). Investigation of the sludge reduction mechanism in the anaerobic side-stream reactor process using several control biological wastewater treatment processes. *Water Research*, XXX, 1-9.
- Chu, L.-B., Yan, S.-T., Xing, X.-H., Yu, A.-F., Sun, X.-L., and Jurcik, B. (2008). Enhanced sludge solubilization by microbubble ozonation. *Chemosphere*, 72, 205-212.
- Chu, L., Yan, S., Xing X.-H., Sun, X. & Jurcik, B. (2009a) Progress and perspectives of sludge ozonation as a powerful pretreatment method for minimization of excess sludge production. *Water Research*, 43, 1811-1822.
- Chu, L., Wang, J., Wang, B., Xing, X.-H., Yan, S., Sun, X. & Jurcik, B. (2009b). Changes in biomass activity and characteristics of activated sludge exposed to low ozone dose. *Chemosphere*, 77, 269-272.
- Chudoba, P. & Capdeville, B. (1991). A possible way towards reduction of waste sludge production, *Sixth IAWPRC Conference on Design and Operation of Large Wastewater Treatment Plants, Prague*.
- Chudoba, P., Chevalier, J.J., Chang, J. & Capdeville, B. (1991). Effect of anaerobic stabilization of activated sludge on its production under batch conditions at various S₀/X₀ ratios. *Water Science and Technology*, 23, 917-926.
- Chudoba, P., Chudoba, J. & Capdeville, B. (1992). The aspect of energetic uncoupling of microbial growth in the activated sludge process: OSA system. *Water Science and Technology*, 26 (9-11), 2477-2480.
- Cook, G.M. & Russell, J.B. (1994). Energy-spilling reactions of *Streptococcus bovis* and resistance of its membrane to proton conductance. *Applied and Environmental Microbiology*, 60, 1942-8.

- Cui, R. & Jahng, D., (2004). Nitrogen control in AO process with recirculation of solubilized excess sludge. *Water Research*, 38, 1159–1172.
- Deleris, S., paul, E., Audic, J.M., Roustan, M. & Debellefontaine, H. (2000). Effect of ozonation on activated sludge solubilization and mineralization. *Ozone, Science and Engineering*, 22 (5), 473-487.
- Deleris. S., Geaugey, V., Camacho, P., Debellefontaine, H. & Paul, E. (2002). Minimization of sludge production in biological processes: An alternative solution for the problem of sludge disposal. *Water Science and Technology*, 46, (10), 63–70.
- Demir, O. & Filibeli, A. (2011). Performance of activated sludge process coupled with ozonation process for reduction of excess sludge production.; In 8th IWA International Symposium on Waste Management Problems in Agro-Industries, 22-24 June Cesme, Turkey.
- Dogrueel, S., Sievers, M., & Germirli-Babuna, F. (2007). Effect of ozonation on biodegradability characteristics of surplus activated sludge. *Ozone: Science & Engineering*, 29, (3), 191-199.
- Dytczak, M. A. & Oleszkiewicz, J.A. (2008). Performance change during long-term ozonation aimed at augmenting denitrification and decreasing waste activated sludge. *Chemosphere*, 73, 1529–1532.
- Dytczak, M.A., Londry, K.L., Siegrist, H. & Oleszkiewicz, J.A. (2006). Extracellular polymers in partly ozonated return activated sludge: impact on flocculation and dewaterability. *Water Science and Technology*, 54 (9), 155–164.
- Dytczak, M.A., Londry, K.L., Siegrist, H. & Oleszkiewicz, J.A. (2007). Ozonation reduces sludge production and improves denitrification. *Water Research*, 41, 543–550.

- Egemen, E., Corpening, J., Padilla, J., Brennan, R. & Nirmalakhandan (1999). Evaluation of ozonation and cryptic growth for biosolids management in wastewater treatment. *Water Science and Technology*, 39 (10-11), 155-158.
- Egemen, E., Corpening, J. & Nirmalakhandan, N. (2001). Evaluation of an ozonation system for reduced waste sludge generation. *Water Science and Technology*, 44, 445–452.
- Egemen Richardson, E., Edwards, F. & Hernandez, J. (2009). Ozonation in sequencing batch reactors for reduction of waste solid. *Water Environment Research*, 81(5), 506-513.
- Ekama, G.A. & Wentzel, M.C. (2008). *Biological Wastewater Treatment Principles, Modelling and Design*.
- EPA (1987). *Design Manual: Dewatering Municipal Wastewater Sludges (EPA/625/1-87/014)*. Cincinnati, Ohio 45268.
- Erden, G. & Filibeli, A. (2010). Improving anaerobic biodegradability of biological sludges by Fenton pre-treatment: Effects on single stage and two-stage anaerobic digestion. *Desalination*, 251, 58–63
- Fabiyi, M., Novak, R. & Marx, R.B. (2008). Reduce excess sludge by Over 50 percent with ozone, praxair technology.
- Foladori, P., Andreottola, G. & Ziglio, G. (2010). *Sludge reduction Technologies in wastewater treatment plants*, IWA Publishing, ISBN 13: 9781843392781, London, UK.
- Frolund B., Palmigren R., Keiding G. K., Nielsen P. H. (1996). Extraction of extracellular polymer from activated sludge using a cation Exchange resin. *Water Research*, 30 (8), 1749-1758.
- Gao, Y., Peng, Y., Zhang, J., Wang, S., Guo, J. & Liu, Y. (2011). Biological sludge reduction and enhanced nutrient removal in a pilot-scale system with 2-step

- sludge alkaline fermentation and A²O process. *Bioresource Technology*, 102, 4091–4097.
- Gaudy, A.F. & Gaudy, E.T. (1980). *Microbiology for Environmental Scientists and Engineers*. McGraw-Hill, New York.
- Ghyoot, W & Verstraete, W. (1999). Reduced sludge production in a two-stage membrane-assisted bioreactor. *Water Research*, 34, 205-215.
- Goel, R.K. & Noguera, D.R. (2006). Evaluation of sludge yield and phosphorus removal in a cannibal solids reduction process. *Journal of Environmental Engineering ASCE*, 132, 1331-1337.
- Goma, G., Rols, J.L. & Pareilleux, A. (1997). Membrane bioreactors for waste water treatment:reduction of sludge production. *Studies in Environmental Science*, 66, 461-467.
- Gonze, E., Pilot, S., Valette, E., Gonthier, Y. and Bernis, A. (2003). Ultrasonic treatment of an aerobic activated sludge in a batch reactor. *Chemical Engineering Process*, 42, 965-975.
- Goodwin J. A. S., Forster C. F. (1985). A further examination into the composition of activated sludge surfaces in relation to their settlement characteristics. *Water Research*, 19 (4), 1038-1046.
- Günder, B. (2001). *The membrane-coupled activated sludge process in municipal wastewater treatment*. Technomic Publishing Company, Inc. ISBN No:1-56676-959-0, Lancaster, Pennsylvania, 17604, USA:
- Guo, X., Liu, J., Wei, Y. & Li, L. (2007). Sludge reduction with Tubificidae and the impact on the performance of the wastewater treatment process, *Journal of Environmental. Science*, 19, 257–263.

- Gürtekin, E. & Şekerdağ, N., (2006). Aktif çamur proseste aşırı çamur üretimini azaltmak için kullanılan yöntemler. Uludağ Üniversitesi Mühendislik-Mimarlık Fakültesi Dergisi, Cilt 11, Sayı 1.
- He, J. Wan, T., Zhang, T.G. & Yang, J. (2011). Ultrasonic reduction of excess sludge from activated sludge system: Energy efficiency improvement via operation optimization. *Ultrasonics Sonochemistry*, 18, 99-103
- He, M-h. & Wei, C-h. (2010). Performance of membrane bioreactor (MBR) system with sludge Fenton oxidation process for minimization of excess sludge production. *Journal of Hazardous Materials*, 176, 597-601.
- He, S., Xue, G. & Wang, B. (2006). Activated sludge ozonation to reduce sludge production in membrane bioreactor (MBR). *Journal of Hazardous Material*, 135, 406–411.
- Heinz, (2007). Scaling up of electrical route. In: Comparative evaluation of Sludge Reduction Routes. Ginestet, P.(ed.). IWA Publishing, London, UK.
- Hendrickx, T.L.G., Elissen, H.J.H., Temmink, H., & Buisman, C.J.N. (2011). Operation of an aquatic worm reactor suitable for sludge reduction at large scale. *Water Research*, 45, 4923- 4929.
- Hendrickx, T.L.G., Temmink, H., Elissen, H.J.H. & Buisman, C.J.N. (2010). Aquatic worms eat sludge: Mass balances and processing of worm faeces *Journal of Hazardous Materials*, 177, 633–638.
- Hirooka, K., Asano, R., Yokoyama, A., Okazaki, M., Sakamoto, A. & Nakai, Y. (2009). Reduction in excess sludge production in a dairy wastewater treatment plant via nozzle-cavitation treatment: Case study of an on-farm wastewater treatment plant. *Bioresource Technology*, 100, 3161–3166
- Huang, X., Liang, P. & Qian, Y. (2007). Excess sludge reduction induced by *Tubifex tubifex* in a recycled sludge reactor. *Journal of Biotechnology*, 127, 443-451.

- Huysmans, A., Weemaes, M., Fonseca, P.A. & Verstraete W. (2001). Ozonation of activated sludge in the recycle stream. *Journal of Chemical Technology and Biotechnology*, 76, 321–324.
- Johnson, B.R., Daigger, G.T. & Novak, J.T. (2008). The use of ASM based models for the simulation of biological sludge reduction processes. *Water Practice and Technology*, 3, 3-11.
- Kamiya, T. & Hirotsuji, J. (1998). New combined system of biological process and intermittent ozonation for advanced wastewater treatment. *Water Science Technology*, 38, (8–9), 145–153.
- Kwon, J.H., Ryu, S.H., Park, K.-Y., Yeom, I.-T. & Ahn, K.-H. (2001). Enhancement of sludge dewaterability by ozone treatment. *Proc. Sludge Management Entering the 3rd Millennium*, Taipei, Taiwan, pp. 119- 124.
- Lee, J.W., Cha, H.Y, Park, K.Y., Song, K.G. & Ahn, K.H. (2005). Operational strategies for an activated sludge process in conjunction with ozone oxidation for zero excess sludge production during winter season. *Water Research*, 39, 1199–1204.
- Li, H., Jin, Y., Mahar, R., Wang, Z., & Nie, Y. (2008). Effects and model of alkaline waste activated sludge treatment. *Bioresour.Technology*, 99, 5140–5144.
- Liang, P., Huang, X., Qian, Y., Wei, Y. & Ding, G. (2006). Determination and comparison of sludge reduction rates caused by microfaunas' predation. *Bioresource Technology*, 97, 854–861
- Lin, S., Jin, Y., Fu, L., Quan, C. & Yang, Y.S. (2009). Microbial community variation and functions to excess sludge reduction in a novel gravel contact oxidation reactor. *Journal of Hazardous Materials*, 165,1083–1090
- Liu, Y. & Tay, J. H. (2001). Strategy for minimization of excess sludge production from the activated sludge process. *Biotechnology Advances*, 19, 97-107.

- Liu, Y. (2000) Effect of chemical uncoupler on the observed growth yield in batch culture of activated sludge. *Water Research*, 34, 2025-2030.
- Low, E.W. & Chase, H.A. (1998). The use of chemical uncouplers for reducing biomass production during biodegradation. *Water Science and Technology*, 37 (4-5), 1119-1132.
- Low, E.W. & Chase, H.A. (1999a). Reducing production of excess biomass during wastewater treatment. *Water Research*, 33 (5), 1119–1132.
- Low, E.W. & Chase, H.A. (1999b). The effect of maintenance energy requirements on biomass production during wastewater treatment. *Water Research*, 33 (3), 847-853
- Mahmood, T. & Elliott, A. (2006). A review of secondary sludge reduction technologies for the pulp and paper industry. *Water Research*, 40, 2093-2112.
- Manterola, G., Uriarte, J. & Sancho, L. (2008). The effect of operational parameters of the process of sludge ozonation on the solubilisation of organic and nitrogenous compounds. *Water Research*, 42, 3191-3197.
- Martinage, V. & Paul, E. (2000). Effect of environmental parameters on autotrophic decay rate. *Environmental Technology*, 21, 31-41.
- Mason, C.A., Hamer, G. & Bryers, J.D. (1986). The death and lysis of microorganisms in environmental processes. *FEMS Microbiology Reviews*, 39, 373–401.
- Mayhew, M. & Stephenson, T. (1998). Biomass yield reduction: is biochemical manipulation possible without affecting activated sludge process efficiency? *Water Science and Technology*, 38 (8-9), 137-144.
- Metcalf & Eddy (2004). *Wastewater Engineering: Treatment, Disposal, Reuse* McGraw Book Company, New York, USA.

- Muller, J.A., Lehne, G., Schwedes, J., Battenberg, S., Naveke, R., Kopp, J., Dicht, N., Scheminski, A., Krull, R. & Hempel, D.C. (1998). Disintegration of sewage sludges and influence on anaerobic digestion. *Water Science and Technology*, 38, (8–9), 425–433.
- Muller, J.A., Winter, A. & Strükmann, G. (2004). Investigation and assessment of sludge pre-treatment processes. *Water Science and Technology*, 49, (10) 97-104.
- Neis, U., Nickel, K. and Lunden, A. (2008). Improving anaerobic and aerobic degradation by ultrasonic disintegration. *Journal of Environmental Science and Health, Part A*, 43 (13), 1541-1545.
- Nickel, K., & Neis, U. (2007). Ultrasonic disintegration of biosolids for improved biodegradation. *Ultrasonics Sonochemistry*, 14, 450–455.
- Novak, J.T., Chon, D.H., Curtis, B. & Doyle, M. (2007). Biological solids reduction using the cannibal process. *Water Environment Research*, 79 (12), 2380-2386.
- Ødegaard, H. (2004). Sludge minimization technologies – An overview. *Water Science and Technology*, 49, (10), 31–40.
- Okey R.W. & Stensel D.H. (1993). Uncouplers and activated sludge-the impact on synthesis and respiration. *Toxicological and Environmental Chemistry*, 40, 235-254.
- Park, K.Y., Lee, J.W., Ahn, K.H., Maeng, S.K., Hwang, J.H. & Song, K.G. (2004). Ozone disintegration of excess biomass and application to nitrogen removal. *Water Environmental Resources*, 76, 162–167.
- Paul, E. & Debellefontaine, H. (2007). Reduction of excess sludge produced by biological treatment processes: effect of ozonation on biomass and on sludge. *Ozone Science. Engineering*, 29, 415–427.
- Paul, E., Camacho P., Sperandio, M. & Ginestet, P. (2006). Technical and economical evaluation of a thermal, and two oxidative techniques for the reduction

- of excess sludge production. *Process Safety and Environmental Protection*, 84(B4), 247–252
- Pe´rez-Elvira, S.I., Nieto Diez, P. & Fdz-Polanco, F. (2006). Sludge minimisation Technologies, Reviews in *Environmental Science and Bio/Technology*, 5, 375–398.
- Pham, T.T.H., Brar, S.K., Tyagi, R.D. & Surampalli, R.Y. (2009). Ultrasonication of wastewater sludge-Consequences on biodegradability and flowability. *Journal of Hazardous Materials*, 163, 891-898.
- Pirt, S.J. (1965). The maintenance energy of bacteria in growing cultures. *Proc. Roy. Soc. London, Ser. B.*, 163, 224-231.
- Rittman, B.E. & McCarty, P. L. (2001). *Environmental Tehnology:Principles and Applications*. Mc-Graw-Hill International Editions. ISBN: 0-07-118184-9, Singapore.
- Rocher, M., Roux, G., Goma, G., Pilas, Begue, A., Louvel, L. & Rols, J.L (2001). Excess sludge reduction in activated sludge processes by integrating biomass alkanline heat treatment. *Water Science and Technology*, 44 (2-3), 437-444.
- Saby, S., Djafer, M. & Chen, G. (2002). Feasibility of using a chlorination step to reduce excess sludge in activated sludge process. *Water Research*, 36, 656–666.
- Saby, S., Djafer, M. & Chen, G.H. (2003). Effect of low ORP in anoxic sludge zone an excess sludge production in oxic-settling-anoxic activated sludge process. *Water Research*, 37, 11-20.
- Sakai, Y., Aoyagi, T., Shiota, N., Akashi, A., and Hasegawa, S. (2000). Complete decomposition of biological waste sludge by thermophilic aerobic bacteria. *Water Science and Technology*, 42 (9), 81-88.

- Sakai, Y., Fukase, T., Yasui, H. & Shibata, M. (1997). An activated sludge process without excess sludge production. *Water Science and Technology*, 36 (11), 163–170.
- Saktaywin, W., Tsuno, H., Nagare, H., Soyama, T. & Weerapakkaron, J., (2005). Advanced sewage treatment process with excess sludge reduction and phosphorus recovery. *Water Research*, 39, 902–910.
- Salsabil, M.R., Prorot, A., Casellas, M. & Dagot, C. (2009). Pre-treatment of activated sludge: Effect of sonication on aerobic and anaerobic digestibility. *Chemical Engineering Journal*, 148, 327–335
- Scheminski, A., Krull, R. & Hempel D.C. (2000). Oxidative treatment of digested sewage sludge with ozone. *Water Science and Technology*, (42), 9, 151-158, IWA publishing.
- Shiota, N., Akashi, A. & Hasegawa, S. (2002). A strategy in wastewater treatment process for significant reduction of excess sludge production. *Water Science and Technology*, 45 (12), 127-134.
- Sievers, M., Ried, A. & Koll, R. (2004). Sludge treatment by ozonation - Evaluation of full-scale results. *Water Science and Technology*, 49, (4), 247–253.
- Song, K-G., Choung, Y-K., Ahn, K-H., Cho, J. & Yun, H. (2003). Performance of membrane bioreactor system with sludge ozonation process for minimization of excess sludge production. *Desalination*, 157, 353-359.
- Strand S.E., Harem G.N. & Stensel H.D. (1999). Activated-sludge yield reduction using chemical uncouplers. *Water Environmental Research*, 71, (4), 454-458.
- Sun, D. D., Khor, S.L., Hay, C. T. & Leckie, J. O. (2007). Impact of prolonged sludge retention time on the performance of a submerged membrane bioreactor. *Desalination*, 208, 101-112.

- Tamis, J., van Schouwenburg, G., Kleerebezem, R. & van Loosdrecht M.C.M. (2011). A full scale worm reactor for efficient sludge reduction by predation in a wastewater treatment plant. *Water Research*, XXX,1-9.
- Tchobanoglous, G., Burton, F.L., and Stensel, H.D. (2003). *Wastewater Engineering: Treatment and Reuse*. Inc. Metcalf & Eddy, McGraw-Hill, 4th edition.
- Tian, Y., Lu, Y., Chen, L. & Lin, H. (2010). Optimization of process conditions with attention to the sludge reduction and stable immobilization in a novel Tubificidae-reactor. *Bioresource Technology*, 101, 6069–6076.
- Tiehm, A., Nickel, K., Zellhorn, M., & Neis, U. (2001). Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. *Water Research*, 35 (8), 2003–2009.
- Turovskiy, I.S. & Mathai, P.K. (2006). *Wastewater sludge processing*. Wiley-Interscience. John Wiley & Sons, Inc., Hoboken, New Jersey.
- Xie, B., Liu, H. & Yan, Y. (2009). Improvement of the activity of anaerobic sludge by low-intensity ultrasound. *Journal of Environmental Management*, 90, 260-264.
- van Loosdrecht M.C.M and Henze, M. (1999). Maintenance, endogenous respiration, lysis, decay and predation. *Water Science and Technology*, 39 (1), 107-117.
- Vergine, P., Menin, G., Canziani, R., Ficara, E., Fabiyi M, Novak, R, Sandon, A., Bianchi, A. & Bergna, G. (2007). Partial ozonation of activated sludge to reduce excess sludge production: evaluation of effects on biomass activity in a full scale demonstration test. In: International Water Association Specialist Conference, Moncton, Canada.
- Wagner, J. & Rosenwinkel, K.H. (2000). Sludge production in membrane bioreactors under different conditions. *Water Science and Technology*, 41 (10-11), 251-258.

- Wang, J., Qingliang, Z., Jin, W. & Lin, J. (2008). Mechanism on minimization of excess sludge in oxic-settling-anaerobic (OSA) process. *Frontiers of Environmental Science and Engineering in China*, 2, (1):36-43.
- Wang, Q., Wang, Z., Wu, Z. & Han, X. (2011). Sludge reduction and process performance in a submerged membrane bioreactor with aquatic worms. *Chemical Engineering Journal*, 172, 929– 935.
- Weemaes, M., Grootaerd, H., Simoons, F. & Verstraete, W. (2000). Anaerobic digestion of ozonized biosolids. *Water Research*, 34, (8), 2330–2336.
- Wei, Y., Houten, R., Borger, A., Eikelboom, D. & Fan, Y. (2003). Minimization of excess sludge production for biological wastewater treatment. *Water Research*, 37, 4453–4467.
- Wei, Y. & Liu, J. (2006). Sludge reduction with a novel combined worm-reactor. *Hydrobiologia*, 564, 213–222.
- Westgarth, W.C., Sulzer, F.T. & Okun, D.A. (1964). Anaerobiosis in the activated sludge process. *Proceedings of the Second IAWPRC Conference*. Tokyo, pp. 43-55.
- Wilen, B.-M., Lumley, D., Mattsson, A. and Mino, T. (2008). Relationship between floc composition and flocculation and settling studied at a full scale activated sludge plant. *Water Research*, 42, 4404-4418.
- Wolff, S. & Hurren, D. (2006). Reduction of excess sludge by up to 80 % with ozone injection-practical experience. In: 11th European Biosolids and Organic Resources Conference, Wakefield, UK.
- Yamamoto, K., Hilasa, M., Mahmood, T. & Matsuo, T. (2001). Direct solid-liquid separation using hollow fibre membrane in an activated sludge aeration tank. *Water Science and Technology*, 21, 43-54.

- Yan, S.Y., Chu, L.B., Xing, X.H., Yu, A.F., Sun, X.L. & Jurcik, B. (2009a). Analysis of the mechanism of sludge ozonation by a combination of biological and chemical approaches. *Water Research*, 43,195-203.
- Yan, S.-T., Zheng, H, Li, A., Zhang, X., Xing, X.-H., Chu, L.B., & Ding, G. (2009b). Systematic analysis of biochemical performance and the microbial community of an activated sludge process using ozone-treated sludge for sludge reduction. *Bioreource Technology*,100, 5002-5009.
- Yang X.-F., Xie M.-L. & Liu Y. (2003). Metabolic uncouplers reduce excess sludge production in an activated sludge process. *Process Biochemistry*, 38, 1373-1377.
- Yasui, H. & Shibata, M., (1994). An innovative approach to reduce excess sludge production in the activated sludge process. *Water Scienceand Technology*, 30 (9), 11–20.
- Yasui, H., Nakamura, K., Sakuma, S., Iwasaki, M. & Sakai, Y. (1996). A full-scale operation of a novel activated sludge process without excess sludge production, *Water Scienceand Technology*, 34, 395–404.
- Ye, F. and Li, Y. (2010). Oxidic-settling-anoxic (OSA) process combined with 3,3',4,5-tetrachlorosalicylanilide (TCS) to reduce excess sludge production in the activated sludge system, *Biochemical Engineering Journal*, 49, 229–234.
- Yoon, S.-H., Kim, H.-S. & Lee, S. (2004). Incorporation of ultrasonic cell disintegration into a membrane bioreactor for zero-sludge production. *Process Biochemistry*, 39, 1923-1929.
- Zhang, G., Yang, J., Liu, H. & Zhang, J. (2009). Sludge ozonation: Disintegration, supernatant changes and mechanisms. *Bioresource Technology*, 100, 1505-1509.
- Zhang, G., Zhang, P., Yang, J. & Chen Y. (2007). Ultrasonic reduction of excess sludge from the activated sludge system. *Journal of Hazardous Materials*, 145, 515-519.

Zhao, Y.X., Yin, J., Yu, H.L., Han, N. & Tian, F.J. (2007). Observations on ozone treatment of excess sludge. *Water Science and Technology*, 56 (9), 167–175

Zhu, H. & Chen, J. (2005). Study of hydrolysis and acidification process to minimize excess biomass production. *Journal of Hazardous Materials*, B127, 221-227.