THE EFFECT OF DISINTEGRATION BY CLASSICAL AND ADVANCED FENTON PROCESSES ON MINIMIZATION AND CHARACTERISTICS OF THE WASTEWATER SLUDGES

by

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ABSTRACT

Wastewater treatment facilities using biological treatment processes produce large quantity of sludge that must be disposed of safely. In recent years researches focused on sludge minimization, during wastewater treatment by using different methods to improve biodegradability of the sludge before biological stabilization.

In this research the role of Advanced Fenton Process (AFP) as a sludge pretreatment method was investigated. In order to demonstrate the efficiency of the Advanced Process, in some experiments Classic Fenton Process was also applied to sludge samples. Batch experiments under different operational conditions were conducted to evaluate the efficiency of Advanced Fenton Process on sludge disintegration. For this purpose, zero valent iron (Fe^0) and hydrogen peroxide (H_2O_2) were used as Fenton reagents. The influence of Advanced Fenton Process on sludge disintegration was analyzed by measuring the increase in soluble chemical oxygen demand (sCOD) and degree of disintegration. Dewatering characteristics of the untreated and pretreated sludge samples were determined by measuring capillary suction time and compactibility in terms of cake solids concentration. Rheological behavior of the sludge samples was analyzed by viscosity measurements.

The results obtained demonstrated that after 1 hour of reaction time, soluble chemical oxygen content of the sludge increased as a result of the disintegration process. The reaction time analysis showed that increase in the reaction time led to an increase in the sCOD concentration and MLSS concentration decreased due to cell disruption. Capillary Suction Time measurements demonstrated that AFP improved sludge dewaterability. Particle size of sludge flocs increased due to coagulant effect of Fenton treatment. Compactibility, in terms of cake solids concentration, also enhanced after Advanced Fenton treatment. On the other hand AFP deteriorated settleability of the sludge samples. Advanced Fenton pretreatment caused to a low increase in viscosity of the sludge samples.

ÖZET

Biyolojik arıtım kullanan atıksu arıtma tesisleri güvenli bir şekilde bertaraf edilmesi gereken yüksek miktarda çamur üretmektedir. Son yıllarda çalışmalar değişik teknikler kullanılarak çamur üretimini azaltmaya ve biyolojik stabilizasyon öncesinde biyolojik parçalanabilirliğini arttırmaya yoğunlaşmıştır.

Bu çalışmada çamur ön arıtım tekniği olarak İleri Fenton Proses yönteminin rolü değerlendirilmiştir. İleri Fenton Oksidasyonunun verimini göstermek amacıyla bazı deneylerde çamur örneklerine Klasik Fenton Prosesi de uygulanmıştır. Değişik deneysel şartlar altında kesikli reaktör prensibiyle İleri Fenton Prosesinin çamur dezentegrasyonuna olan etkisi incelenmiştir. Bu amaçla Fenton reaktifi olarak sıfır değerlikli elementer demir tozu ve hidrojen peroksit kullanılmıştır. İleri Fenton Oksidasyonun çamur dezentegrasyonuna ola etkisi çözünmüş kimyasal oksijen (KOİ) değerindeki artış ve dezentegrasyon derecesi ölçülerek analiz edilmiştir. Ön arıtım uygulanmış ve ham çamurun susuzlaştırma özellikleri kapiler emme süresi ve kompakt edilebilirlik parametrelerinin ölçülmesiyle belirlenmiştir. Çamurun reolojik özellikleri viskozite ölçümüyle analiz edilmiştir.

Elde edilen sonuçlar 1 saatlik reaksiyondan sonra dezentegrasyon prosesinin bir sonucu olarak çözünmüş kimyasal oksijen değerinde artış olduğuna işaret etmiştir. Reaksiyon süresi analizi reaksyon süresindeki artış çözünmüş KOİ değerinin arttırmış, ve aynı anda askıda katı madde (AKM) oranı hücrelerin parçalanması nedeniyle azalmıştır.

Kapiler emme süresi analizi İleri Fenton Prosesinin çamurun susuzlaştırma özelliğini iyileştirdiğini ortaya koymuştur. İleri Fenton oksidasyonundan sonra ön arıtım uygulanmamış çamura gore daha düşük kapiler emme süresi gözlemlenmiştir. Çamur floklarının partikül boyutu Fenton oksidasyounun koagülant etkisi nedeniyle artmıştır. Kompakt edilebilirlik, kek katı konsantrasyonu açısından, İleri Fenton arıtımından sonra artış göstermiştir. İleri Fenton oksidasyonu partikül boyutundaki artışa bağlı olarak çamurun çökelebilirliğini zayıflatmıştır. İleri Fenton Porsesi, çamur örneklerinin viskozite değerlerinde bir miktar artışa neden olmuştur

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LIST OF SYMBOLS/ABBREVIATIONS

Symbols	**Explanation**	**Unit used**
AFP	Advanced Fenton Process	
AOP	Advanced Oxidation Processes	
CFP	Classic Fenton Process	
COD	Chemical Oxygen Demand	mg/L
CST	Capillary Suction Time	s
DD_{COD}	Degree of Disintegration	%
MLSS	Mixed Liquor Suspended Solids	mg/L
MLVSS	Mixed Liquor Volatile Suspended Solids	mg/L
ORP	Oxidation Reduction Potential	mV
sCOD	Soluble Chemichal Oxygen Demand	mg/L
SVI	Sludge Volume Index	ml/g
TCOD	Total Chemical Oxygen Demand	mg/L
TS	Total Solids	mg/L
ZVI	Zero Valent Iron	

1. INTRODUCTION

Wastewater sludges are produced as a result of biological practices and they must be disposed of safely. Increasing human population leads to a gradual increase in the production of wastewater treatment sludges urging the application of sludge minimization methods in the wastewater treatment plants

In recent years researches have been focused on the minimization of excess sludge using mechanical, biological and chemical methods. 'Sludge Disintegration' is the general term used to indicate all of these methods. Sludge Disintegration can be defined simply as the destruction of cell wall of the microorganisms. When cell wall is destroyed, intracellular materials, such as proteins and carbohydrates, are released into the bulk solution of the sludge. This method can be implemented in different part in wastewater treatment facility. As an innovative approach, an activated sludge system coupled with disintegration in biomass recycle system has been developed to achieve zero discharge of excess sludge (Tokumura et al., 2007). Beside this concept, disintegration methods can also be used prior to digestion process. Release of intracellular materials increases soluble biodegradable part of the WAS. Hence, the amount of methane, produced after anaerobic digestion, increased and it can be used to supply electrical energy of the treatment plant. Disintegration process also affects dewaterability and settleability characteristics of the excess sludge. Previous studies proved that the influence of disintegration on these characteristics varies according to technique used.

Advanced Fenton Process (AFP) is a novel approach that can be used in sludge pretreatment. This method is generally used to remove dye particles from wastewaters (Fu et al., 2009, Shu et al., 2009). Classic Fenton Process consists of the reaction of ferrous iron (Fe^{2+}) and hydrogen peroxide (H_2O_2) to produce highly oxidant hydroxyl radicals. As an innovative approach in Advanced Fenton Process zero valent iron (Fe^0) is used with hydrogen peroxide to provide Fenton oxidation. The main advantage is that zero valent iron causes faster recycling of iron species during Fenton Process, thus more hydroxyl radicals are produced. Generally Fenton Process has been used to treat wastewaters with high organic pollutant content. Only a few researches have focused on the influence of Classic Fenton Process on excess wastewater sludge treatment.

This study investigates the effect of Advanced Fenton Process, as a novel technique, on excess sludge treatment. In order to demonstrate the efficiency of the Advanced Process, in some experiments Classic Fenton Process was also applied to sludge samples. Sludge samples were obtained from a wastewater treatment facility of an oil refinery. In order to analyze the efficiency of AFP on disintegration different iron and hydrogen peroxide concentrations were used. The influence of AFP on the increase in the soluble organic fraction of the sludge was evaluated by the degree of disintegration. Various operational parameters, such as pH, mixing rate, MLSS concentration, were investigated to find out the performance of AFP on sludge disintegration. Dewaterability properties of untreated and pretreated sludge samples were examined in terms of filterability and compactibility analyses. In order to observe particle size distribution after Advanced Fenton oxidation particle size analyses were conducted. Settleability was determined by measuring sludge volume index. Viscosity of the untreated and pretreated sludge was measured to observe the change in the rheology of the sludge samples.

2. THEORETICAL BACKGORUND

2.1. Disintegration of Wastewater Sludges

2.1.1. Definition and General Characteristics

Conventional municipal sewage treatment plants use mechanical and biological processes for the wastewater treatment. The activated sludge process is the most widely used for biological wastewater treatment, but it results in the generation of a considerable amount of excess sludge that has to be disposed of (Perez-Elvira et al., 2006). Perez-Elvira et al., 2006, pointed out that this sludge consisted of high fractions of volatile solids (VS) and large amounts of water (> 95% by weight), leading to the large volumes of residual solids produced, and significant disposal costs. For the year 2010 it is estimated that sludge production will exceed 10 million tons (dry weight) (Perez-Elvira et al., 2006).

In recent years studies have focused on the minimization of excess sludge. The most widely used minimization technique is the sludge disintegration. ‘Sludge Disintegration’ can be defined as the destruction of sludge by external forces resulting in numerous changes in the sludge properties including destruction of floc structures and disruption of the cell walls of the microorganisms present in the wastewater sludge (Müller, 2003b). This process causes to the release of intracellular material increasing the biodegradable part of the bulk sludge.

The figure below explains the basics of this mechanism.

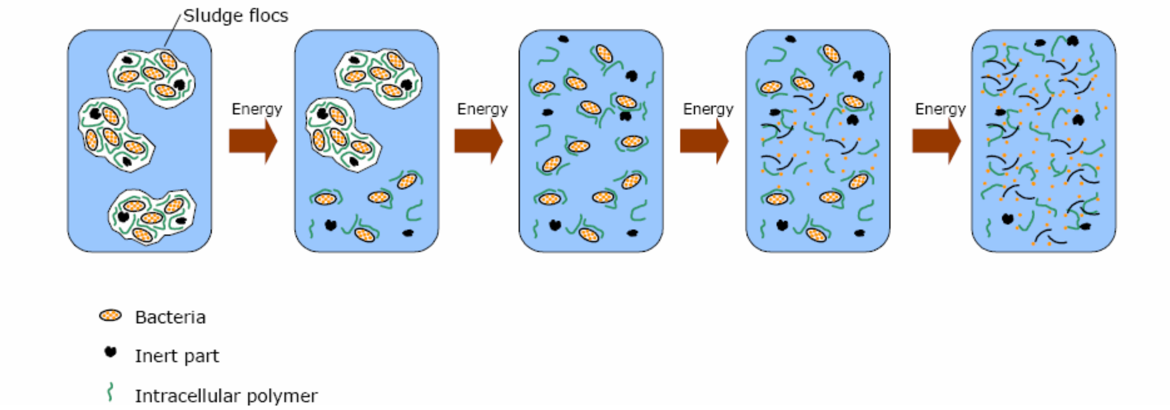


Figure 2.1. Effect of increased energy input on disintegration of sludge (Luning et al., 2008)

Within a wastewater treatment plant sludge disintegration can be implemented at a number of locations. In some cases it was applied prior to digestion to increase the soluble fraction of the organic materials and to produce more methane as energy source. On the other hand it can also be implemented in recycle line and it can be sent to aeration tank for microorganisms to decompose released materials from disrupted cells.

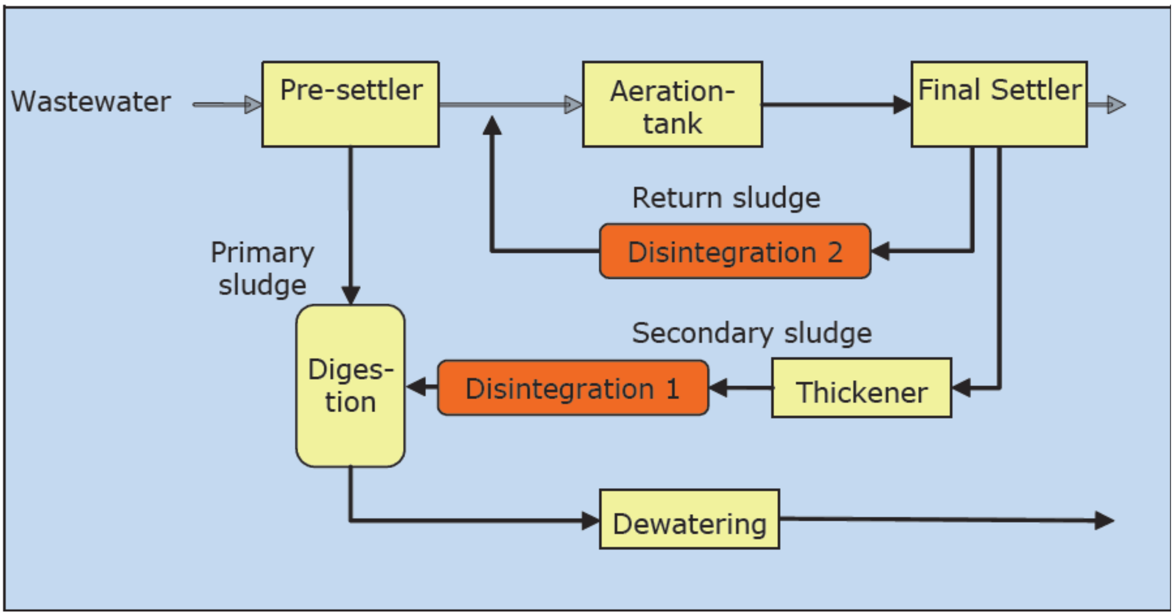


Figure 2.2. Possible implementation of the sludge disintegration method (Kopp et al., 1997, Luning et al., 2008)

In the next section different sludge disintegration methods are investigated and the results of the related studies are examined

2.1.2. Sludge Disintegration Methods

Sludge disintegration methods can be classified into four categories:

a) Mechanical Sludge Disintegration
b) Chemical Sludge Disintegration
c) Thermal Sludge Disintegration
d) Biological Sludge Disintegration

2.1.2.1. Mechanical Sludge Disintegration. Mechanical disintegration is a well-established process to obtain intracellular products such as proteins or enzymes from biotechnological applications. Applying mechanical shear and pressure forces into a sewage sludge will result in disintegration of the sludge structure. Sludge flocs as well as cell membranes of the microorganisms can be destroyed by mechanical disruption (Müller, 2003a). Some of the mechanical disintegration methods are explained below.

Stirred Ball Mill.

Winter (2002) investigated stirred ball mill for sludge disintegration. Stirred ball mills consist of a cylindrical grinding chamber which is almost completely filled with grinding beads. A rotor forces the beads into a rotational movement. The microorganisms are disintegrated between the beads by shear and pressure forces. Bead diameter is one of the major parameters for stirred ball mill. With decreasing bead diameter less energy is needed to reach certain degree of disintegration (Lehne et al., 2001). Winter (2002) used two types of stirred ball mills. Stirred ball mill with a relatively low energy input caused a disintegration degree of 25%. On the other hand stirred ball mil with high energy input caused high disintegration degree (60%). The author also noted that using grinding beads with smaller diameters improved efficiency. An average increase of 21% in specific biogas production was achieved from the 6th week of the study due to disintegration. Due to decrease in sludge particle size dewaterability of the sludge was deteriorated. Both specific resistance to filtration (SRF) and capillary suction time (CST) increased compared to untreated sludge. The author also noticed that polymer demand increased slightly due to disintegration.

High Pressure Homogenizer

The high-pressure homogenizer was originally constructed for homogenizing milk products but the robust nature of this homogenizer has enabled its diversified laboratory and industrial applications. The pressure of homogenization is the most influential parameter for the disintegration performance of the high-pressure homogenizer. As the sludge flows through the homogenizing valve, rapid velocity increase and pressure decrease cause turbulence, cavitation and liquid stress to the cells. Collision of these cavitation bubbles creates an energetic shear stress to disrupt the sludge cells (Onyeche and Schafer, 2003).

Rai and Rao (2009) used high pressure homogenizer for sludge disintegration. The authors stated that as the applied energy increased particle size decreased. At high energy input from 14252 to 17815 kJ/kg a significant decrease in the particle size was observed. Rai and Rao (2009) found that soluble COD increased steadily as the input increases. At the lower energy input of 3563 kJ/kg 8% increase in the sCOD was obtained. In energy range from 7126 to 17815 kJ/kg, 18–29% increase in the COD was observed. It was shown that sludge inactivation efficiency increased from 53 to 84-98% for the specific energy from 10689 to 17815 kJ/kg. It was also observed that increase in degree of inactivation led to an increase in the growth reduction. At 45% inactivation a growth reduction to an extent of 92% was achieved. Rai and Rao (2009) showed that there was a mass reduction with increased specific energy due to disruption of the cells.

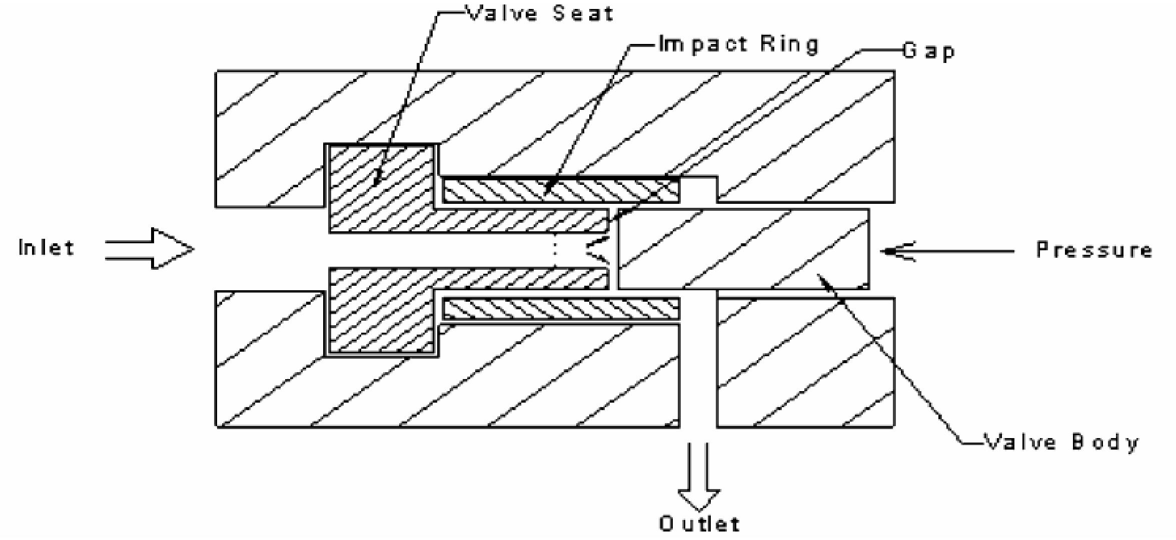


Figure 2.3. Schematic view of high pressure homogenizer (Rai and Rao, 2009)

Ultrasound

Ultrasound is the most widely used method for sludge disintegration. Many researchers have focused on the effect of ultrasound on sludge structure (Neis and Nickel. 2007, Zhang et al., 2009, Pham et al., 2010). The impact of ultrasound waves on a liquid causes the periodical compression and rarefaction of the medium. Cavitation occurs above a certain intensity threshold, when gas bubbles are created, they first grow in size before violently collapsing within a few microseconds. The temperature and pressure inside the collapsing cavitation bubbles rise up to about 5000K and several hundred atmospheres (Tiehm et al., 2000). This mechanism leads to the disruption of the cell walls in sludge.

Bougrier et al. (2005) examined the disintegration of excess sludge by ultrasound. According to their result, specific energy over 1000 kJ/kg TS solubilization and degree of disintegration significantly increased. Percent increase in the sCOD was reached to 35% at an energy input of 15000 kJ/kg TS. For specific energy input under 1000 kJ/kg TS, change in the sCOD and DD_{COD} was low, 8% and 14% respectively. The author found that for supplied energies of 7000 and 15000 kJ/kg TS, biogas production was almost the same. Biogas volume was 1.4 times higher than that for untreated sludge. It was also shown that as specific energy increased particle size decreased. For untreated sludge d_{50} particle size was 31,99 µm and it decreased to 12.7 µm for specific energy of 14550 kJ/kg TS.

Dewil et al. (2006) investigated effect of ultrasound on dewatering characteristics of the sludge. They stated that ultrasound caused poorer dewaterability. CST value of the untreated sludge was below 15 s while CST of the ultrasonicated sludge was above 30 s at 20 kHz. The main reason was the decrease in floc size caused by ultrasound.

Lysate Centrifuge

The centrifugal forces created in this thickening centrifuge are deliberately applied to cell destruction. This disruption takes place using a special beater (ring) which is integrated into the centrifugal thickener and which dissipates the kinetic energy provided by the centrifuge. Cell destruction takes place in the centrifuge effluent following thickening, thus the effluent is not loaded any higher as compared to normal centrifugation (Perez-Elvira et al., 2006). Müller et al. (2004) observed different mechanical disintegration techniques including lysate centrifuge for a full-scale application. They found that when lysate centrifuge was used % increase in COD, ammonia and polymer demand was below %10. Similarly % degree of disintegration and % increase in DD_{COD} were below % 15. The authors concluded that lysate centrifuge showed little increase of the degree of degradation, but therefore has a lower energy demand compared to other mechanical systems.

2.1.2.2 Chemical Sludge Disintegration

Ozone Treatment

Ozone is a strong chemical oxidant widely used in water and sludge treatment processes. Ozone attacks on sludge particles and causes to the destruction of cell wall of the microorganisms by leading to the reduction in MLSS concentration and to an increase in the sCOD content (Saktaywin et al., 2005). Dytczak et al. (2007) analyzed the effect of ozone on sludge reduction. They found that for a moderate dose of ozone (0.05 mg O_3/mg TSS) the average decrease in excess sludge in alternating reactor was 14.7%. It was shown that for the same dose of ozone the increase in sCOD was 125% and 200% for the aerobic and alternating reactors respectively. The authors indicated that ozonation of 20% of the RAS reduced the amount of excess solids in the reactors receiving ozonated sludge sample. It was demonstrated that sCOD, released after ozonation, provided good carbon source for denitrification process. Chu et al. (2009) stated that recommended ozone dose ranges from 0.03 to 0.05 g O_3/g TSS.

Alkali Treatment

Alkali treatment is a harsh disintegration method (Erdincler and Vesilind, 2000). During the alkaline pre-treatment, the pH of the sludge increased up to 12 (Perez-Elvira et al., 2006). As a result of that process cell wall of the microorganisms are disrupted and intracellular materials are released. This method can also be used to hydrolyze and decompose lipids, hydrocarbons and proteins into smaller soluble substances such as aliphatic acids, polysaccharides and amino acids (Chiu and Chang 1997).

Dogan and Sanin (2009) used alkaline solubilization combined with microwave irradiation. The authors observed that for sludges pretreated at pH 12.5, sCOD concentration increased from 50 mg/L to 3300 mg/L. When it was combined with microwave irradiation, sCOD concentration increased to approximately 4000 mg/L. It was also observed that with increasing pH values sCOD value significantly increased. The authors analyzed oxygen uptake rate of the sludge samples. At high pH, considerable decrease in oxygen uptake rate was observed. It means that because of high pH, mass reduction occurred. Similarly to sCOD values, Dogan and Sanin (2009) found that as pH increased concentration of protein and carbohydrate increased due to cell disruption. Therefore when it was combined with microwave irradiation important increase in proteins was seen. For biogas production in terms of methane yield, at the end of 53rd days the control reactor achieved 143.5 L CH_4 /kgVS and pretreated reactor achieved 219.8 L CH_4 /kgVS corresponding to a 53.2% improvement in biogas production.

Hydrogen Peroxide Oxidation

Hydrogen peroxide (H_2O_2), as one of the oxidation process like ozone, was used for excess sludge disintegration. Kim et al. (2009) studied the effect of hydrogen peroxide for sludge minimization. Kim et al. (2009) used different H_2O_2 concentrations in molar basis. They combined hydrogen peroxide treatment with alkaline solubilization and they found that at pH 11 and 1.6 M H_2O_2 the concentration of total solids decreased from 14850 mg/l to 7410 mg/L after 2 hours of reaction (49% removal). Moreover, when the same concentrations were used, the sCOD/TCOD of sludge increased from 28.3% to 60.8%, indicating high amount of release in the intracellular materials. The authors also observed effect of hydrogen peroxide on particle size and they stated that hydrogen peroxide decreased median size of the sludge particles from 34.5 μm to 13.5 μm (decrease of 61%). Kim et al. (2009) showed that settleability was enhanced after hydrogen peroxide treatment. SVI of the untreated sludge decreased from 67.2 mL/g to 62.9 mL/g (7% improvement was obtained).

Fenton Process is examined in detailed form in Sections 2.3 and 2.4.

2.1.2.3. Thermal Treatment. Thermal pre-treatment in the low temperature ranging from 60 to 180 °C destroys the cell walls and release organic materials for biological degradation. The input of thermal energy is applied by using heat exchangers or by application of steam to the sludge (Neyens and Baeyens, 2003).

Bougrier et al. (2006) investigated the effect of thermal treatment for sludge solubilization with different methods. The authors used 170°C and 190°C for sludge treatment. According to their results, both temperatures caused an increase higher than 50 % in the sCOD concentration. It was observed that viscosity of untreated sludge decreased after thermal treatment from 0.034 Pa.s to 0.003 Pa.s. Bougrier et al. (2006) stated that thermal treatment caused to an increase in the particle size of the sludge flocs. Median diameter of untreated sludge particles was 36.1 μm and it increased to 77.1 μm after thermal pretreatment at 190 °C. In terms of methane production after anaerobic digestion, thermal process was the most effective method compared to ultrasound and ozone. They noticed that methane production of untreated sludge at the end of 24 days was 221 L CH_4 /g COD while that of thermal treatment was 328 L CH_4 /g COD for 190 °C.

2.1.2.4. Biological Sludge Disintegration. Biological sludge disintegration process is based on the addition of enzymes in the system. The enzymatic lysis cracks the compounds of the cell wall by an enzyme catalyzed reaction (Perez-Elvira et al., 2006). Barjenbuch and Kopplow (2003) added externally carbohydrase enzyme for VS and foaming reduction. The authors stated that enzyme treatment did not show any positive effect on foaming problem. It was found that there was an improvement of 15% and 3% for DD_{COD} and gas production respectively. It was also indicated that enzyme treatment decreased CST value and improved sludge dewaterability.

In another study by Hasegawa et al. (2000) a thermophilic producing extracellular enzyme was added to system. The authors observed 40% increase in the soluble organic fraction of the sludge after treatment for 1–2 days and the amount of gas generated was increased by 1.5 compared to that of the untreated sludge.

2.2 Effects of Sludge Disintegration on Dewaterability

The dewatering process of the sewage sludge is an important part of the wastewater treatment. Dewatering greatly reduces the volume of sludge requiring handling and disposal and is a necessary process for disposal options. (Houghton et al., 2000). In literature many researchers, investigating the effect of disintegration on the increase in the sCOD content of the sludge, examined effect of disintegration on dewaterabilty of secondary sludge as well (Feng et al., 2009, Huan et al., 2009, Dewil et al., 2006, Bougrier et al., 2006). Results found in these studies showed discrepancies according to method used. Disintegration process changes water distribution and EPS properties in sludge. These parameters are essential factors to determine sludge dewaterability.

2.2.1. Sludge Water Distribution

Commonly, water in sludge is divided into two categories: free (bulk) and bound (non-free) water. However, the “bound water” term does not have a uniform meaning, and its operational definition depends upon the measurement method of the bound water (Erdincler and Vesilind, 2000).

Biological sludge contains various fractions of water;

-Free water: water that is not associated with and not influenced by the suspended solid particles.

-Interstitial water: water that is trapped in the crevices and interstitial spaces of the flocs and microorganisms.

-Vicinal water: water that is associated with the multiple layers of water molecules held tightly to the particle surface. This water can be within cells as well, as long as it is associated with a solid surface.
-Water of hydration: water that is chemically bound to the particles and can only be removed by thermal destruction of the particles (Erdincler and Vesilind, 2000).

Disintegration process helps to release of interstitial and vicinal water. Bougrier et al. (2006) analyzed the effect of different disintegration methods on dewaterabillity of sludge. The authors demonstrated that ultrasound and ozone deteriorated dewaterability whereas thermal treatment enhanced in terms of filterability. According Bougrier et al. (2006) the principal reason was that ozone and ultrasound decreased particle size but it was increased by thermal treatment. Contrary to Bougrier et al. (2006), Na et al. (2007) showed that ultrasound enhanced dewaterability of the sludge in terms of filterability.

Erdincler and Vesilind (2003) investigated effect of cell disruption on dewaterability in terms of compactibility. The authors found that the improvement in the compactibility in terms of the increase in the cake solids content of sonicated and heat-treated sludges were 653% and 127%, respectively. Erdincler and Vesilind (2003) related this improvement to the hydrolysis of extracellular and intracellular materials destructing the colloidal properties of these macromolecules. The author observed no strong relationship between CST values and unfreezable water content of the biological sludge.

2.2.2. Effect of EPS

Extracellular polymeric substances are organic polymers, being produced by bacterial cell wall, surrounding the cell wall as a hydrated capsule (Flemming and Wingender 2001). Extracellular polymeric substances have a very heterogeneous chemical composition mainly containing protein, carbohaydrate, lipids, humic acids and nucleic acids (Cetin and Erdincler 2004).

Chen et al. (2000) investigated pretreatment of sludge with sulfuric acid and surfactant. The authors observed that the centrifugal dewatering efficiency was increased with the decrease in the sludge pH value, and which was further improved if the surfactant was simultaneously applied. The authors stated that when sludge was conditioned with the surfactant at pH 2.5 and then filtered, a 73.99% of water content was obtained. Chen et al. (2001) noticed that sludge sedimentation was accelerated at pH 2.0 with the addition of surfactant. They concluded that the reason of the enhancement in dewaterability and settleability was the reduction in the EPS concentration.

Feng et al. (2009) investigated the effect of EPS on sludge dewatering characteristics. They showed that at an energy input of 35000 kJ/kg TS the increase in the levels of proteins and polysaccharides was 394% and 413% respectively. This was probably because these two substances are released simultaneously upon cellular disruption (Feng et al., 2009). The authors found that at approximately 400-500 mg/l of EPS concentration both CST and SRF values decreased, indicating an improvement in the dewatering property of the sludge samples. Similarly Sanin and Vesilind (1994) noticed that above relatively low levels could improve the extent of sludge flocculation. Above this concentration poorer results are obtained and an increase in the both CST and SRF values was observed (Feng et al., 2009).

2.3. Fenton Process

Advanced Oxidation Processes (AOPs) are defined as the oxidation processes that generate hydroxyl radicals in sufficient quantity to effect wastewater treatment. Most of the AOPs use a combination of strong oxidants like ozone, oxygen or hydrogen peroxide with catalysts like transition metals, irons, semiconductor powders, radiation or ultrasound. Typical AOPs includes O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV, H_2O_2/Fe(II), TiO_2/UV, and TiO_2/H_2O_2/UV (Zhang et al.,2005).

In the Fenton process, hydrogen peroxide is added to wastewater in presence of ferrous salt to generating species that are strongly oxidative with respect to organic compounds present (Deng and Englehardt, 2006). The ferrous iron (Fe^{+2}) reacts and catalyses the decomposition of H_2O_2, leading to the generation of hydroxyl radicals (Neyens and Baeyens, 2003). These hydroxyl radicals are strong chemical oxidants being responsible to oxidize wide variety of pollutant found in wastewater.

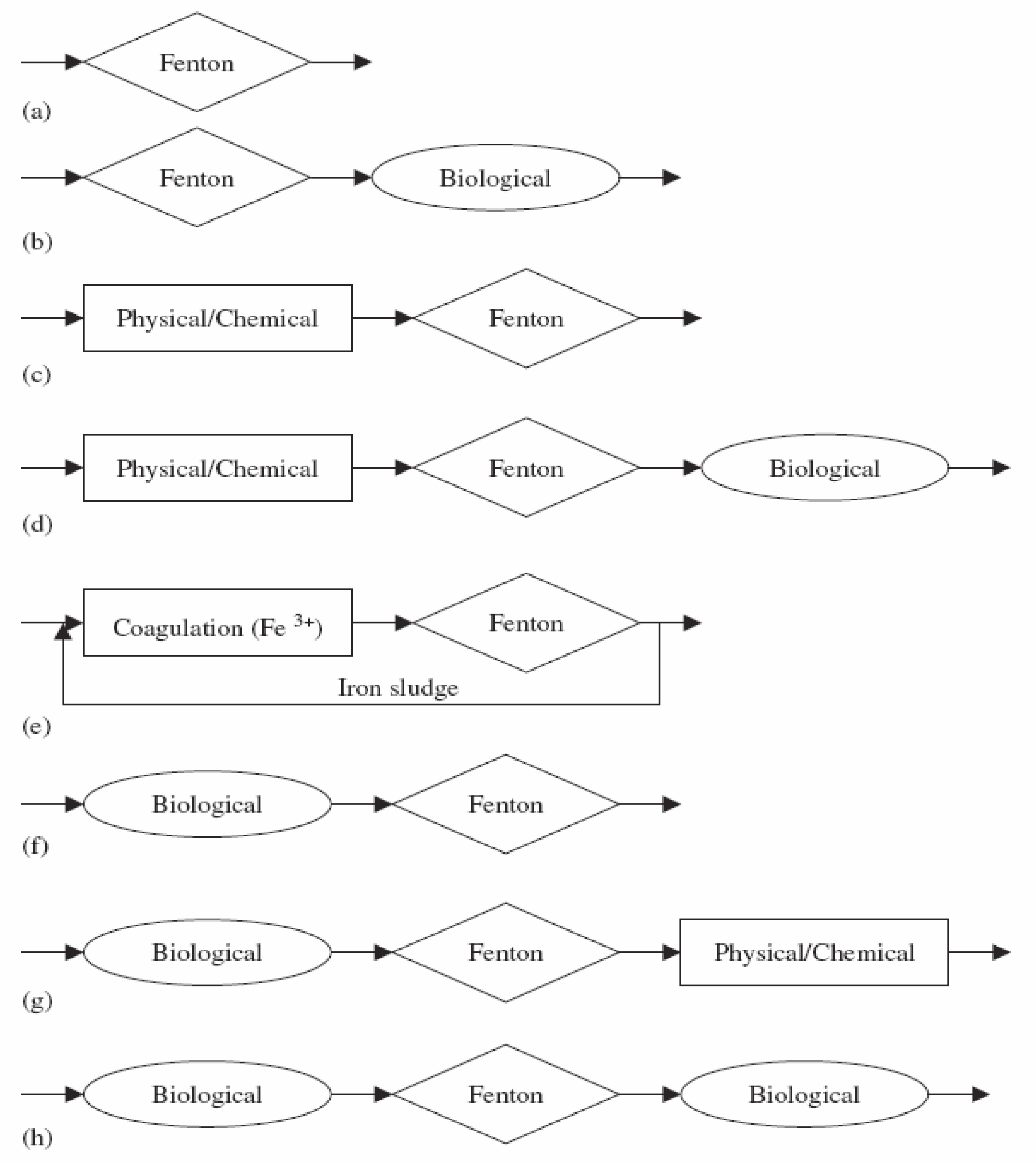


Figure 2.4. Possible Fenton applications in wastewater treatment (Deng and Englehardt, 2009)

2.3.1. Mechanisms of Fenton Process.

The Classical Fenton mechanism, in the absence of organic compounds mainly contains the reactions below (Deng and Englehardt, 2006);

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^{-} \tag{2.1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^{+} \tag{2.2}$$

$$\cdot OH + H_2O_2 \rightarrow HO_2 + H_2O \tag{2.3}$$

$$\cdot OH + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \tag{2.4}$$

$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + O_2H^{+} \tag{2.5}$$

$$Fe^{2+} + HO_2 + H^{+} \rightarrow Fe^{3+} + H_2O_2 \tag{2.6}$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \tag{2.7}$$

Deng and Englehardt (2006) reported that hydroxyl radicals were rapidly generated through Eq. (2.1). In the above reactions, iron cycles between Fe^{2+} and Fe^{3+}, and plays the role of catalyst. The reaction of HO· with organic compounds leads to the formation of carbon-centered radicals. The hydroxyl radical reacts with organic compounds, principally by abstracting H from C–H, N–H, or O–H bonds, adding to C=C bonds, or adding to aromatic rings (Pignatello et al., 2006).

$$O\cdot + R{-}H \rightarrow H_2O + R^{\bullet} \tag{2.8}$$

$$HO\cdot + C{=}C \rightarrow HO{-}C{-}C^{\bullet} \tag{2.9}$$

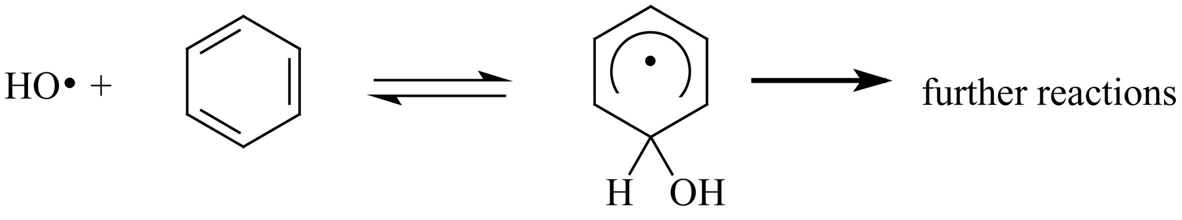


Figure 2.5. Mechanism of OH radicals with organic compounds (Pignatello et al., 2006)

Two energetically enhanced Fenton processes are applied for the treatment of the wastewaters. First, the photo-Fenton process, using ultraviolet (UV) radiation, can enhance reduction of dissolved Fe^{3+} complexes to Fe^{2+}, and generate additional OH radical via photolysis. Tokumura et al. (2007) explained basic mechanism of photo-Fenton process;

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^{-} \qquad (2.10)$$

$$Fe(OH)^{2} + hv \rightarrow Fe^{2+} + \cdot OH \qquad (2.11)$$

The reaction (2.11) is followed by reaction (2.10) and iron cycle between Fe^{2+} and Fe^{3+} occurs by the light irradiation. In other words, Fe^{3+} ions are constantly reduced to Fe^{2+} ions under irradiation and the Fenton reaction is improved by the participation of photogenerated Fe^{+2}. Hydroxyl radicals generated in reactions (2.10) and (2.11) react with target organic pollutants (Tokumura et al., 2007).

Second, the electro-Fenton process, in which either or both of H_2O_2 and Fe^{2+} can be generated electrochemically, is an indirect electrochemical oxidation that employs OH radical generated by the Fenton reaction to oxidize organic compounds (Deng and Englehardt, 2006). Oturan (1999) stated that it was sufficient to apply a low cathodic potential to the working carbon electrode to start the production of radicals. At this potential, dissolved dioxygen is reduced to superoxide ion ($O^{-2\bullet}$) which reacts quickly with H^{+} in protic medium to produce peroxyl radical HO_2. This radical is unstable and leads through disproportionation to the formation of hydrogen peroxide (Oturan, 1999).

$$O_2 + 2H^{+} + 2e^{-} \leftrightarrow H_2O_2 \qquad (2.12)$$

Oturan (1999) also pointed out that at the applied potential which reduced O_2, a second cathodic reaction took place simultaneously; the reduction of ferric ion to ferrous ion.

$$Fe^{3+} + e^{-} \leftrightarrow Fe^{2+} \qquad (2.13)$$

The Fenton's reagent, which is electrochemically generated, leads to the OH radical production by the following reaction in solution (Oturan, 1999).

$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O$ (2.14)

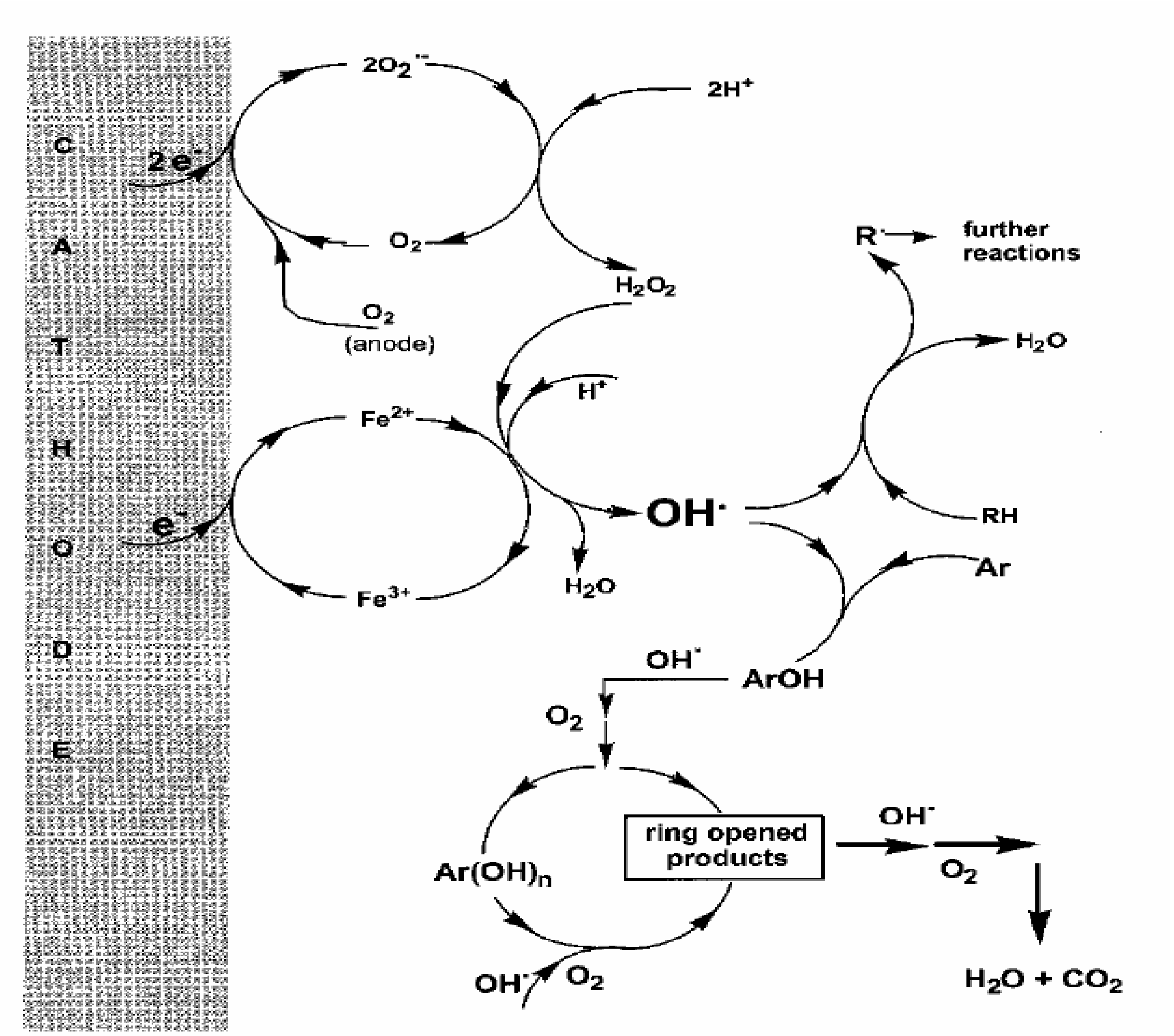


Figure 2.6. Scheme of the electrocatalytic Fenton's reagent generation and homogenous OH· radical production in aqueous solution (Oturan, 1999).

2.3.2. Fenton-like Process

Wang et al. (2008) described Fenton-like reaction as the reaction of ferric ion Fe^{3+} with hydrogen peroxide. For aqueous Fe^{3+}, the following reactions have been identified spectrophotometrically by (Pignatello et al., 2006):

$Fe^{3+} + H_2O_2 \leftrightarrow Fe(HO_2)^2 + H^+$ (2.15)

$FeOH^{2+} + H_2O_2 \leftrightarrow Fe(OH)(HO_2) + H^+$ (2.16)

According Pignatello et al. (2006) it was meaningless to distinguish both processes, because Fe^{2+} and Fe^{3+} are found simultaneously in the reactions of the Fenton Process. If a large molar excess of H_2O_2 is present, all initially added Fe(II) will quickly be oxidized to Fe(III) and thereafter the system will behave independent of the initial oxidation state of iron (Pignatello et al., 2006). However, a great difference in practice is that a greatly quick generation of hydroxyl radicals may occur at the beginning of Fenton oxidation, whereas Fenton-like oxidation has a slow generation rate of hydroxyl radicals. The reason is that the rate constant in Eq. (2.1) (the main reaction at the initial stage of Fenton oxidation) is much higher than that in Eq. (2.15) (the main reaction at the initial stage of Fenton-like oxidation), such that the latter reaction becomes a rate limiting step and slows down the release of hydroxyl radicals (Deng and Englehardt, 2006).

2.3.3. Factors Affecting the Fenton Process

As a chemical process Fenton oxidation is influenced by many different factors including pH, iron and hydrogen peroxide dosage, presence of inorganic salts, dissolved oxygen. The effect of these parameters are explained in next sections

2.3.3.1 Effect of pH. According to Neyens and Baeyens (2003) pH is the one of the most important parameter for the Fenton reaction. At high pH values, the oxidation efficiency of Fenton's reagent may decrease due to possibility of the formation of ferric ions. When the pH is too low and the concentration of hydrogen ions is too high, the formation of $FeOOH^{2+}$ will be slowed down causing to a decrease in the production rates of ferrous ions and hydroxyl radicals (Neyens and Baeyens, 2003). Deng and Englehardt (2006) summarized the effect of extremely low and high pH values on Fenton reaction by using various studies in literature; at extremely low pH values, the $[Fe(H_2O)]^{2+}$ reacts slowly with H_2O_2, producing less OH· radical and low pH can also inhibit reaction between Fe^{2+} and H_2O_2. A pH value at neutral and alkaline range also inhibits Fenton reaction. The absence of H^+ can inhibit the decomposition of H_2O_2 (Deng and Englehardt, 2006). For these reasons mentioned above the optimal pH value for the Fenton reaction was found to be pH 3 by various researchers (Tokumura et al., 2007, Neyens and Baeyens 2003).

2.3.3.2 Effect of Inorganic Salts. Pignatello et al. (2006) stated that the Fenton and the photo-Fenton reactions were inhibited by the presence of phosphate, sulfate, organo-sulfonate, fluoride, bromide, and chloride ions, depending on their concentrations. The authors noticed that these anions could be present initially in the wastewater or formed as end products of the compounds due to the degradation. The main reason of inhibition by these compounds is precipitation of iron, scavenging of OH·, or coordination to dissolved Fe^{3+} to form a less reactive complex (Pignatello et al., 2006).

2.3.3.3. Iron and Hydrogen Peroxide Dosages. Determination of optimum hydrogen peroxide and iron concentrations are important factors for the treatment system efficiency. Generally, removal of organics increases with increasing concentration of iron salt (Deng and Englehardt, 2006). The use of high initial ferrous ion in Fenton system produces an important amount of OH· within a short period of time (Yoon et al., 2001). Lin and Lo (1997) found that in terms of absolute COD concentration, an increase in the amount of $FeSO_4$ is definitely highly beneficial. The authors attributed the increase in the COD removal efficiency with increasing $FeSO_4$ concentration to the enhancement of the redox reaction in the presence of higher amounts of ferrous iron. However an enormous increase in the ferrous ions will lead to an increase in the unutilized quantity of iron salts, which will contribute to an increase in the TDS content of the effluent (Gogate and Pandit, 2004). Moreover ferrous iron (Fe^{2+}) itself is an OH· scavenger, high amount of iron can affect efficiency of the Fenton process negatively (Yoon et al., 2001). Hydrogen peroxide dosage is also an important factor for Fenton process. Lin and Lo (1997) found that, similarly to iron, COD removal efficiency increased with increasing H_2O_2 concentration. They also showed that the excessive amount of hydrogen peroxide caused extra COD loading in the system (Lin and Lo, 1997). Another negative effect of hydrogen peroxide is that in large quantities it acts as a scavenger for the generated hydroxyl radicals (Gogate and Pandit, 2004).

2.3.3.4 Temperature. Rivas et al. (2001) investigated the effect of temperature. Rivas and co-workers, (2001) stated that in the range of temperatures from 284 to 314K no influence of this parameter was noticed. However Rivas et al. (2003a) determined that when temperature was raised from 10 to 30°C positive influence on the COD removal rate in landfill leachate was exerted. Lin and Lo (1997) found that optimum COD removal was observed at 30°C.

2.4 Advanced Fenton Process

As described in the previous section, Classic Fenton Process involves the reaction of ferrous iron (Fe^{2+}) with hydrogen peroxide (H_2O_2) under acidic conditions to produce hydroxyl radicals for the degradation of hazardous pollutants in wastewaters. The basic equation Eq(2.1) was given as follows;

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^{-} \qquad (2.1)$$

In recent years researches have focused on the generation of hydroxyl radicals by using zero valent iron (ZVI) (Fe^0) instead of ferrous iron (Fe^{2+}) in the Fenton reaction. This application is referred to as Advanced Fenton Process (AFP) (Devi et al., 2009). In acidic conditions, the surface of the ZVI corrodes and generates in situ ferrous ions, which can lead to Fenton reactions in the presence of hydrogen peroxide .The ZVI surface can then reduce the ferric ions down to ferrous ions. The basic mechanisms of AFP are given below (Fu et al., 2010, Bremner et al., 2006).

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (2.17)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^{-} \qquad (2.18)$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \qquad (2.19)$$

Many researchers investigated the efficiency of AFP for removal of the pollutants (Shu et al., 2009, Lee et al., 2008, Fu et al., 2009, Bremner et al., 2006). Bremner et al. (2006) analyzed phenol degradation by using zero valent iron and hydrogen peroxide. The authors found that after 15 min, all of the free organic compounds have disappeared except an unidentified compound. In order to observe the effect of pH on the degradation, the reaction was repeated in the absence of added acid. However the degradation of phenol was much slower and it completely disappeared after 2 h of reaction (Bremner et al., 2006).

Fu et al. (2010) studied degradation of C.I. Acid Red by AFP. Different zero valent iron and hydrogen peroxide concentrations were used in their research. Fu and co-workers, (2009) found that optimum concentrations of ZVI and H_2O_2 are 0.3 g/l and 2.0mM for discoloration process respectively. No significant change was observed when ZVI and H_2O_2 were exceeded their optimum concentration. The effect of pH value on the AR 73 discoloration was assessed at four initial pH values, 2.0, 3.0, 4.0 and 5.0 Fu et al. (2009). When pH rose to 5.0, the residual concentration decreased from 200 mg/L to 171.3 mg/L after 30 min. However when the pH of the sample was 3.0 concentration of Acid Red was 6.4 mg/L (Fu et al., 2010). The authors explained that ZVI was easily dissolved in acidic conditions and produced Fe^{2+} ions, and these ferrous ions reacted with hydrogen peroxide to generate hydroxyl radicals. When pH values increased, Fe^{2+} ions originating from the ZVI can form ferrous hydroxide precipitates, and suppresses the reaction (Fu et al., 2010).

Devi et al. (2009) investigated the degradation of methyl orange azo dye by AFP. For 10 ppm of azo dye the authors used different dosages of iron and hydrogen peroxide. At lower iron dosages of 10–30 mg, rapid discoloration of the dye was achieved. However on further increase of Fe^0 dosage up to 200 mg considerable decrease in the degradation rate was observed due to the inhibition effect shown by iron ions (Devi et al., 2009). The authors evaluated the effect of pH on the discoloration of methyl orange azo dye. Devi and co-workers observed that when the pH of the medium was increased from 4 to 9.2, the discoloration of the dye could not be achieved even after 1 h of irradiation. Under lower acidic condition of pH 2.0 and 3.0, the bands in the visible region disappeared completely in 20 min and 15 min respectively, indicating the complete discoloration of the dye (Devi et al., 2009).

2.4.1. Advantages and Disadvantages of ZVI

Use of zero valent iron in Fenton Process can be considered as a new method to remove pollutants in wastewater. The main advantage is the faster recycling of iron as shown in the Eq(19) (Brehmer et al., 2006);

$$2Fe^{3+} + Fe^{0} \rightarrow 3Fe^{2+} \qquad (2.19)$$

As a result of the equation above more OH radicals are produced and oxidation efficiency was improved.

According to Kusic et al. (2007) implementation of iron powder (Fe^{0}) instead of iron salts prevents the unnecessary loading of aquatic system with counter anions. Fu et al. (2010) noticed that when ZVI is used as iron source no further treatment is needed because of the low iron concentration in the effluent.

On the other hand there are some disadvantages of the use of ZVI. According to Devi et al. (2009) the disadvantages of using iron metal are that:
- ZVI requires acidic condition,
- Higher dosage of iron powder generates significant levels of Fe^{2+} ions causing secondary pollution.

2.5. Fenton Process as a Sludge Treatment Method

Generally, studies investigated Fenton process focused on the treatment of the wastewater. This process was widely used to treat wastewaters with high organic loading content like landfill leachate. However the oxidative property of Fenton was also analyzed by many researchers for the sludge disintegration process. Some of these studies are briefly explained below.

Tokumura et al. (2007) studied photo-Fenton process for excess sludge disintegration. They observed effect of iron, hydrogen peroxide, pH, initial MLSS concentration. Soluble fraction of the COD increased and reached the maximum concentration after 6 hours of reaction when 40 mg/L of iron and 4 g/L of H_2O_2 were added to sludge samples as Fenton reagents at pH 3.0 (Tokumura et al., 2007). The authors observed that after 6 hours of reaction COD began to decrease due to mineralization of dissolved organic substances by photo-Fenton process. It was found that the MLSS decreased from the initial value of 3000 to 912 mg/L after 10 h of photo-Fenton reaction. Tokumura et al. (2007) noted that for the MLSS of 2000 and 3000 mg/L, the dissolved COD increased, reached the maximum after around 7 and 22 h of the reaction time respectively and then decreased. However they noticed that for MLSS of 4000 mg/L COD value for the monotonously increased during the course of photo-Fenton oxidation of 38 h. The authors investigated the effect of iron and hydrogen peroxide dosages. They observed faster increase in the sCOD and mineralization at iron dosage of 40 mg/L. For 2 g/L of hydrogen peroxide no mineralization was seen even at the end of 14 hours (Tokumura et al., 2007). For the initial pH the experiments were performed at the pH of 3.0 and 6.8 (neutral) by maintaining other process parameters constant (Tokumura et al., 2007). They found that at initial pH value of 3.0 COD increased until t = 6 h however when the solution pH was natural (pH 6.8), COD increased at lower rate and then decreased gradually with the reaction time.

Tokumura et al. (2009) investigated disintegration of excess sludge using solar photo-Fenton reaction. In their study Tokumura et al. (2009) used solar light instead of artificial UV light. The experiment with solar light was performed at the initial MLSS concentration of 1000 mg/L, H_2O_2 dosage of 4000 mg/L and Fe dosage of 60mg/L. They indicated that the dissolved COD increased by 3.7 times the initial COD value. When COD concentration reached maximum value after 17 hours of reaction, COD began to decrease due to mineralization. The MLSS continuously decreased with accumulated energy and as a result of that about 40% reduction in MLSS was achieved. Tokumura and co-workers concluded that disintegration with solar light was significantly faster and higher than that with UV light. They noted that for solar light irradiation the dissolved COD values increased by 3.7 and 4.5 times the initial COD value, while the increase was 2.0 and 2.9 times the initial value for UV light irradiation.

Pham et al. (2010) compared ultrasound and Fenton treatments in terms of disintegration and rheological characteristics of the wastewater sludges. They used a ratio of $[H_2O_2]_0/ [Fe^{2+}]_0 = 150$ at pH 3.0 for Fenton treatment. The authors found that both

Fenton Process and ultrasonication decreased apparent viscosity of the sludge samples. At constant shear rate over 102 min, the apparent viscosity decreased from 159.9 to 100; and 121.8 to 79.9mPa.s for ultrasonicated and Fenton oxidized sludge samples respectively. Pham et al. (2010) observed an increase in the particle size of Fenton oxidized sludge compared to that of untreated sludge. The authors also found that CST of the sludge decreased after Fenton treatment and dewaterability was enhanced due to increased due to agglomeration of the sludge flocs (Pham et al., 2010). They observed that for 10 g/L of TS solubilization of sludge was approximately 80% and as TS concentration increased solubilization decreased. Therefore they also stated biodegradability of sludge was improved depending on the increase in organic materials.

3. MATERIALS AND METHODS

3.1. Sludge Source and Experimental Set-up

In this study sludge samples were obtained from an industrial facility. The treatment system of the facility consists of physical, chemical and biological treatment. For water reuse tertiary treatment is also applied. Sludge samples were taken from the recycle line of the activated sludge system. SRT of the system was adjusted to 10 days. Maximum storage period of sludge was 1 week at 4 ± 1 ºC to minimize microbial degradation.

In this study Advanced Fenton Process (AFP) was applied as sludge disintegration technique. Batch experiments were conducted. Three hundred milliliters of each wastewater sludge samples were acidified to pH 3 by using 0.5 N H_2SO_4 and placed in a 600 ml flask. All experiments were carried out without adding any buffers for pH adjustments during the process. To initiate Fenton oxidation, known amount of iron and hydrogen peroxide were added to the sludge samples. The Fenton oxidation was carried out at the ambient temperature for 1 h by using a Jar test machine for mixing at 120 rpm.

For Classic Fenton Process, iron(II) sulfate heptahydrate ($FeSO_4.7H_2O$) was used as a source of iron. For Advanced Fenton Process zero valent iron was supplied from Hepure-USA (H-200) zero valent iron in powder form. Hydrogen peroxide (H_2O_2) was supplied form Sigma-Aldrich. The purity of hydrogen peroxide was 30%.

The characteristics of the waste activated sludge samples obtained from the wastewater treatment facility are given in the table below;

Table 3.1. The characteristics of the waste activated sludge

Parameter	**Value**
pH	6.8
COD (mg/L)	5217 (mg/L)
sCOD (mg/L)	67.4 (mg/L)
TS (mg/L)	15817 (mg/L)
MLSS (mg/L)	9714 (mg/L)
MLVSS (mg/L)	7510 (mg/L)
ORP (mV)	34 (mV)

The values above are the average value of the data obtained between 15/02/2010 – 28/06/2010.

3.2. Analytical Methods

Analytical methods used in this study are shown in Table 3.2.

Table 3.2. Analytical methods used in the study.

Analysis	**Method**	**Instrument**	**Reference**
COD (mg/L)	Dichromate Closed Reflux Method	HACH OD Digester HACH DR/2010 Spectrophotometer	APHA-AWWA-WPCF Methods for the Examination of Water and Wastewater, 1975
pH and ORP(mV)	4500-HB Method Electrometric	WTW Inolab pH meter Level 2	APHA-AWWA-WPCF Methods for the Examination of Water and Wastewater, 1975
TS (mg/L)	Gravimetric Method	Julabo Ecotemp TW 12 Evaporater, oven (103°C), desiccator	APHA-AWWA-WPCF Methods for the Examination of Water and Wastewater, 1975
MLSS (mg/L)	Gravimetric Method	Oven (103°C), desiccator	APHA-AWWA-WPCF Methods for the Examination of Water and Wastewater, 1975
MLVSS (mg/L)	Gravimetric Method	Furnace (600°C), desiccator	APHA-AWWA-WPCF Methods for the Examination of Water and Wastewater, 1975
sCOD (mg/L)	Centrifugation and Gravimetric Method	Hettich Universal 16A Centrifuge HACH OD Digester HACH DR/2010 Spectrophotometer	APHA-AWWA-WPCF Methods for the Examination of Water and Wastewater, 1975 Bougrier et al., 2008
SVI	Settling Colones	Imhoff Cones	APHA-AWWA-WPCF Methods for the Examination of Water and Wastewater, 1975
CST (s)	Instrumental Method	CST Instrument	Vesilind, 1988
Viscosity(cP)	Instrumental Method	Brookfield DV-I Prime	
Particle Size Analysis	Instrumental Method	Mastersizer 2000	
Compactibility as Cake Solids Concentration	Centrifugation	Hettich Universal 16A Centrifuge	Erdincler and Vesilind, 2000, Vesilind, 1978

3.2.1. Chemical Oxygen Demand Analysis

Chemical Oxygen Demand (COD) analysis was conducted by using dichoramte closed reflux method according to the *Standard Methods for the Examination of Water and Wastewater*. Samples were refluxed with potassium dichoramte ($K_2Cr_2O_7$) and sulfuric acid for two hours at 150°C in HACH COD digester. Interference from chloride was prevented by using mercury sulfate ($HgSO_4$). Silver sulfate (Ag_2SO_4) was used as catalyst. Absorbance values were measured using HACH DR/2010 Portable Data Logging at 600 nm for colorimetric COD measurement. Calibration curve was prepared using potassium hydrogen phthalate (KHP).

3.2.2. Soluble Chemical Oxygen Demand Analysis

Soluble Chemical Oxygen Demand method (sCOD) was conducted as described by Bougrier et al. (2008). 40 ml of sludge samples were centrifuged at 2850 rpm for 15 minutes. Supernatant was taken by using a syringe. The supernatant was analyzed by using dichoramte closed reflux method, according to *Standard Methods for the Examination of Water and Wastewater*.

3.2.3. pH and ORP Analysis

WTW Inolab pH meter was used for both analyses.

3.2.4. Total Solids Analysis

Total Solids (TS) analysis was performed according to Standard Methods. 50 ml of well-mixed samples of 50 ml were evaporated on the steam bath (Julabo Ecotemp TW 12) and then dried for one hour at 103°C in oven. Afterwards, they were cooled in desiccator for 30 minutes and then were weighed. The TS content of the sludge was found by measuring difference between the weight of (dry residue + dish) and the weight of dish divided into the volume of sludge sample.

3.2.5. Mixed Liquor Suspended Solids (MLSS) Analysis

The sludge sample was filtered through a pre-weighed glass-fiber filter paper (Whatman GF/C) and dried for 1 hour at 103°C in oven. The filter paper was cooled in desiccator for 30 minutes and weighed. The difference between the dry weight of (residue + filter paper) and the weight of filter paper was divided into the volume of the sample to calculate MLSS in the sludge sample.

3.2.6. Mixed Liquor Volatile Suspended Solids (MLVSS) Analysis

Mixed Liquor Volatile Suspended Solids (MLVSS) Analysis was performed by igniting the residue on the filter paper used in MLSS analysis in a crucible for 30 minutes at 550±50 °C in furnace. The crucible with filter paper and inorganic residue on the filter paper were cooled in desiccator and weighed. In order to measure the concentration of MLVSS in the sludge sample, the difference between the weight of (sample residue + filter paper + crucible) before and after ignition was divided by the volume of the sample.

3.2.7. Sludge Volume Index (SVI) Analysis

The Sludge Volume Index (SVI) is the volume in milliliters occupied by one gram of activated sludge after the mixed liquor has settled for 30 minutes. 1 liter of mixed liquor was allowed to settle in a graduated cylinder for 30 minutes and sludge volume index was calculated by using following equation;

$$\text{SVI} = \text{settled sludge volume (ml/L)} \times 1000/\text{suspended solids (mg/L)} \qquad (3.1)$$

3.2.8. Dewaterability Tests

Dewaterability of the sludge samples measured in terms of filterability and compactibility. Filterability is measured by CST analysis and compactibility is measured by centrifugation.

3.2.8.1. Capillary Suction Time (CST) Analysis. As described by Vesilind (1988) the filterability of sludges was measured by Capillary Suction Time (CST) Analysis. To measure the sludge filterability, high and low CST values are compared. High CST values indicate the slow releasing of the liquid part of the sludge and low CST values indicate the easy separation of sludge water.

The CST apparatus consist of two plastic blocks, a stainless-steel collar, three electrical sensors fixed on the upper plastic block, a piece of filter paper and an electrical timer. CST filter paper was obtained from Venture Innovations, Inc. (Part No: IFP-9052). The paper was placed between these plastic blocks. Two milliliters of sludge sample is poured into the collar and flowed through the paper circularly forming a wet blot in the filter paper. The diameters of the first circle having two sensors and second circle on which one sensor was present, were 3.2 cm and 4.6 cm, respectively. When the sample reached the inner circle, the electrical timer started to count with a signal. After a period, the sensor of outer circle perceived the liquid part of the sludge sample and the timer stopped. The period of reaching from the inner circle to the outer was called as ‘Capillary Suction Time’ (CST) in seconds.

The CST test depends on the sludge solids concentration and the instrument used. Temperature also affects the test due to its effect on viscosity (Vesilind, 1988). Temperature of the sludge samples was adjusted to 25 °C. The tests were duplicated and the average values were reported as CST value in seconds.

3.2.8.2. Sludge Compaction Analysis. Compactibility of the sludge samples were measured by centrifugation in terms of cake solids content. Compaction tests were performed by centrifuging 10 ml of sludge samples at 2800 g (4850 rpm) for 30 minutes in a centrifuge (Hettich Universal 16A). The solid content and heights of compacted sludge cake were measured (Erdinçler 1996, Erdinçler and Vesilind, 2000)

3.2.9. Particle Size Analysis

Particle size analysis was performed using Mastersizer 2000 (Malvern) particle size analyzer. During entire analysis ultrasonic function was kept off not to disturb the sludge flocs. The speed of the stirrer was adjusted to 600 rpm in order to minimize the damage of the sludge particles (Pham et al., 2010). In the particle size analysis approximately 5 ml of sludge sample was added to 800 ml of deionized water. Obscuration was adjusted to 10-20% after preliminary studies. The method used in the analysis is based on Fraunhoffer scattering. All of the measurements were triplicated and the average values were reported. The results were recorded as d_{10}, d_{50}, d_{90} particle sizes

3.2.10. Degree of Disintegration

The disintegration degree of the sludge samples were calculated according to following formula described by Müller and Pelletier (1998), Bougrier et al. (2005).

$$DD_{COD} = (sCOD - sCOD_0) / (sCOD_{NaOH} - sCOD_0) \times 100 \qquad (3.2)$$

where;

DD_{COD} : Degree of Disintegration

sCOD : COD in the supernatant of the pretreated sludge, mg/L

$sCOD_0$: COD in the supernatant of the untreated sludge, mg/L

$sCOD_{NaOH}$: COD in the supernatant of the chemically disintegrated sludge in 1mol/L NaOH for 24 h at ambient temperature 20±1 °C. In this study $sCOD_{NaOH}$ value was found as 2961 mg/L.

3.2.11. Viscosity Analysis

Viscosity analysis were performed by using Brookfield DV-I Prime viscometer. Viscosity of the 500ml sludge samples was measured by using Spindle No:4. All measurements were carried out at ambient temperature of 25° C.

4. RESULTS AND DISCUSSION

This study investigates the role of the both Advanced and Classic Fenton Processes on the disintegration of excess wastewater sludges. Different iron and hydrogen peroxide concentrations ranging between 20-100 mg/L and 2000-6000 mg/L were applied to sludge samples respectively. In this study sludge samples obtained from treatment plant of a petrochemical facility. The increase in the soluble organic content of the sludge samples was measured in terms of soluble chemical oxygen demand (sCOD).

In Fenton Process pH, mixing rate and MLSS concentrations are important factors affecting the degree of sludge disintegration. In order to show the effect of pH and mixing rate experiments were conducted at different pH values, mixing rates and MLSS concentrations.

In this study the effect of AFP on dewaterability of the wastewater sludges was also analyzed in terms of filterability and compactibility. CST of the samples was measured using different MLSS concentration as in the study of Pham et al. (2010). In order to show the relation between the dewaterability and particle size distribution, particle size analyses were conducted after Fenton Process applications.

The settleability of the sludge was carried out to untreated and Fenton oxidized sludge. Experiments were conducted under same MLSS values for each sample by using Imhoff cones.

Rheological behavior of the untreated and Fenton pre-treated sludges was analyzed by measuring the viscosity of the sludge samples.

4.1. Effect of Iron Concentration

During the experiments, different iron concentrations ranging from 20 to 100 mg/L were applied to the sludge samples. The experiments were evaluated under the same mixing rate, pH and MLSS concentration. The effect of the iron dosage on the disintegration of excess wastewater sludges is given in Figure 4.1.

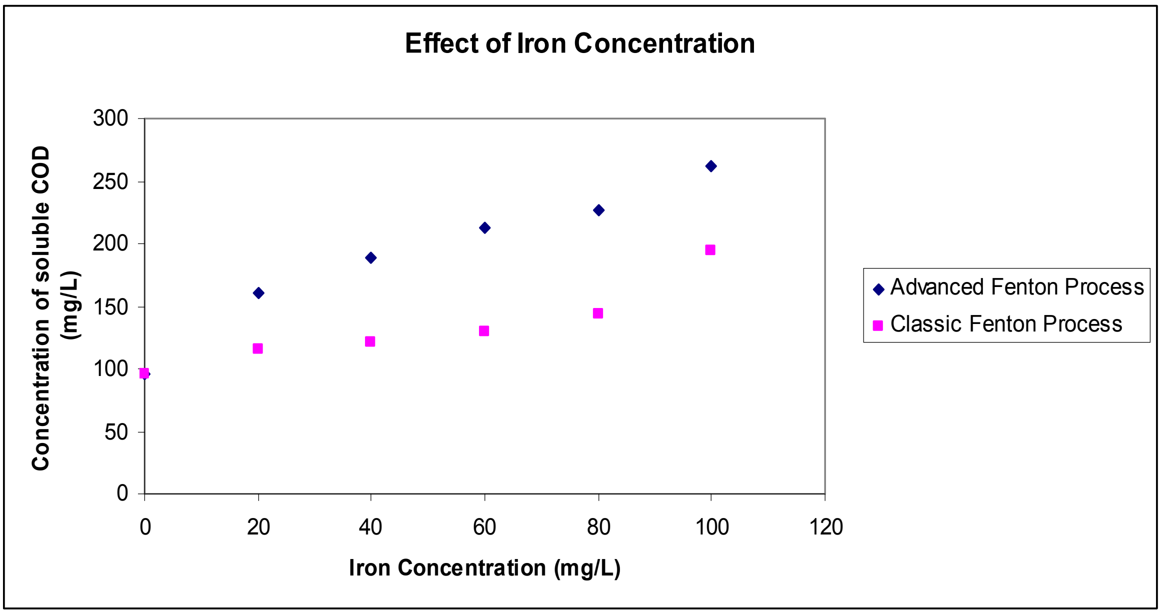


Figure 4.1. Effect of Iron dosage on the disintegration of excess sludge (a) increase in concentration of sCOD, (b) % increase in sCOD. H_2O_2 = 4g/L, initial pH=3, MLSS = 10200 mg/L, reaction time = 1 hour, initial sCOD = 96,2 mg/L

The results obtained demonstrated the effect of different iron concentrations on the sludge disintegration. The sCOD concentration of the untreated sludge was 96, 2 mg/L. It was observed that after the application of Classic Fenton pretreatment at different iron concentrations of 20, 40, 60, 80, 100 mg/L, the concentration of the soluble COD increased to 115.99, 120.6, 130, 144 and 194 mg/L respectively. However Figure 4.1.a showed that the highest sCOD concentrations were obtained after Advanced Fenton Process application to the sludge samples. For the iron concentrations of 20, 40, 60, 80, 100 mg/L the sCOD increased to 161.2, 189.4, 212.8, 226.9, 262,2 mg/L respectively. The main reason for the increase in the sCOD concentration is the release of intracellular materials due to the disruption of the cell walls of the microorganisms. Fenton reactions destructed bacterial cell membranes, discharged biomass particulates and transformed them into a soluble composition such as proteins, lipids and polysaccharides (Tokumura et al., 2007). The results also indicated that as iron concentration increased the sCOD concentration of the sludge samples increased. The highest sCOD concentration were observed, for both Classic and Advanced Fenton pretreatment, at iron concentration of 100 mg/L. Lin and Lo (1997) explained that the increase in the iron concentration facilitated redox reaction in the Fenton Process. The production of OH radicals from H_2O_2 depended on the concentration of the iron because of the catalyzing effect of the iron in the Fenton Process (Kim and Vogelpohl, 1998). Similarly, Yoon et al. (2000) indicated that the use of high initial ferrous ion produced a considerable amount of hydroxyl radicals.

These results also demonstrated that Advanced Fenton oxidation led to higher sCOD concentrations. The main advantage of the Advanced Fenton Process is the zero valent iron utilization in the reaction. ZVI cause to the faster recycling of iron as shown in equations below. Because of the faster iron recycling, in Advanced Fenton Process, more hydroxyl radicals were produced and more cells were disrupted by releasing intracellular materials into the bulk sludge.

$$Fe^{0} + 2H^{+} \rightarrow Fe^{2+} + H_2 \qquad (2.17)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^{-} \qquad (2.18)$$

$$2Fe^{3+} + Fe^{0} \rightarrow 3Fe^{2+} \qquad (2.19)$$

Degree of Disintegration was calculated according to Eq(3.2) for both Advanced and Classic Fenton pretreatment by using the sCOD values obtained in Figure 4.1.a. The results are shown in Figure 4.2.

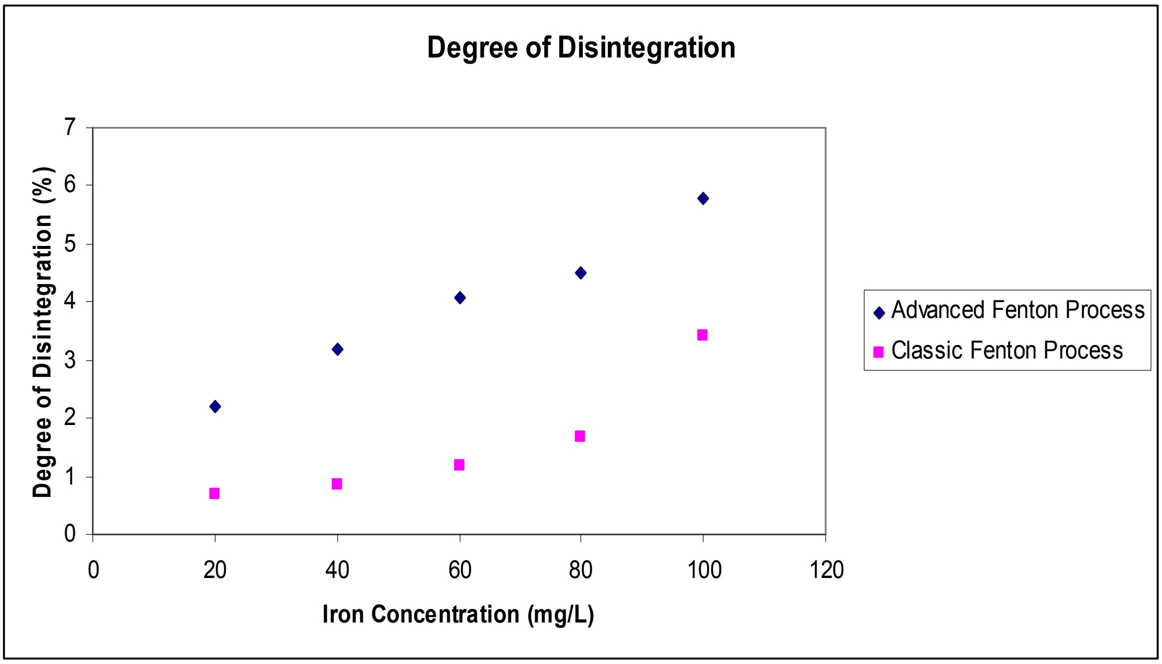


Figure 4.2. Degree of Disintegration H_2O_2 = 4g/L, Fe = 100 mg/L, initial pH=3, MLSS = 10200 mg/L, mixing rate = 120 rpm, reaction time = 1 hour

The results shown in Figure 4.2 demonstrated that the highest DD_{COD} results were obtained after Advanced Fenton sludge pretreatment process. It was observed that for 20, 40, 60, 80, 100 mg/L of Fe^{2+} concentrations, the measured DD_{COD} values for Classic Fenton pretreatment were 0.69%, 0.85%, 1.18%, 1.68%, 3.42% respectively. In Figure 4.1 it was shown that the sCOD concentrations obtained after Advanced Fenton pretreatment were higher than those of Classic Fenton pre-treatment. As a result of that DD_{COD} values of the Advanced Fenton oxidized sludge samples were higher and for 20, 40, 60, 80, 100 mg/L of Fe^0 concentrations DD_{COD} values were calculated as 2.2%, 3.2%, 4.07%, 4.5%, 5.8% respectively.

4.2. Effect of Hydrogen Peroxide (H_2O_2) Concentration

Initial concentration of H_2O_2 plays an important role in the Fenton reaction because of the reasons described in section 2.3.3.3. In this study hydrogen peroxide experiments were performed using 2, 4 and 6 g/L of hydrogen peroxide for fixed iron concentration of 100 mg/L. The results obtained are shown in Figure 4.3.

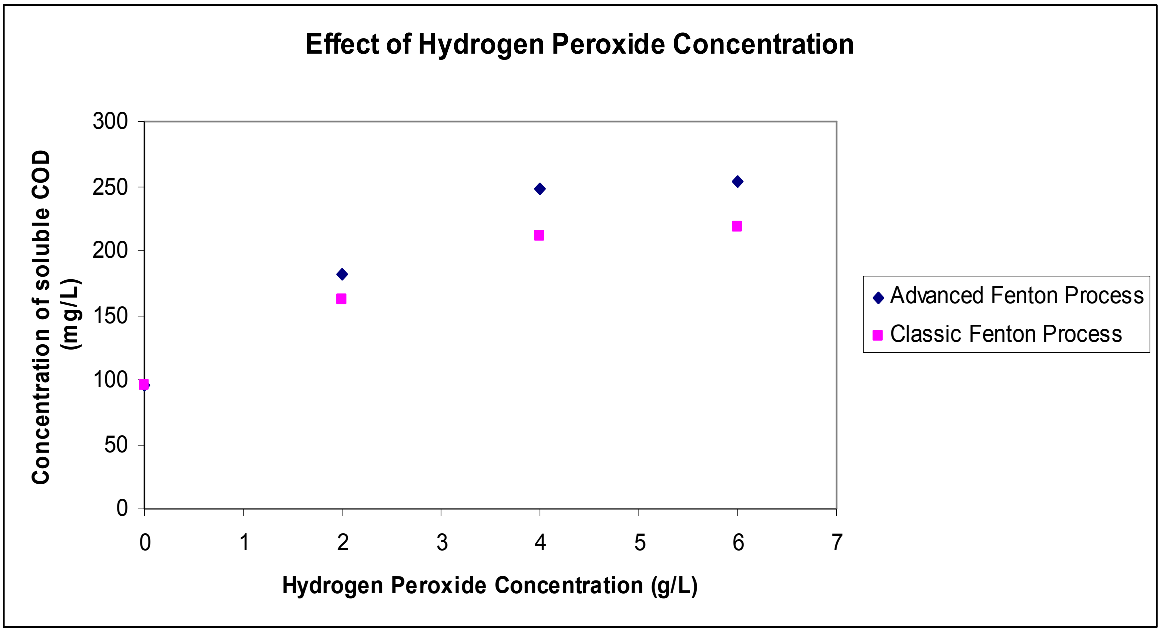


Figure 4.3. Effect of hydrogen peroxide concentration on excess sludge disintegration. Increase in concentration of sCOD, Fe = 100mg/L, initial pH=3, MLSS = 10200 mg/L, mixing rate = 120 rpm, reaction time = 1 hour, initial sCOD = 96 mg/L.

In these experiments both Classic and Advanced Fenton pretreatment methods were applied to the untreated sludge samples. The initial sCOD of the untreated sludge sample was 96 mg/L. The results demonstrated that after Classic Fenton Process, soluble COD of the sludge samples increased from 96 mg/L to 162, 211.3, 218.4 mg/L as a result of the addition of 2, 4, 6 mg/L of hydrogen peroxide respectively. For Advanced Fenton oxidation the results of the soluble COD were 181.4, 247.4, 254 mg/L for the hydrogen peroxide concentrations of2, 4, 6 mg/L respectively. According to these results percent increase in the sCOD concentrations for 2, 4, 6 g/L H_2O_2 were calculated as 82.7%, 157.7%, 164.5 % for Advanced Fenton Process and 68.75%, 120.1%, 124.5 % for Classic

Fenton Process respectively. The increase in the sCOD of the sludge samples can be explained by the destruction of the cell membrane of the microorganisms found in the sludge. As a result of that the organic materials inside the cells of microorganisms were released by leading to an increase in the sCOD concentration of the sludge.

The results obtained showed that the increasing hydrogen peroxide concentration cause to an improvement in the soluble COD concentration due to the increase in the hydroxyl radical concentration by the addition of H_2O_2 (Tokumura et al., 2007). These results are in accordance with the studies in literature. Lin and Lo (1997) found that in the treatment of a landfill leachate, increasing hydrogen peroxide concentration enhanced the COD removal. Lopez et al. (2004) demonstrated that the COD values of the treated leachate regularly decreased with increasing amounts of H_2O_2. Tokumura et al. (2007) noticed that the increase in the initial H_2O_2 concentration was found to enhance the sludge disintegration rate.

These results also demonstrated that, in sludge disintegration experiments at different hydrogen peroxide concentrations, Advanced Fenton Process led to higher sCOD concentrations. Because of the faster iron recycling mechanism, due to the utilization of zero valent iron, of the Advanced Fenton process more hydroxyl radicals were produced and more cells were disrupted by releasing organic materials into bulk sludge.

The results also demonstrated that for both Classic and Advanced Fenton processes there was not a very big difference between the sCOD values of the sludge samples dosed with 4 and 6 g/L H_2O_2. The increase in sCOD values of the sludge samples for hydrogen peroxide dosages of 4 and 6 g/L were found to be 157.7%, 164.5% and 120.1, 124.5% for Advanced Fenton and Classic Fenton process respectively. As a result of that the optimum hydrogen peroxide concentration was found as 4 g/L for this study. The obtained results agree with the studies done by Lopez et al. (2004) and Zhao et al. (2004). It seems that, in the presence of excess of hydrogen peroxide and hydroxyl radicals, some competitive reactions may take place and a part of hydrogen peroxide is consumed before the oxidation process. Zhao et al. (2004) also observed that after a certain hydrogen peroxide concentration, addition of more hydrogen peroxide decreased the degradation efficiency.

4.3. Effect of Initial pH

The initial pH of the sludge sample is one of the most important parameter for Fenton Process. During the experiments, pH of the sludge samples were adjusted to 2.0, 3.0, 4.0, 5.0, and 6.8 (neutral pH value of the untreated sludge sample) by using 0.5 N H_2SO_4 solution. The effect of the pH on the efficiency of the Fenton Process for sludge disintegration was shown in figure 4.4.a and b.

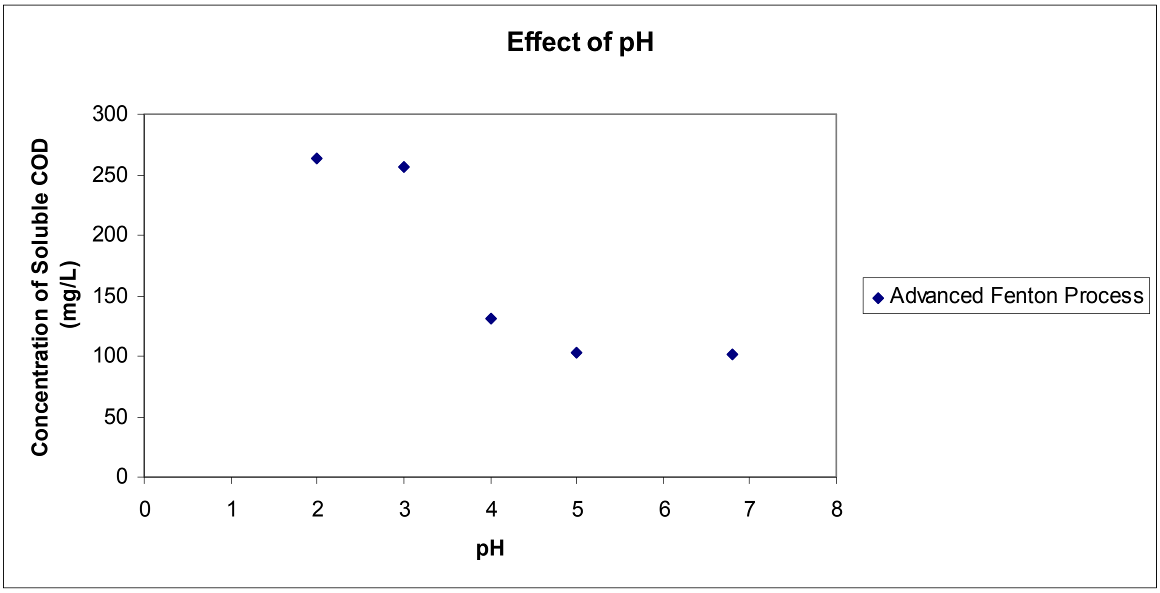


Figure 4.4. Effect of pH on excess sludge disintegration. Increase in concentration of sCOD, Fe = 100 mg/L, MLSS = 11730 mg/L, H_2O_2 = 4 g/L, reaction time = 1 hour, mixing rate = 120 rpm, initial sCOD = 100.9 mg/L

The results given in Figure 4.4. showed that COD solubilization was improved with decreasing pH of the sludge sample. At pH 5.0 and pH 6.9 the sCOD concentrations were measured as 102 and 103.5 mg/L respectively. For pH value of 4.0 a low increase was observed and sCOD was found as 130.8 mg/L. The highest sCOD values measured to be 256 and 264 mg/L for the sludge samples treated with Advanced Fenton Process at pH 3.0 and 2.0 respectively.

These results demonstrated that when Advanced Fenton pretreatment was applied at pH values of 5.0 and 6.9, the sCOD of the sludge samples remained constant. Tokumura et al. (2007) indicated the reason of this observation as that for pH ≥ 4, iron precipitated as $Fe(OH)_3$ and as a result, its potential ability to catalyze H_2O_2 was lowered. At high pH values, ferrous hydroxide precipitated on the surface of ZVI, occupied the reactive sites and suppressed the Advanced Fenton Process (Fu et al., 2010). Kim and Vogelpohl (1998) also reported that the precipitation of ferric hydroxide decreased the regeneration rate of the iron during the reaction. On the other hand the highest increase in the sCOD was measured at pH 3.0 and 2.0 as 154.6% and 162.5% increase respectively. Fu et al. (2010) explained that ZVI was easily dissolved in acidic conditions and hence produced Fe^{2+} ions. The produced ferrous ions reacted with hydrogen peroxide to generate hydroxyl radicals in order to break up cell walls of the microorganisms. At pH 4.0 the increase in the sCOD was measured as 29.7%. In agreement with this result, Devi et al. (2009) and Zhang et al. (2009) reported 40% and 50% color removal at pH 4.0 after Advanced Fenton oxidation. These observations demonstrated that at pH 4.0 Fenton reaction could take place but not with total efficiency due to precipitation of iron as ferric hydroxide.

The results of these experiments also showed that there was not a big difference between the sCOD values of the sludge samples treated at pH 2.0 and 3.0. It can be concluded that optimum pH value for the Advanced Fenton sludge pretreatment was 3.0. Similarly, Fu et al. (2010) reported that no difference was seen at pH 2.0 and 3.0 in terms of degradation of C.I Acid Red compound. Zhang et al. (2009) and Devi et al. (2009) also concluded that optimum pH value was 3.0 for the Advanced Fenton Process.

4.4 Effect of MLSS Concentration

The influence of the MLSS concentration on the Advanced Fenton Process was examined by using MLSS concentrations of 5000, 10000 and 15000 mg/L at fixed iron and hydrogen peroxide dosages. In order to obtain 5000 mg/L of MLSS, the untreated sludge was diluted by using the effluent of the wastewater treatment plant of the petrochemical facility and to adjust 10000 and 15000 mg/L of MLSS the known amount of supernatant of the untreated sludge was discarded. The results obtained are illustrated in Figure 4.5.

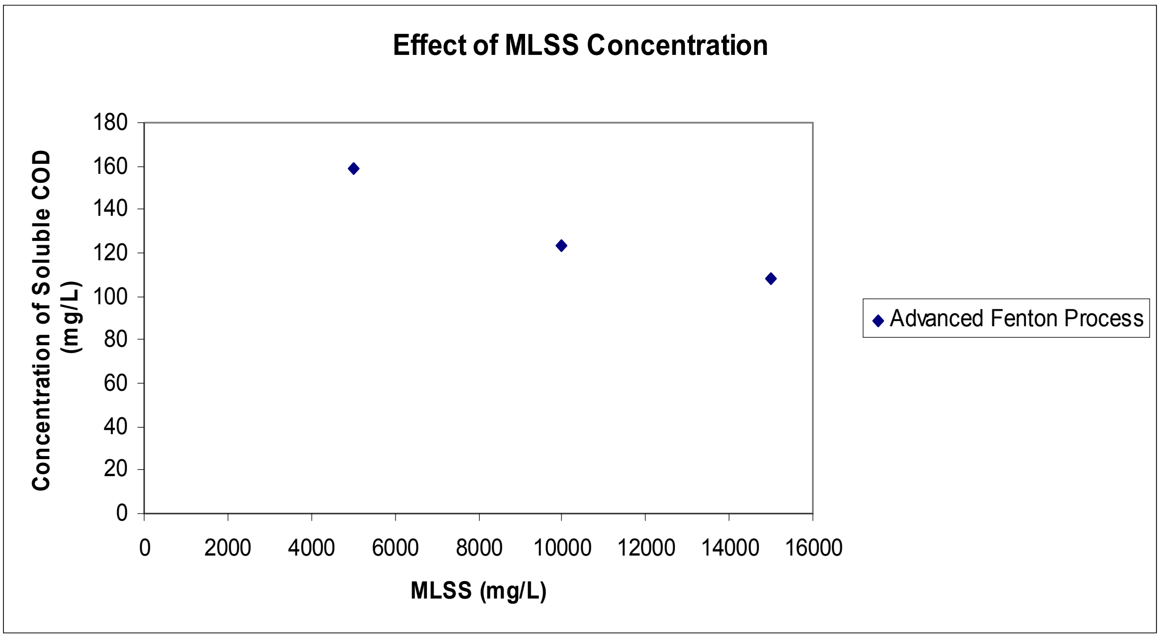


Figure 4.5. Effect of MLSS concentration on sludge disintegration. Increase the in concentration of sCOD, Fe = 100 mg/L, H_2O_2= 4 g/L, pH = 3.0, reaction time = 1 hour, mixing rate = 120 rpm, initial sCOD = 46.9 mg/L.

Figure 4.5.a showed that concentration of the sCOD of the sludge samples decreased with increasing MLSS concentration after Advanced Fenton pretreatment. At the end of 1 hour of Advanced Fenton reaction, soluble COD concentrations increased from 46.9 mg/L to 158.5, 123.1 and 108.04 mg/L for sludge samples containing 5000, 10000 and 15000 mg/L of MLSS concentrations respectively. The highest increase in the sCOD of about %237 was observed at 5000 mg/L of MLSS concentration. For the sludge samples having MLSS concentrations of 10000 and 15000 mg/L, the rate of the increase in the sCOD were 160.3% and 130.4 % respectively. Tokumura et al. (2009) evaluated effect of MLSS on solar photo-Fenton reaction. In their study Fenton reaction was performed for initial MLSS concentrations of 1000, 2000 and 3000 mg/L. The authors obtained the highest increase in sCOD at 1000 mg/L of MLSS concentration. As a result of these obtained measurements, it can be concluded that higher MLSS concentrations suppressed Advanced Fenton reaction. This can be explained as that the increase in the MLSS concentration increased the number of cells but OH· radical concentration remained constant and the disintegration rate of the sludge samples decreased (Tokumura et al., 2007). Similarly, Pham et al. (2010) examined the effect of TS concentration on Fenton Process for sludge disintegration. They

used different TS concentrations ranging from 10 to 40 g/L. The authors observed the minimum disintegration rate at 40 g/L of TS concentration. Fu et al. (2010) and Devi et al. (2009) reported that the degradation efficiency of Advanced Fenton Process decreased with increasing pollutant concentration. This mechanism can be explained as that the •OH radicals found in the system could not increase proportionally with the increased pollutant concentration (Fu et al., 2010).

4.5 Effect of Mixing Rate

In order to observe the influence of mixing rate on the efficiency of Advanced Fenton Process for sludge disintegration, the experiments were performed at different mixing rates ranging between 0-120 rpm. Other operational parameters were kept constant for each sludge sample. Initial sCOD of the untreated sludge sample was 100.9 mg/L. Results obtained are shown in Figure 4.6.

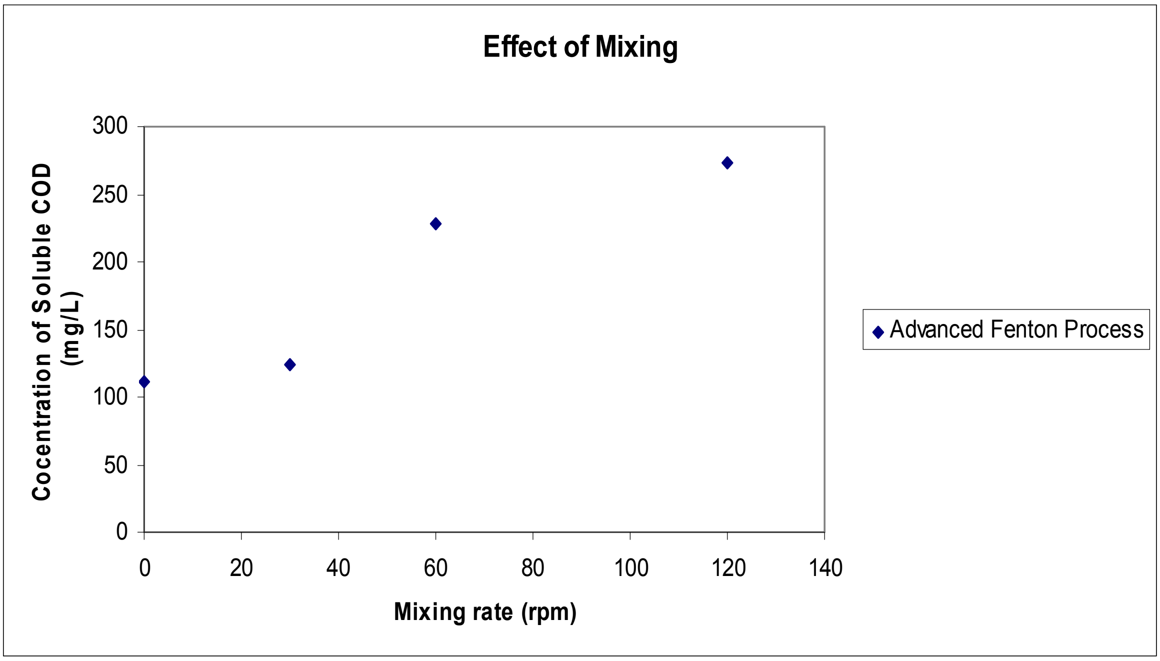


Figure 4.6. Effect of Mixing Rate on sludge disintegration. Increase in the concentration of sCOD, Fe = 100 mg/L, H_2O_2= 4 g/L, pH = 3.0, reaction time = 1 hour, initial sCOD = 100.9 mg/L

The results obtained from Figure 4.6 clearly demonstrated that when there was no mixing, the value of the sCOD increased from 100.9 mg/L to 111.5 mg/L corresponding to an increase of 11.2% in the sCOD. However it was observed that disintegration rate begun to increase with increasing mixing rate. At 30 rpm the increase in sCOD was approximately 20 % and at the end of 1 hour of Advanced Fenton reaction, the concentration of the sCOD reached to 124 mg/L. It was demonstrated that at 60 rpm sCOD value increased to 227.8 mg/L corresponding to an increase of 125.7% in the sCOD. The highest disintegration rate was observed at 120 rpm. At this mixing rate soluble COD was measured as 273 mg/L and percent increase in the soluble COD was calculated as 170.5%.

The results obtained showed that increasing mixing rate led to an improvement in the disintegration efficiency of the Advanced Fenton Process. Fu et al. (2010) analyzed influence of mixing on the degradation of the dye. They indicated that the discoloration efficiency of the Advanced Fenton treatment increased with increasing mixing rate. The authors stated that increasing mixing rate decreased the mass resistance and increased the mobility of the system. Pham et al. (2010) applied a mixing rate of 150 rpm to analyze the efficiency of Fenton Process on sludge solubilization. Tokumura et al. (2009) applied a mixing rate of 300 rpm to ensure complete mixing of the Fenton reagents during sludge disintegration experiments. The benefit of the mixing can be explained as that high mixing rates provides a complete dispersion of the Fenton reagents (Fe^0, H_2O_2) in the system and lead to the production of hydroxyl radicals causing to disruption of the cell walls of microorganisms. Kim et al. (2009) also reported that mixing prevented sludge settling.

4.6 Effect of Reaction Time and Decrease in MLSS

In order to analyze the effect of reaction time, during the AFP, the sCOD of the sludge samples were measured in every 2 hours. At the same time, the decrease in the MLSS concentration of these sludge samples was also measured to investigate the influence of the AFP on the sludge cell disruption. The results obtained were given in Figure 4.7.

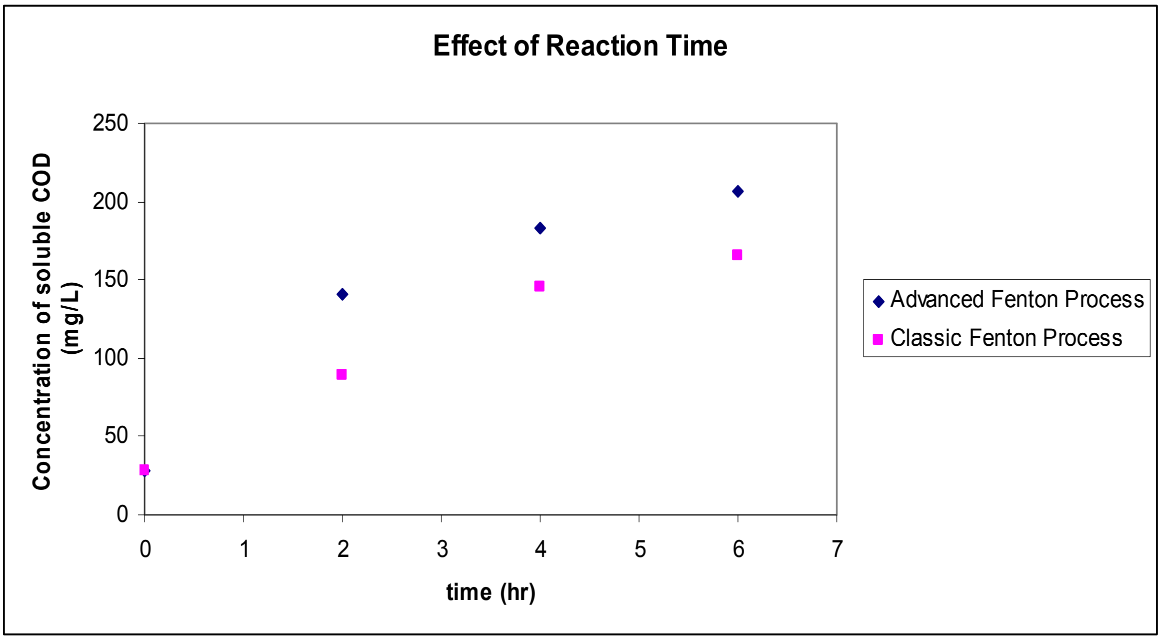


Figure 4.7. Effect of Reaction Time on sludge disintegration, Increase in the concentration of sCOD Fe = 100 mg/L, H_2O_2= 4 g/L, pH = 3.0, initial sCOD = 28.1 mg/L, mixing rate = 120 rpm, initial MLSS = 7200 mg/L

Advanced Fenton pretreatment, increased the soluble COD of the sludge samples from 28.1 mg/L to 140.3, 182.6 and 206.7 mg/L at the end of 2, 4 and 6 hours of reaction time respectively. These values correspond to an increase of 399%, 549.8%, 633.4% in the sCOD for 2, 4, 6 hours of reaction respectively. However, Classic Fenton Process caused to an increase of 219.5%, 420.2%, 489.6% in the sCOD for 2, 4, 6 hours of reaction time respectively. These results demonstrated that Advanced Fenton Process led to higher degree of organic solubilization compared to that of Classic Fenton Process due to the faster iron recycling. During 6 hours of Advanced Fenton pretreatment, Fenton oxidation provided the destruction of the cell walls of the microorganisms, leading to the release of a part of the intracellular materials into the bulk solution and so the increase in the soluble COD concentration of the sludge samples. The sCOD values increased rapidly until the end of 4th of the Advanced Process. In between 4th and 6th hours of the reaction the increase in the sCOD was slower.

In order to show that the reason of the increase in the sCOD was the destruction of the cell walls of the microorganisms, the decrease in the MLSS concentration was measured at the end of every two hours. The results obtained were given in Figure 4.8.

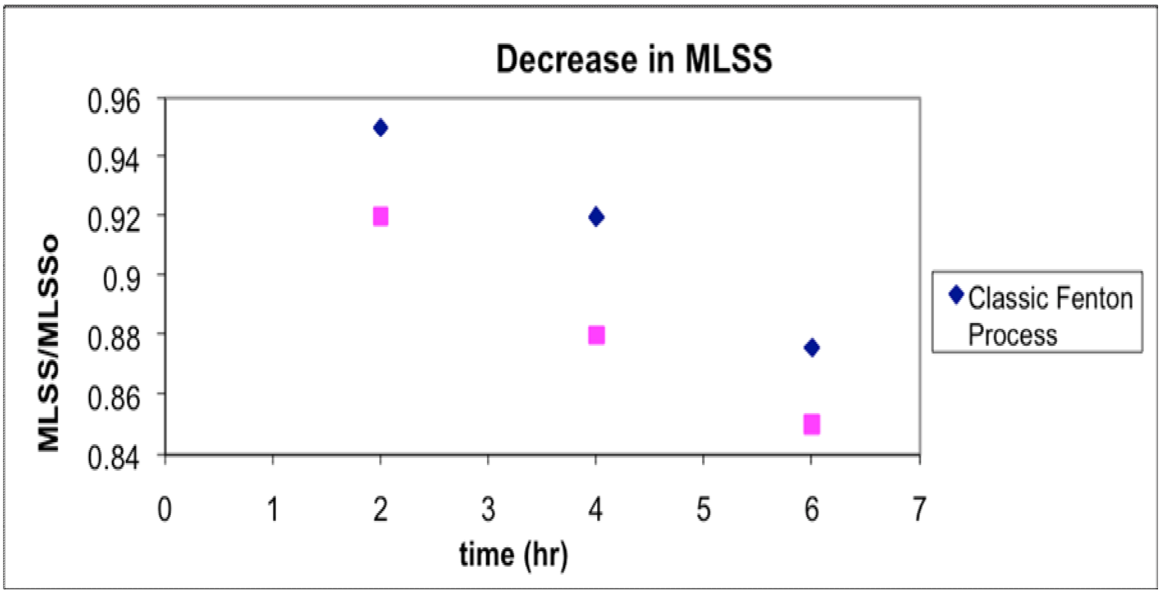


Figure 4.8. Decrease in the MLSS concentration after Fenton Processes. Fe = 100 mg/L, H_2O_2= 4 g/L, pH = 3.0, initial SCOD = 28.1 mg/L, mixing rate = 120 rpm, initial MLSS = 7200 mg/L

Figure 4.7. demonstrated that MLSS concentrations of the pretreated sludge samples decreased from 7200 mg/L to 6020 mg/L and 6310 mg/L after applications of Advanced Fenton and Classic Fenton pretreatment respectively. Kim et al. (2009) investigated the efficiency of hydrogen peroxide oxidation for total solids reduction. They noticed that total solids content of the sludge was decreased from 14850 mg/L to 9960 mg/L when 1.6M hydrogen peroxide was added to sludge sample. In the same way, Dytczak et al. (2007) investigated a decrease in the TSS concentration by applying ozone treatment to the sludge samples.

These results also showed that more hydroxyl radicals were produced for the disruption of cell walls due to faster recycling of iron species in Advanced Fenton Process. Because more cells were disrupted, high amount of intracellular materials were released and higher sCOD values were obtained after Advanced Fenton application. By observing these data it can be concluded that there is a correlation between the disruption of cell wall and the increase in the soluble COD (Dytczak et al., 2007). Similarly, Tokumura et al.

(2007) observed that after 10 hours of photo-Fenton reaction MLSS concentration of the pretreated sludge sample decreased from 3000 mg/L to 912 mg/L.

4.7 Effect of Advanced Fenton Process on Sludge Dewaterability

4.7.1 Capillary Suction Time Analysis

The influence of Advanced Fenton Process on sludge dewaterability, in terms of filterability, was analyzed by measuring CST of the sludge samples having different MLSS concentrations.

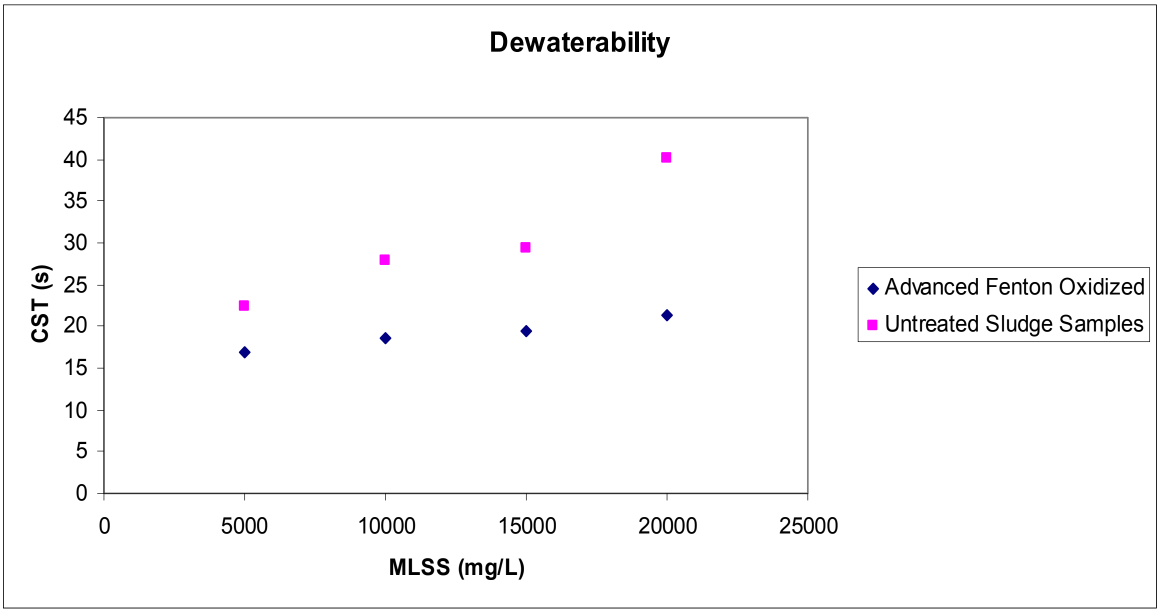


Figure 4.9. Effect of Advanced Fenton Process on the CST value of the sludge samples. Fe = 100 mg/L, H_2O_2= 4 g/L, reaction time =1 hour, pH = 3.0, mixing rate = 120 rpm

The CST results shown in Figure 4.8. demonstrated that Advanced Fenton oxidation led to a reduction in the CST values of the sludge samples. It was observed that at MLSS concentration of 20000 mg/L, CST of the untreated sludge sample was 40.2 s. However the CST value decreased to 21.3 s after Advanced Fenton oxidation. The decrease in the CST values indicated that the dewaterability of the Advanced Fenton oxidized sludge samples was improved. The main reason of the improvement in sludge filterability can be explained by the fact that Fenton oxidation caused to an increase in particle size of the sludge samples due to acidic pH conditions and generation of ferric hydroxide and ferric hydroxo complexes. Similarly, Lu et al. (2004) also concluded that Fenton pretreatment process led to an improvement in the sludge dewaterability characteristics.

The CST values also demonstrated that as the solid concentration increased sludge dewaterability deteriorated. Pham et al. (2010) stated that higher solid content meant more particles which may cause to an increase in the values of the CST measurements.

In order to show the influence of different disintegration methods on CST values of the sludge samples, CST analysis were performed after Classic Fenton Process, Advanced Fenton Process and only Hydrogen Peroxide (H_2O_2) oxidation. The results are given in Table 4.1. Operating conditions were as follows; Fe = 100 mg/L, H_2O_2= 4 g/L, mixing rate = 120 rpm, reaction time = 1 hour, pH = 3.0 (only for Fenton applications), MLSS = 10260 mg/L.

Table 4.1. Effect of different disintegration techniques on CST of the sludge samples having 10260 mg/L of MLSS concentration.

Sludge Type	**CST (s)**
Untreated Sludge	25.2
Classic Fenton Oxidized	21.9
Advanced Fenton Oxidized	19.1
Hydrogen Peroxide Oxidized (without pH adjustment)	39.3

The results in Table 4.1. clearly showed that both Advanced and Classic Fenton Processes enhanced sludge dewaterability. Therefore there was not an important difference between the CST values of the Advanced and Classic Fenton oxidized sludge samples. However when only hydrogen peroxide was added to the sludge sample, CST value increased from 25.2s to 39.3s. This observation demonstrated that, contrary to Fenton Process, hydrogen peroxide pretreatment caused to the deterioration of the sludge dewaterability. The main reason was that hydrogen peroxide application caused to the decrease in particle size. As a result of the decrease in the particle size, bound water content increased leading to an increase in the CST values. In agreement of this observation Chu et al. (2000) also stated that high amount of water could be attached on the large surfaces provided by the small particles causing to the increase in the CST values and poorer dewaterability characteristic of the sludge samples.

4.7.1.1 Particle Size Analysis. In order to investigate the influence of the particle size distribution on sludge dewaterability, particle size analysis was carried out after the application of Advanced Fenton Process and hydrogen peroxide oxidation to the untreated sludge samples. Results were given in Figure 4.9. and Figure 4.10.

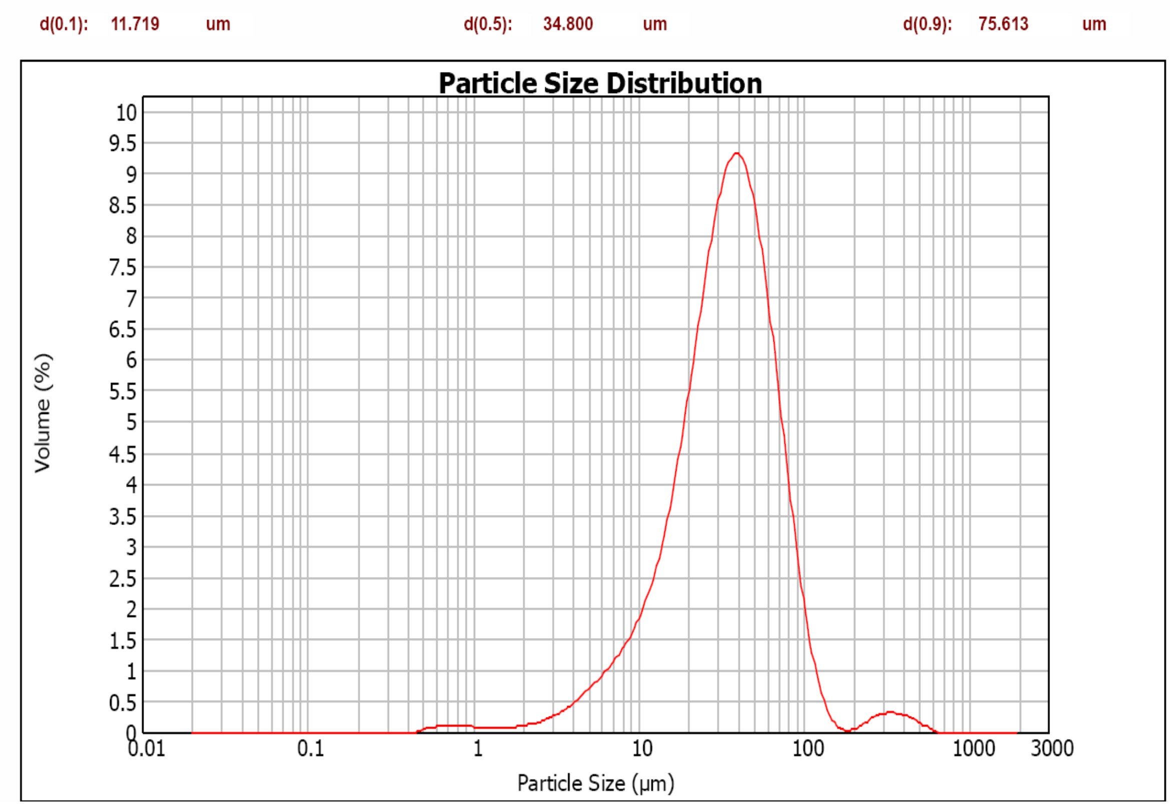
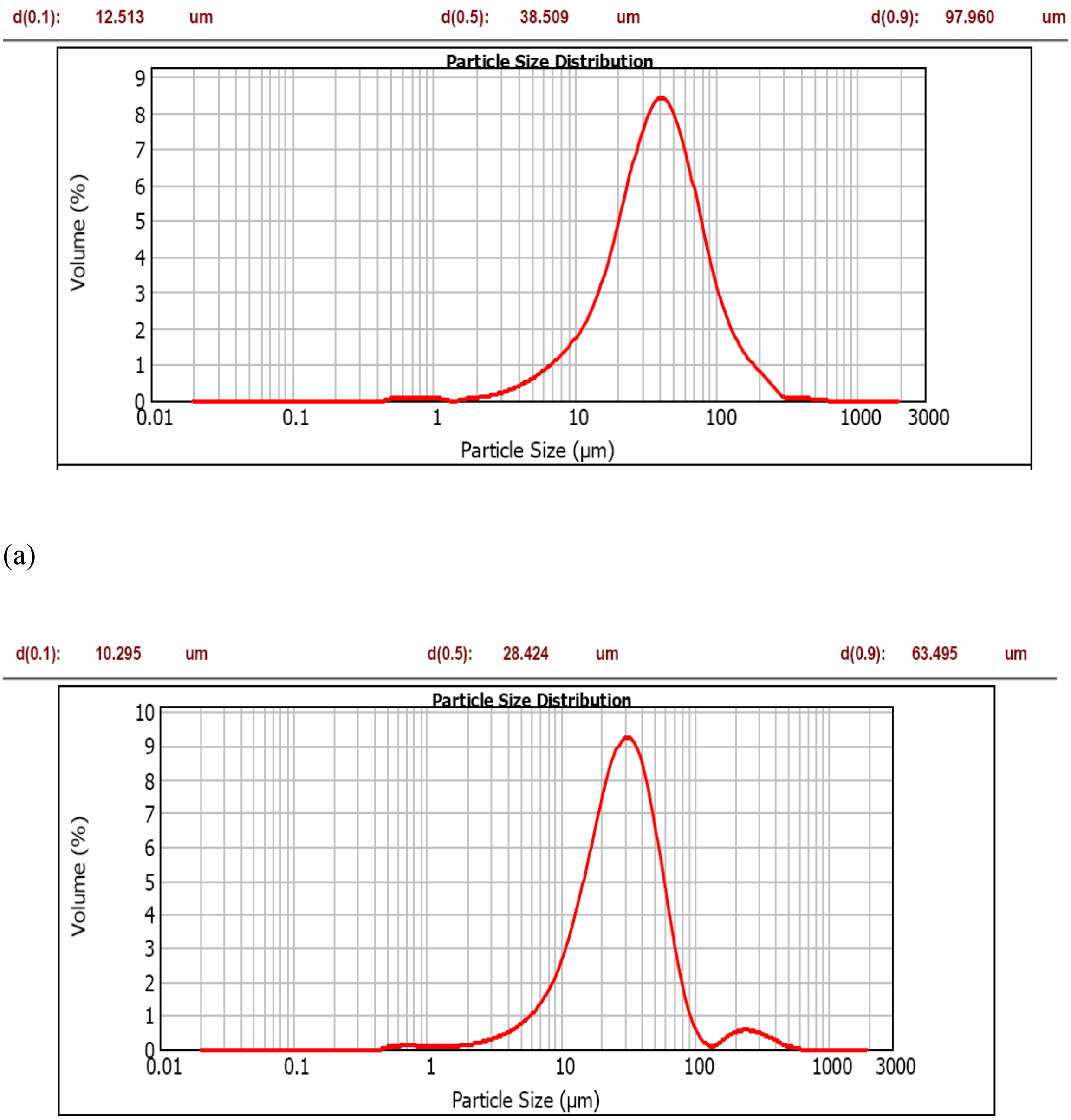


Figure 4.10. Particle Size distribution of the untreated sludge sample. MLSS = 10000 mg/L

Figure 4.9 showed that sludge particles in the range of 10-100 µm occupied the highest volume of the sludge solids found in the untreated sludge sample. This particle size range occupied approximately 9.5% by volume. It was also observed that there was an unimportant volume occupied by the sludge particles in the range of 100-1000 µm. The cut-off diameter (d_{50}) particle size was measured as 34.8 µm. The change in the particle size distribution after hydrogen peroxide and Advanced Fenton oxidation was shown in Figure 4.10. For hydrogen peroxide oxidation 4 g/L of hydrogen peroxide was used and no pH adjustment was applied. To perform Advanced Fenton Process 100 mg/L of zero valent iron, and 4 g/L of H_2O_2 were used.



(a)

(b)

Figure 4.11. Change in particle size distribution. (a) Advanced Fenton oxidation Fe = 100 mg/L, H_2O_2= 4 g/L, pH = 3.0, reaction time = 1 hour, mixing rate 120 rpm. (b) Hydrogen peroxide oxidation H_2O_2= 4 g/L, reaction time = 1 hour, mixing rate = 120 rpm

Figure 4.10.a demonstrated that Fenton Process cause to an increase in particle size while hydrogen peroxide cause to a decrease. The cut-off diameter (d_{50}) particle size of the untreated sludge sample was measured as 34.8 µm. However after Advanced Fenton oxidation d_{50} particle size increased to 38.509 µm but it decreased to 28.424 µm as a result

of hydrogen peroxide oxidation. The results obtained in Figures 4.9 and 4.10 were summarized in Table 4.2.

Table 4.2. Particle Size Distribution of untreated and pre-treated sludge samples.

Sludge Type	d_{10} particle size (µm)	d_{50} particle size (µm)	d_{90} particle size (µm)
Untreated Sludge	11.719	34.800	75.613
Hydrogen Peroxide Oxidized (without pH adjustment)	10.295	28.424	63.495
Advanced Fenton Oxidized	12.513	38.509	97.960

Pham et al. (2010) explained that ferric hydroxide and ferric hydroxo complexes generated by Fenton reaction caused to coagulation of sludge particles and thus particle size of sludge increased. The authors observed that particle size of Fenton oxidized sludge sample increased compared to that of the untreated sludge. Pham et al. (2010) also analyzed the dewaterability in terms of CST and they found that CST values decreased after Fenton treatment. The main reason for the decrease in CST values can be attributed to the increase in particle size. The decrease in the particle size after hydrogen peroxide oxidation can be explained as that hydroxyl radicals attacked on sludge particles led to disruption of cells of the microorganism. Similarly, Kim et al. (2009) found that median size of the untreated sludge was around 34.5 µm and it was reduced to 13.5 µm after hydrogen peroxide oxidation.

4.7.2. Sludge Compactibility Analysis

Sludge compaction analysis was performed for both Advanced and Classic Fenton oxidation and hydrogen peroxide oxidation. Compactibility of sludge samples were measured by centrifuging the sludge samples at 2800 g (4850 rpm) for 30 minutes. After centrifugation, the volume of the sludge cakes was measured. The experiments were conducted by using 100 mg/L of iron and 4 g/L of H_2O_2. The results obtained were given in Table 4.3.

Table 4.3. Effect of different disintegration techniques on sludge compactibility. MLSS = 10260mg/L.

Sludge Type	**Compactibility Cake solid concentration (%)**
Untreated Sludge	7.4
Hydrogen Peroxide Oxidized (without pH adjustment)	9.5
Classic Fenton Oxidized	10.3
Advanced Fenton Oxidized	10.3

Sludge dewaterability in terms of CST was enhanced for Fenton oxidation. CST of the sludge samples decreased after the application of Advanced Fenton Process. On the other hand sludge compactibility, in terms of cake dry solid content, increased by Fenton oxidation indicating an improvement in the sludge dewatearbility. The results given in Table 4.3. showed that cake dry solid content of the centrifuged sludge samples increased from 7.4 % to 10.3 % for both Advanced and Classic Fenton Processes. These results showed that Advanced and Classic Fenton applications caused to similar effects on the sludge compaction. In agreement with these results, Neyens et al. (2003) also reported a 30% increase in the cake dry solid content as a result of the Fenton pretreatment. Similarly Lu et al. (2004) observed a reduction in the moisture content of the sludge samples related to the Fenton oxidation. The increase in the cake dry solid content can be attributed to the change in the water distribution of the biological sludge by releasing a considerable amount of interstitial water trapped inside microorganisms due to the cell disruption (Erdincler and Vesilind 2000).

The results also demonstrated that hydrogen peroxide application also led to an improvement in the cake dry solid content of the sludge. As shown in previous section hydrogen peroxide oxidation caused poorer dewataerability by increasing CST value of the untreated sludge. However compactibility results indicated that sludge dewaterability by centrifugation could be enhanced by hydrogen peroxide oxidation.

4.8. Effect of Advanced Fenton Process on Settleability

In order to investigate effect of AFP on settleability, Sludge Volume Index (SVI) of the sludge samples were measured. Before measuring SVI values, MLSS concentrations of the sludge samples were adjusted to 5000 mg/L by using effluent of the wastewater treatment facility of the petrochemical plant.

The SVI of the untreated sludge was measured as 57 ml/g. When only 4 g/L of hydrogen peroxide was added to the sludge sample, without pH adjustment, the SVI of the sludge decreased to 51.2 ml/g indicating an enhancement in settleability. Kim et al. (2009) related this improvement in settleability to the decrease in particle size after hydrogen peroxide oxidation. The authors observed that SVI of the hydrogen peroxide oxidized sludge decreased to 62.9 ml/g, while the SVI of the untreated sludge sample was 67.6 ml/g. Figure 4.11 shows the effect of hydrogen peroxide oxidation on the sludge settleability.

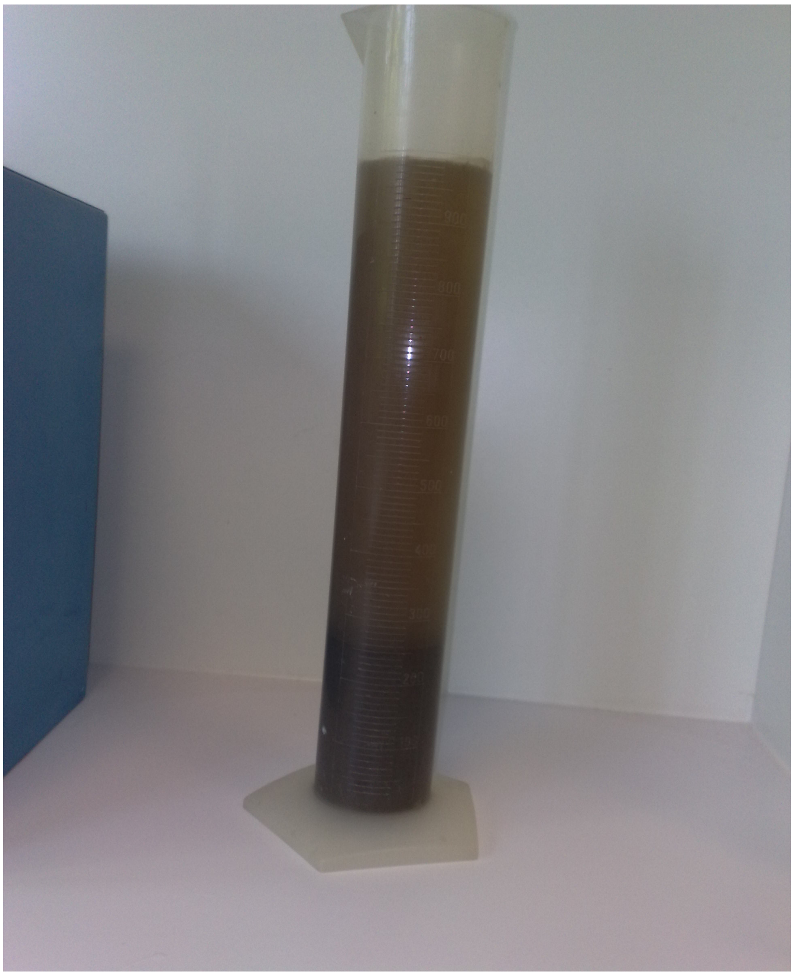


Figure 4.12. Effect of Hydrogen Peroxide oxidation on the sludge settleability. H_2O_2 = 4 g/L, MLSS = 5000 mg/L, reaction time = 1 hour, mixing rate = 120 rpm, pH = 6.9

The SVI result of the Advanced Fenton oxidized sludge sample could not be measured due to the deterioration in the settleability of the sludge caused by Advanced Fenton Process. It was observed that some part of the sludge particles settled properly but the other part floated on the surface of the graduated cylinder. Figure 4.12. demonstrates the influence of the Advanced Fenton Process on sludge settleability

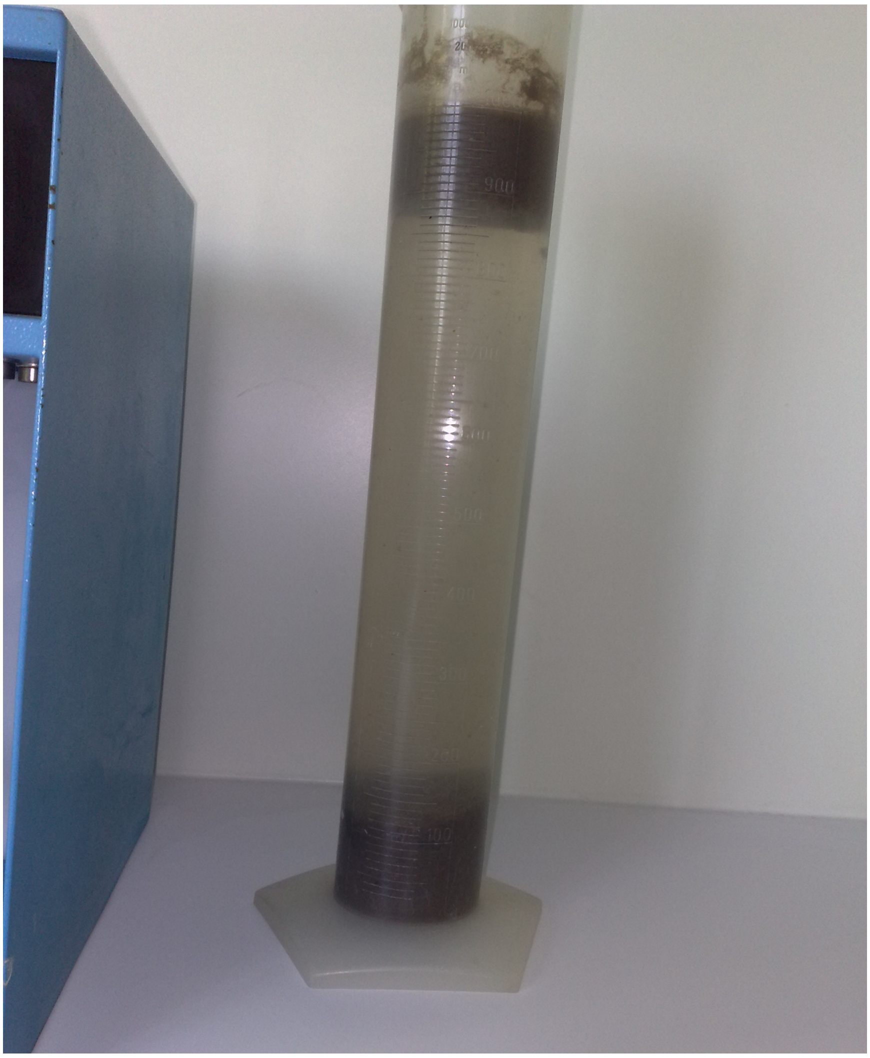


Figure 4.13. Effect of Advanced Fenton Process on sludge settleability. Fe = 100 mg/L H_2O_2 = 4 g/L, MLSS = 5000 mg/L, reaction time = 1 hour, mixing rate = 120 rpm, pH = 3.0

Particle size distribution analysis showed that AFP cause to an increase in sludge particle size due to the coagulant effect of ferric hydroxides complexes. Jin et al. (2003) observed that large flocs caused poorer settleability characteristic. The authors observed that SVI value increased with increased particle size. This can be explained as that due to increase in the particle size caused to fluffy floc structure and prevented sludge settling.

4.9 Effect of Advanced Fenton Process on Viscosity

The influence of the Advanced Fenton Process on the rheology of the sludge was analyzed by measuring viscosity of the sludge samples. The influence of different methods on viscosity is given in Table 4.4. During experimental procedure both Classic and Advanced Fenton oxidation was conducted by using 100 mg/L of iron and 4 g/L of hydrogen peroxide. The MLSS concentration of the samples was 10000 mg/L and the reaction time was 1 hour. Because viscosity is highly affected by the temperature, all measurements were carried out at ambient temperature of 25 °C.

Table 4.4. Effect of different disintegration methods on viscosity. MLSS = 11200 mg/L

Sludge Type	**Viscosity (cP)**
Untreated Sludge	21.6
Hydrogen Peroxide Oxidized (without pH adjustment)	24.3
Classic Fenton Oxidized	25.6
Advanced Fenton Oxidized	26.4

The results obtained demonstrated that viscosity of the sludge samples increased depending on the disintegration method used. The highest value was measured after applying Advanced Fenton pretreatment to the sludge sample. However the results obtained were very close to each other and an important change in viscosity values was not observed. Contrary to the results obtained in this study, many researchers concluded that disintegration caused to a reduction in viscosity of the sludge. Kim et al. (2009) reported that viscosity of the sludge samples decreased after hydrogen peroxide application. Pham et al. (2010) also found that viscosity of the sludge samples decreased after 100 minutes of the Classic Fenton reaction. According to Pham et al. (2010) degradation of the EPS and interaction cleavage due to the free hydroxyl radicals and acid hydrolysis during Fenton reaction caused to a decrease in strength of sludge flocs and decreased in viscosity. Tixier et al. (2003) observed that as pH decreased viscosity of the sludge samples decreased. The decrease in electrostatic repulsions between flocs at low pH values, allowed a favorable flow and was responsible for the decrease in the viscosity (Tixier et al. 2003).

Sanin (2002) observed that as the pH increased viscosity increased considerably. Sanin (2002) reported that expanded floc structure at high pH value created a higher resistance to flow due to an increase in the exposed cross-sectional area. For that reason at low pH values viscosity is lower compared to that of high pH values.

The low increase observed in viscosity, in the present study, can be linked to the slimy structure of the sludge samples due to the release of intracellular materials out of the sludge cells.

5. CONCLUSIONS

This study investigates the effect of Advanced Fenton Process on excess wastewater sludge disintegration. 100 mg/L of iron (Fe^0) and 4 g/L of hydrogen peroxide (H_2O_2) were used as Fenton oxidation reagents. Increase in soluble COD was measured to show the influence of AFP on sludge disintegration. Different operational parameters, pH, mixing rate, Fenton reagent dosages, reaction time, affecting the efficiency of AFP were studied. Dewaterability was determined by measuring CST values. Compactibility was determined by measuring cake solids concentration. The effect of AFP on particle size distribution was analyzed by instrumental method. Rheology analysis was carried out by measuring viscosity of the sludge samples.

Based on the results of the study the following results can be drawn;

- Advanced Fenton pretreatment process caused to disintegration of the sludge samples and improved biodegradability by leading to an increase in the soluble COD of the sludge samples.

- The disintegration degree of the sludge sample was 5.8% when 100 mg/L of zero valent iron and 4 g/L hydrogen peroxide were used. The increasing iron and hydrogen peroxide concentrations caused to an increase in the soluble COD due to the formation of hydroxyl radicals.

- Fenton Process is highly dependent on pH of the sample. At ph values ≥4 Fenton Process was suppressed due to the precipitation of iron as $Fe(OH)_3$. The optimum value of pH for Advanced Fenton Process was found to be 3.0.

- Mixing rate also affects the efficiency of AFP. Experiments demonstrated that when mixing rate increased to 120 rpm soluble COD value increased about 171%. However not an important increase in the sCOD was observed in the unmixed sludge sample.

- The increase in MLSS concentration caused to a decrease in the disintegration efficiency of the Advanced Fenton Process. The highest increase in the sCOD was observed at the lowest MLSS concentration.

- A correlation was found between reaction time and decrease in MLSS concentration of the sludge sample. As the reaction time of the AFP increased soluble COD concentration increased continuously. Experiments demonstrated that MLSS concentration decreased simultaneously with the increase in sCOD related to destruction of the cell wall of the microorganisms by releasing intracellular material to bulk solution.

- Particle size analysis showed that the Advanced Fenton Process increased the particle size of the sludge flocs due to the coagulant effect of ferric hydroxide.

- Advanced Fenton Process caused to an enhancement in sludge dewaterability. The CST values of the Advanced Fenton oxidized sludge samples decreased compared to those of untreated samples. The increase in particle size was considered as the main reason for the improvement in the dewaterability.

- Compactibility tests, based on centrifugation, showed that AFP improved sludge compactibility in terms of cake dry solids content. Cake dry solids content of the sludge samples increased after Fenton oxidation.

- Advanced Fenton Process deteriorated the settling properties of the sludge samples.

APPENDIX A: CALIBRATION CURVE

The calibration curve prepared for chemical oxygen demand analysis is given in Figure A.1.

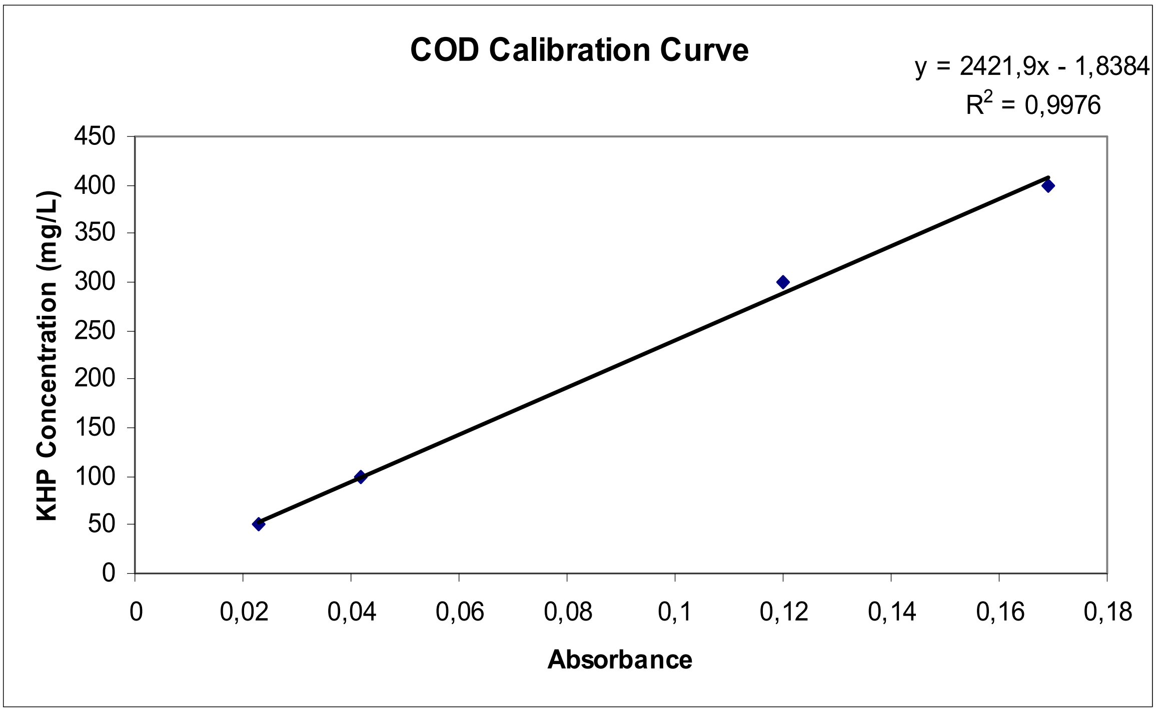


Figure A.1. Calibration curve prepared for COD analysis

APPENDIX B: SUMMARY OF THE DISINTEGRATION RESULTS

Table A.1. Effect of Advanced Fenton Process on Sludge Disintegration

Iron Concentration (mg/L)	Hydrogen Peroxide Concentration (g/L)	sCOD Concentration (mg/L)	Increase in the sCOD (%)	pH	DD_{COD}(%)
20	4	161.2	67.5	3	2.2
40	4	189.4	96.8	3	3.2
60	4	212.8	121.2	3	4.07
80	4	226.9	135.8	3	4.5
100	4	262.2	172.5	3	5.8

Table A.2. Effect of Classic Fenton Process on Sludge Disintegration

Iron Concentration (mg/L)	Hydrogen Peroxide Concentration (g/L)	sCOD Concentration (mg/L)	Increase in the sCOD (%)	pH	DD_{COD}(%)
20	4	115.99	20.5	3	0.69
40	4	120.6	25.3	3	0.85
60	4	130	35.1	3	1.18
80	4	144	49.6	3	1.68
100	4	194	101.6	3	3.42

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