SONOLYTIC AND SONO-FENTON PRETREATMENT OF WASTE ACTIVATED SLUDGE

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Başak Savun

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SONOLYTIC AND SONO-FENTON PRETREATMENT OF WASTE ACTIVATED SLUDGE

APPROVED BY:

Prof. Dr. Orhan Yenigün ....
(Thesis Advisor)

Prof. Dr. Nilsun H. İnce ....
(Thesis Co-advisor)

Prof. Dr. Işıl Balcıoğlu ....

Prof. Dr. Ferhan Çeçen ....

Prof. Dr. Beyza Üstün ....

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ABSTRACT

The pretreatment of waste activated sludge (WAS) to facilitate solubilization and biodegradability is most common using thermal, mechanical (e.g. ultrasound, high pressure homogenization), chemical (oxidation) and alkali methods. Ultrasonic disintegration is one of the most effective one owing to the capacity of ultrasound to break-up microbial cells and extract the intracellular material. The mechanism involves deagglomeration of biological flocs and disruption of large organic particles via the shear forces produced by high pressure waves during the implosion of cavitation bubbles. A less common method of WAS pretreatment is the Fenton process, in which the production and diffusion of hydroxyl radicals through the microbial cell membrane lead to the oxidative decomposition of the cell wall. Moreover, hydroxyl radicals are highly effective in oxidation of recalcitrant compounds in the sludge, the biodegradable products of which are further subject to biochemical treatment.

The objective of this study was to examine the impact of low-frequency ultrasound (US) on disintegration and dewatering characteristics of waste activated sludge originating from municipal wastewater treatment plants, and to enhance the efficiency of the process by combining it with either the classical Fenton or an "advanced" Fenton process that utilizes metallic zero-valent iron powder instead of ferrous iron as the chemical reagent.

The results of the study showed that pretreatment of WAS by short wave ultrasonic irradiation in the presence of Fe^{2+}/H_2O_2 or Fe^0/H_2O_2 is far more effective than each single process in terms of the degree of solubilization and bacterial inactivation. It was also found that US with the advanced-Fenton process was more efficient than US with the classical-Fenton, because closely equivalent yields were achieved by using a two-fold lower dose of hydrogen peroxide in the former. The finding was attributed to the power of ultrasound to disintegrate heterogenous surfaces, thus increasing surface defects and the number of active sites while inducing a continuous cleaning action.

ÖZET

Aktif çamurun çözünürlük ve biyolojik parçalanabilirliğinin arttırılması amacıyla ön arıtımı en yaygın olarak termal, mekanik (ultrason, yüksek basınçlı homojenleştirme), kimyasal (oksidasyon) ve alkali yöntemlerle yapılmaktadır. Ultrasonik ön arıtım ultrasonun mikrobiyal hücre duvarını bozarak çözünür maddelerin hücre dısına salınması kapasitesine bağlı olarak en etkili ön arıtım yöntemlerinden biridir. Sistemin mekanizması kavitasyon balonlarının patlaması sırasındaki yüksek basınç dalgalarıyla oluşan kesme kuvvetlerinin biyolojik flokların dispersiyonunu ve büyük organik materyallerin parçalanmasını içermektedir. Aktif çamur ön arıtımında daha nadir kullanılan bir yöntem olan Fenton prosesi ise hidroksil radikalleri oluşmakta ve mikrobiyal hücre membranına difüze edilerek hücre duvarının oksidatif bozunmasını sağlamaktadır. Hidroksil radikalleri çamur içersindeki bozunmaya dirençli bileşiklerin biyokimyasal arıtma öncesinde biyolojik olarak parçalanabilir ürünlere okside edilmesinde oldukça etkilidir.

Bu çalışmanın temel amacı düşük dalga boylarında ultrasonik ön arıtımın kentsel aktif çamurun parçalanma ve susuzlaştırma karakteristiklerindeki etkisinin değerlendirilmesidir. Çalışmanın ikinci amacı ise aktif çamurun münferit ultrason ve Fenton oksidasyonu ile ön arıtımının verimini arttırmak üzere ultrason, klasik Fenton veya demirin iki değerlikli ferrous formu yerine sıfır değerlikli metalik parçacıklarının kullanıldığı “ileri” Fenton oksidasyon proseslerini içeren hibrid bir proses ile ön arıtımının çalışılmasıdır.

Çalışma kısa-dalga ultrason ile klasik ya da “ileri” Fenton reaksiyonunu içeren hibrit tekniklerin çamurun parçalanması ve bakterileri etkisiz hale getirmesi bakımından bu iki tek prosesten daha etkili olduğunu göstermiştir. İleri Fentonun ultrasonla kombinasyonu prosesinde klasik Fentona göre iki kat düşük hidrojen peroksit dozu kullanılmasına rağmen oldukça yakın sonuçların elde edilmesi ultrasonun heterojen yüzeyleri parçalama böylece yüzey bozukluklarını ve aktif bölgeleri arttırarak sürekli bir temizleme hareketi yaratma gücünden kaynaklanmaktadır.

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LIST OF SYMBOLS/ABBREVIATIONS

Symbols	Explanation	Unit used
AD	Anaerobic Digestion	
AS	Activated Sludge	
BSA	Bovine Serum Albumin	
BU	Boğaziçi University	
COD	Chemical Oxygen Demand	mg L^{-1}
CST	Capillary Suction Time	s
DD_{COD}	Degree of Disintegration	%
DOC	Dissolved Organic Carbon	mg L^{-1}
DS	Dry Solids	mg L^{-1}
DW	Distilled Water	
ODS	Organic Dry Solids	mg L^{-1}
EPS	Extracellular Polymeric Substances	
PS	Primary Sludge	
sCOD	Soluble Chemical Oxygen Demand	mg L^{-1}
SR	Specific Resistance	
TCOD	Total Chemical Oxygen Demand	mg L^{-1}
TDN	Total Dissolved Nitrogen	mg L^{-1}
TS	Total Solids	mg L^{-1}
TUHH	Technical University of Hamburg Harburg	
US	Ultrasonication	
VS	Volatile Solids	mg L^{-1}
WAS	Waste Activated Sludge	
ZVI	Zero Valent Iron	

1. INTRODUCTION

Conventional activated sludge processes for wastewater treatment transform organic pollutants into CO_2, water and biomass. Due to stringent sludge disposal regulations worldwide, processing and ultimate disposal of excess biomass known as waste activated sludge (WAS) is one of the major problems in biochemical wastewater treatment, because it accounts for approximately 35-60% of the whole operation cost (Neyens et al., 2003). As a consequence, there are numerous studies world-wide on the development of low-cost WAS treatment or stabilization technologies. The most favorable of all so far has been anaeorobic digestion, which is well recognized with its capability for energy-production.

The cost-effectiveness of anaerobic digestion (AD) is not only based on its capacity to produce "renewable" energy in form of methane gas, but also for rendering high degrees of mass reduction and stabilization. However, the process has a major drawback with its slow hydrolysis step, which leads to large fermenters and excessive space requirements. Thus, the only way to enhance the performance and efficiency of AD processes is to accelerate the rate-limiting hydrolysis step (Mao et al., 2004; Eastman and Ferguson, 1981), which is possible by pre-treatment of the sludge to improve the biodegradability of the solids.

Pretreatment of WAS for enhanced solids biodegradability is possible by biological, thermal, mechanical (ultrasound, high pressure, lysis), chemical (oxidation, ozonation) and alkali methods (Carrérea et al., 2010). Amongst them, ultrasonic pretreatment has become very popular due to several inherent merits of US, such as no chemical requirements, efficient sludge disintegration, and improvements in digester stability (Tiehm et al., 2001).

Ultrasonic disintegration of waste activated sludge is a well-known method of breaking up microbial cells to extract the intracellular material in them (Harrison, 1991). Ultrasound de-agglomerates biological flocs and disrupts large organic particles into smaller size particles by the formation and implosion of cavitation bubbles. The shear forces produced by high pressure waves break down bacterial cell walls and release intracellular substances into the aqueous phase (Tiehm et al., 2001). Moreover, ultrasonic pretreatment improves volatile solids reduction and biogas production. The only disadvantage of ultrasonic methods is that they require substantial energy for effective disintegration of high-solid wastes. However, the high energy requirements can be reduced by combining ultrasonication with chemical processes to allow different mechanisms of action for disintegration.

The classical Fenton process is well-known for its outstanding performance in the destruction of organic pollutants contained in wastewaters, sludge and contaminated soils. The process involves cyclic reactions between H_2O_2 and Fe^{2+} to produce hydroxyl radicals, which are highly capable of oxidizing recalcitrant organic pollutants. Research on the pre-treatability of WAS by the Fenton process has shown that it improves the disintegration and dewatering characteristics of sludge (Neyens et al., 2003; Takumura et al., 2009; Pham et al., 2010).

The objective of this study was to test the pretreatability of WAS by low frequency ultrasound via the mechanical shear forces that are effective for microbial cell disintegration, and to increase the effectiveness of the method by combining it with either the classical or the “advanced” Fenton process that utilizes zero valent iron in powder form. The literature shows that ultrasonication and classical Fenton process have been tested separately for sludge pretreatment, but the two has not been applied together so far. Moreover, there is no study that reports advanced Fenton applications to WAS, nor its combination with ultrasound.

The following sections present a literature review on the theory of cavitation, principles of sludge pretreatment and improved sludge properties following either ultrasonic or classical Fenton pretreatment.

2. THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1. Types of Sludge from Municipal Wastewater Treatment Plant

The most common suspended-growth process used for municipal wastewater treatment is the activated sludge process as shown in Figure 2.1. Sludge generated from municipal wastewater treatment plants are mainly primary sludge (PS) and activated sludge (AS). After handling them in anaerobic or aerobic treatment plants, the end-product is called “digested sludge”, which is associated with gas output (Hanjei, 2010). Table 2.1 shows values of gas production from primary and activated sludge.

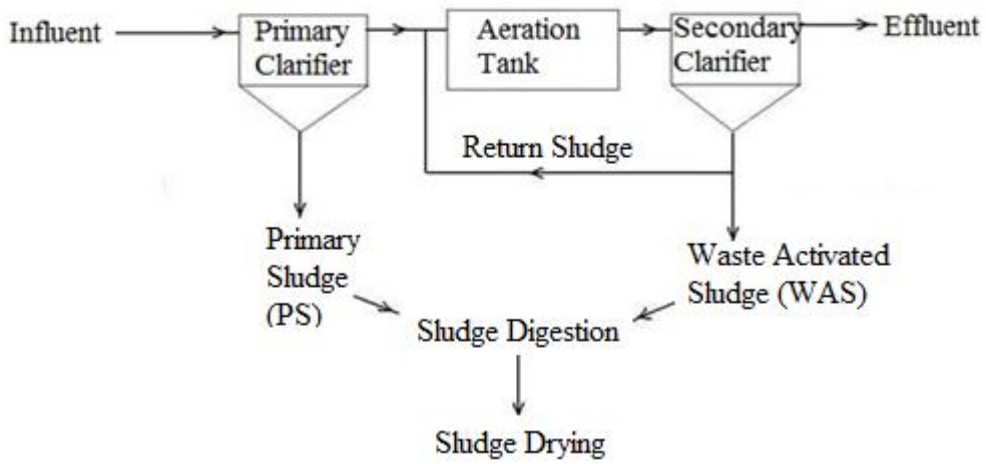


Figure 2.1. The typical layout of an activated sludge process

Primary sludge also called “raw sludge” comes from the bottom of the primary clarifier. It is more easily biodegradable due to the presence of more easily digestible carbohydrates and fats, compared to AS, which consists of complex carbohydrates, proteins and long chain hydrocarbons (Gary et al., 2007). Hence, the production of biogas is also easier from PS than from AS (Hanjei, 2010).

AS also called “excess sludge” or “waste activated sludge” comes from the secondary wastewater treatment process. It is the result of overproduction of microorganisms in the activated sludge process. AS consists largely of biological mass, mainly protein (30%), carbohydrate (40%) and lipids (30%) in particulate form (Lin et al., 1999).

After anaerobic digestion of primary and activated sludge, the residual product is digested sludge. The digested sludge is lighter in mass, less odorous, safer with respect to pathogens and more easily dewatered than the primary and activated sludge (Ek, 2005).

Table 2.1. Gas production from primary sludge and activated sludge (Hanjei, 2010).

Reference	**Gas production (mL g VS^{-1})**	
	Primary sludge	**Activated sludge**
Sato et al. (2001)	612	380
Speece (2001)	362	281
Rittman and McCarty (2000)	375	275

2.2. Sludge Stabilization in a Wastewater Treatment Plant

The activated sludge process has been widely applied to treat wastewater since it has advantages of low running cost and high degradation efficiency. However, proper management of excess sludge poses considerable challenge to the wastewater treatment operators due to the stringent disposal regulations. Treatment and disposal of excess biomass produced during biological treatment of wastewater mainly contribute to its total operation costs reaching as high as 50–60% . Therefore, treatment of excess sludge is very important in activated sludge wastewater treatment system.

The objectives of the overall sludge treatment is to remove its organic material and water, to reduce volume and mass, to remove biodegradable material thus to prevent subsequent odours and pathogens. Among all stabilization methods anaerobic digestion (AD) is the most commonly applied process because it has the ability to produce a net energy gain in form of methane gas. In many cases, sufficient digester gas can be produced by anaerobic digestion of municipal wastewater to meet most of the energy needs for plant operation (Metcalf and Eddy, 2002). The advantages/disadvantages of anaerobic processes over aerobic processes for wastewater and sludge treatment are summarized in Table 2.2.

Table 2.2. Advantages and disadvantages of anaerobic processes compared to aerobic processes (Metcalf and Eddy, 2002).

Advantages	**Disadvantages**
Less energy required	Longer start-up time to develop necessary biomass inventory
Less biological sludge production	May require alkalinity and/or specific ion addition
Fewer nutrients required	May require further treatment with an aerobic treatment process to meet discharge requirements
Methane production, a potential energy source	Biological nitrogen and phosphorus removal is not possible
Smaller reactor volume required	Much more sensitive to the adverse effect of lower temperatures on reaction rates
With acclimation most organic compounds can be transformed	May be more susceptible to upsets due to toxic substances
Rapid response to substrate addition after long periods without feeding	Potential for production of odors and corrosive gases

2.3. Mechanism of Anaerobic Digestion

As mentioned previously, the primary aim of anaerobic digestion of wastewater sludges is stabilization of organic matter with a concurrent reduction in odor, pathogen concentration and the mass of organic material. Conversion of biodegradable organic compounds to methane (CH_4) and carbon dioxide (CO_2) involves several groups of bacteria carrying out rather specific reactions (Parkin and Owen, 1986).

Methane formation in anaerobic digestion occurs in three stages namely (i) Hydrolysis (ii) Fermentation (also known as acidogenesis); and (iii) Methanogenesis. Five groups of bacteria, each deriving energy from a number of biochemical reactions, are thought to be involved. (Parkin and Owen, 1986). The three-stage scheme, involving five groups of bacteria, is shown in Fig 2.2.

Hydrolysis and liquefaction are conversion of complex and/or insoluble organic materials and higher molecular mass compounds into soluble organic materials by the help of extracellular, hydrolytic enzymes produced and excreted by the bacterial population for this specific purpose (Parkin and Owen, 1986). By such, organics become bioavailable for use by the bacteria of the next stage. Bioavailability refers to those materials that can pass through the cell wall due to their proper form and size. The hydrolysis step is significant because it provides food for the bacteria as bioavailable organics.

After hydrolysis the next step is fermentation. In the fermentation process, amino acids, sugars, and some fatty acids are degraded further. The principal products of fermentation are acetate, hydrogen, CO_2, and propionate and butyrate. The propionate and butyrate are also fermented further to produce hydrogen, CO_2, and acetate. Thus, the final products of fermentation and precursors of methanogenesis are acetate, hydrogen and CO_2. However, these steps are only conversion processes and therefore do not result in further stabilization (McCarty and Smith, 1986).

The last and the most important step is “methane formation” which provides actual stabilization of organic material in sludge. This step involves utilization of acetic acid and hydrogen (that form in the previous step) by methane-forming archaea to produce methane and carbon dioxide (Parkin and Owen, 1986). Figure 2.2 is a schematic diagram of the anaerobic digestion process, and the names of microorganisms that are responsible for each step.

The primary drawbacks of AD technology are high retention times and large digester volumes, which are consequences of low microbial conversion rates. Hence, pretreatment of sludge before AD is very important in order to increase the efficiency of the process by means of accelarating the slow hydrolysis step.

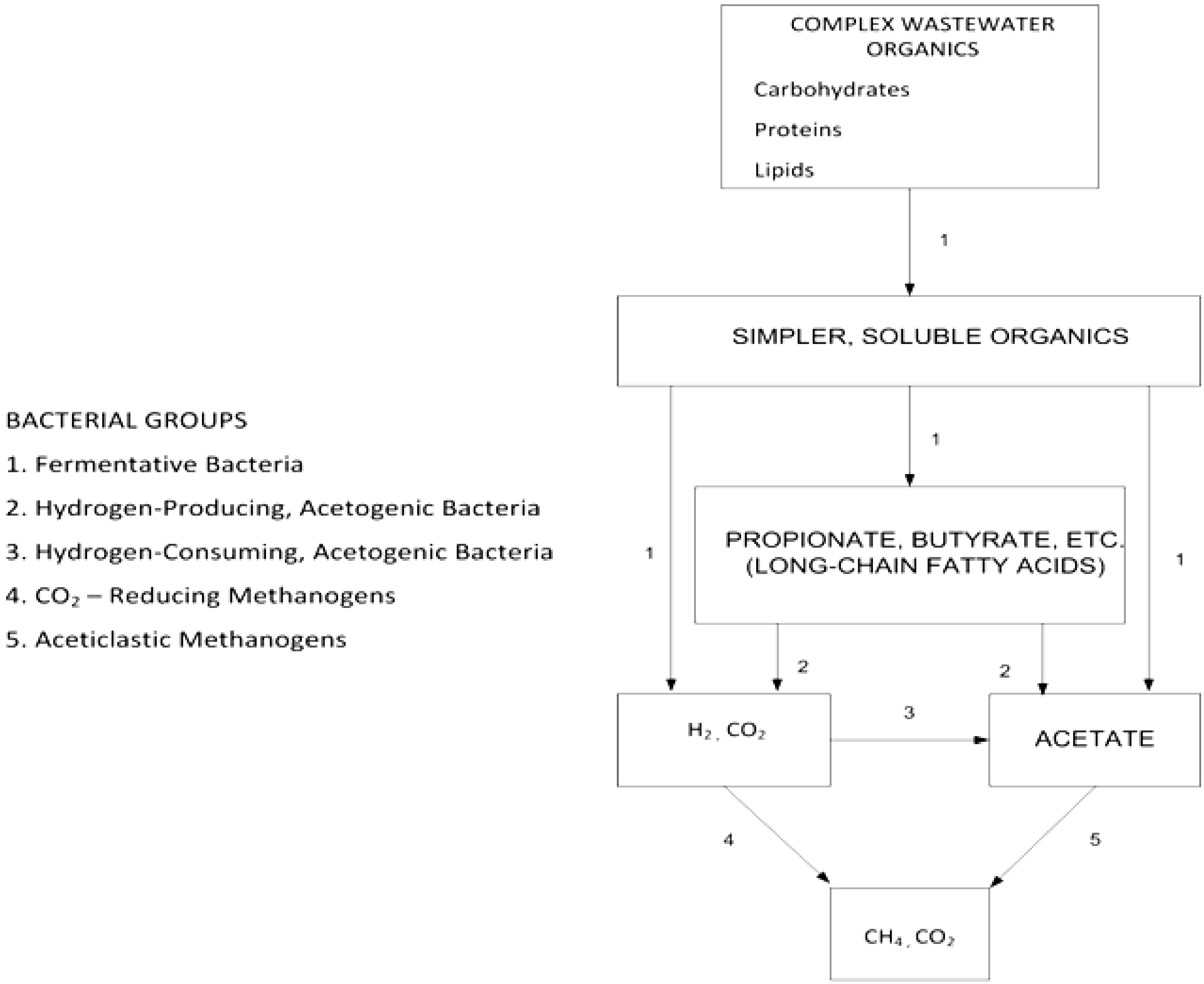


Figure 2.2. Three-stage Anaerobic Digestion Scheme (Parkin and Owen, 1986).

2.4. Overview of Sludge Pretreatment Methods

Waste activated sludge contains primarily large quantities of water, biomass and extracellular polymeric substances (Wang et al., 2006). Due to the rate-limiting cell lysis step, WAS is more difficult to digest than primary solids (Lafitte and Forster, 2002; Li and Noike, 1992). This is because the cell wall and the membrane of prokaryotic organisms are composed of complex organic materials which are recalcitrant to biodegradation (Pelczar et al., 1993).

Sludge pretreatment is an additional stage prior to the main digestion process, which is needed to solubilize and reduce the size of organic compounds in order to make them more easily biodegradable. The key point of sludge pretreatment is to rupture the cell wall and to facilitate the release of intracellular matter in order to produce bioavailable substrates to the AD process. Therefore, sludge pretreatment primarily aims to accelarate the first and also the rate-limiting step of anaerobic digestion, hydrolysis. Thus to reduce the retention time and to increase the biogas production.

The effectiveness of sludge pretreatment is expressed in terms of enhanced biodegradability of solids. Major techniques of biodegradability enhancement in sludge are mechanical, chemical, thermal and biological pretreatment.

2.4.1. Mechanical Pretreatment

Mechanical stress of the solids results in tensions and deformations. The cell of the microorganism resists the stress as long as the tension is lower than the strength of the cell wall. Mechanical methods of pretreatment include the following techniques:

- Stirred ball mill: Causes disintegration by the crushing of patricles.
- High Pressure Homogeniser: Causes disintegration by cavitation effects due to sudden pressure release.
- Ultrasound: Acoustically generates cavitation, which leads to sludge disintegration.
- Lysate Centrifuge: The partial destruction of excess activated sludge cells is achieved during sludge thickening by means of a centrifuge equipped with a disintegrating device. The disintegrating gear is mounted at the end of the flow of thickened sludge and does not influence the centrate quality (Dohányos et al., 1997).

The most popular mechanical means of sludge pretreatment is ultrasonication (US). Like all other mechanical methods (high pressure homogenization, ball milling, lysate centrifuge), ultrasound requires no chemicals but intensive energy (Weemaes and Verstraete, 1998). Ultrasound technique is discussed in detail in section 2.5.

2.4.2. Chemical Pretreatment

Most common chemical pretreatment methods are alkaline hydrolysis and chemical oxidation (ozonation and peroxidation).

2.4.2.1. Alkaline Hydrolysis. Amongst the chemical pretreatment methods, alkaline treatment is the most common due to its high efficiency. Alkali treatment destroys floc structures and cell walls by hydroxy anions. Chemical degradation and ionization of the hydroxyl groups lead to extensive swelling and subsequent solubilization of gels in sludge. After the destruction of extracellular polymer substances (EPS) the cell walls exposed to high pH can not withstand the appropriate turgor pressure. As such, cells are disrupted with the release of intracellular substances (Yiying et al., 2009). Arising from easy manipulation with no heating requirement alkali treatment is an easy and effective technique which can be operated at ambient temperature (Bunrith, 2008). Further advantages of the method are that it is compatible with the subsequent biological treatment process.

2.4.2.2. Oxidation. Ozone is a very strong oxidizing agent, which causes the hydrolysis and partial oxidation of organic matter in WAS. A complete oxidation is not expected (Goel et al., 2003, Carballa et al., 2007). Hydrogen peroxide (H_2O_2), is also an oxidant, but not as strong as ozone. Transition metal salts (e.g. iron salts), ozone and UV-light can activate H_2O_2 to form hydroxyl radicals, which are much stronger oxidants.

The main drawback of chemical pretreatment is that after chemical addition and hydrolysis, subsequent neutralisation is required. The cost of chemicals represents 54% of the total running cost (Weemaes and Verstraete, 1998). A less common chemical method is “thermochemical”, which utilizes excess chemicals and heat, and is therefore not cost-effective.

2.4.3. Thermal Pretreatment

Thermal pretreatment has been studied using a wide range of temperatures ranging from 60 to 270°C. Temperatures over 200°C have been found to result in the formation of refractory compounds (Climent et al., 2007). The most common treatment temperatures are between 60 and 180°C. Thermal pre-treatment in the temperature range from 60 to 180°C destroys the cell walls and makes the proteins accessible for biological degradation. The input of thermal energy is mostly realized by heat exchangers or by application of steam to the sludge (Neyens, 2003).

2.4.4. Biological Pretreatment

Biological pretreatment of sludge generally uses enzymes that are capable of increasing the degradation rate of activated sludge. Enzymic hydrolysis process was proposed by Mayhew et al. (2002) and was first used to kill pathogens. However, the enhancement of biogas production during anaerobic digestion aroused interest of researchers (Hanjei, 2010). Hydrolysis of the complex organic structures in sludge with the hydrolytic enzymes like glucosidases, lipases, and proteases is one of the applied methods and appears to be an efficient alternative. The only difficulty in this process is that the processed sludge is poor in dewaterability so that further chemical addition is necessary in dewatering units (Mayhew et al., 2002).

2.5. Ultrasonic Pretreatment

2.5.1. Ultrasound

Ultrasound is defined as any sound wave at a frequency above the normal hearing range of human ear (i.e. above 16 kHz). The relative frequencies of sound waves are shown in Figure 2.3.

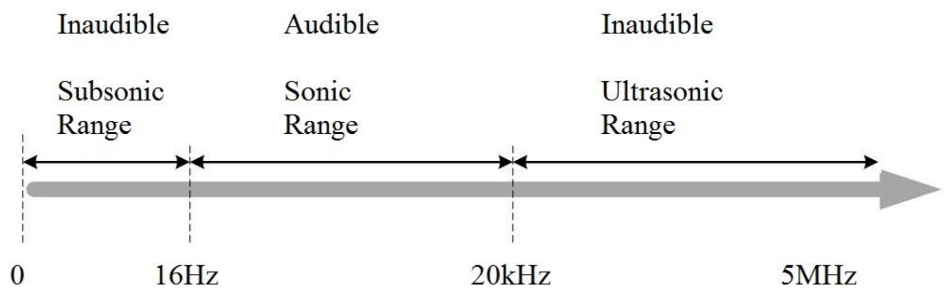


Figure 2.3. Nomenclarute of sound waves at different frequencies (Khanal et al., 2007).

<u>2.5.1.1.Ultrasonically-Induced Cavitation.</u> When ultrasound waves propagate in a medium such as sludge, they generate a repeating pattern of compressions and rarefactions in the medium to supply energy to the liquid phase. The phenomenon called "acoustic cavitation" consists of at least three distinct and successive stages: i) nucleation, ii) bubble growth (expansion), iii) implosive collapse (Suslick, 1990).

The first stage is a nucleated process, by which cavitational nuclei are generated from microbubbles trapped in microcrevices of suspended particles within the liquid (Suslick, 1990; Reisse, 1995). In the second stage, the bubbles grow and expand in a manner restricted by the intensity of the applied sound wave. With high-intensity ultrasound, a small cavity occurs through "rectified diffusion", proceeding in a much slower rate, and lasting many more acoustic cycles before expansion (Suslick, 1990). The third stage of cavitation occurs only if the intensity of the ultrasound wave exceeds that of the "acoustic cavitational threshold" (typically a few watts cm^{-2} for ordinary liquids exposed to 20 kHz). At this condition, the microbubbles overgrow to the extent where they can no longer efficiently absorb energy from the sound environment to sustain themselves, and implode violently, therefore, in a so called "catastrophic collapse" (Mason 1990; Suslick et al. 1990; Ince and Tezcanlı, 2001). During this collapse stage, the temperatures and pressures released are in such extremes that the entrapped gases undergo molecular fragmentation (Ince et al.,2001). Pressure and temperature conditions are extreme enough in these localized "hot spots" to cause cell lysis (Hogan et al., 2004).

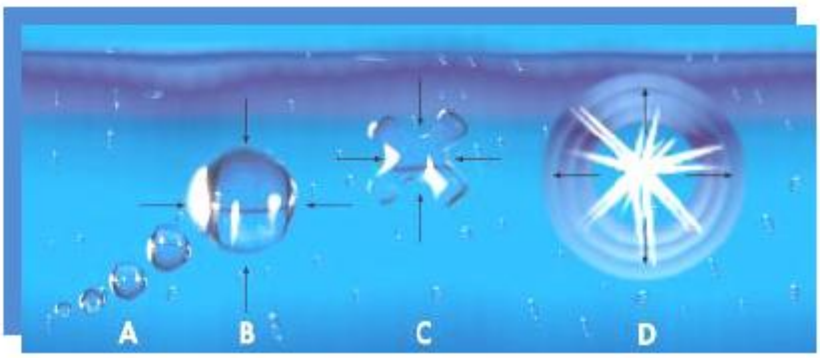


Figure 2.4. Formation, growth and implosion of a cavitation bubble (Suslick, 1994).

The high temperature produced during bubble collapse decomposes water (H_2O) into extremely reactive hydrogen atoms (H^+), and hydroxyl radicals (•OH). These radicals recombine to form hydrogen peroxide and molecular hydrogen in the cooling phase. Hence, the following reactions occur as a result of cavitation collapse in water:

H_2O+))) → •OH + •H (thermolysis) (2.1)

•OH + •H → H_2O (2.2)

•OH +•OH → H_2O_2 (2.3)

2•OH → H_2O + •O (2.4)

In heterogeneous systems, when cavitation occurs in a liquid near a solid surface, the dynamics of cavity collapse changes dramatically. In pure liquids, the cavity remains spherical during collapse because its surroundings are uniform. Approaching to a solid boundary, cavity collapse is very asymmetric and generates high-speed jets of liquid (Suslick, 1994). Liquid jets drive into the heterogeneous surfaces with velocities of roughly 400 km h^{-1}. This process can cause severe damage at the point of impact and can produce newly exposed, highly reactive surfaces (Suslick, 1994).

The disintegration mechanism during sonication of sludge follows one or more of the following pathways (Pilli et al., 2010):

a) Hydro-mechanical shear forces
b) Oxidizing effect of •OH, •H, •N, and •O produced under ultrasonic irradiation
c) Thermal decomposition of volatile hydrophobic substances in the sludge
d) Increase of temperature during ultrasonic activated sludge disintegration

The oxidizing effect of •H, •N and •O is less than •OH and negligible during ultrasonication. As their quantity is very low in the sludge the effect of the volatile hydrophobic substances is also negligible. Therefore, sludge disintegration is expected to occur mainly by hydro-mechanical shear forces and the oxidizing effect of •OH. Wang et al. (2005) have evaluated the effect of •OH and hydro-mechanical shear forces on sludge disintegration and the results showed that the disintegration of the sludge occurs mainly by hydro-mechanical shear forces produced by cavitation bubbles.

2.5.2. Effects of Ultrasonic Pretreatment on Solubilization of Organics

Effects of various ultrasonication parameters, including frequency, duration and intensity, and their effects on the characteristics of sludge have been studied by many researchers.

2.5.2.1. Sonication Frequency. Both hydromechanical shear forces and the sonochemical effects can contribute to the ultrasonic disintegration of sewage sludge. According to Portenlanger (1999) macromolecules with a molar mass above 40000 are disrupted by the hydromechanical shear forces produced by ultrasound and the mechanical forces are most effective at frequencies below 100 kHz. Sonochemical degradation processes can occur in a broad ultrasound frequency range from 20 kHz up to about 1 MHz. The highest efficiency of sonochemical reactions was observed at more than 100 kHz. (Hua and Hoffmann, 1997). Thiem et al. (2001) studied at different frequencies and within the range of explored frequencies between 41 and 3217 kHz, the disintegration of WAS was most effective at the lower end, showing that ultrasonic sludge disintergration is most effective at low ultrasound frequencies and hydromechanical shear forces produced by ultrasonic cavitation are predominantly responsible for sludge disintegration.

2.5.2.2. Energy/Power Input and Sonication Time. The economy of an ultrasound system is primarily governed by the power (W or kW) or energy (J or kJ) input supplied. Thus, quantification of energy/power input needed to obtain a desired degree of disintegration is a key factor in selecting the ultrasound system for field application. The power or energy supplied for sludge disintegration can be expressed in a number of ways as shown in Table 2.3.

Table 2.3. Expressions of ultrasonic energy supplied for disintegration (E_S: Specific energy; P: Power (kW); t: Sonication time; V: Volume of sludge; TS: Total solids concentration (kg L^{-1}); A:Surface area of the probe (cm^2))

Parameter	Expression	Unit
Specific energy	$E_S = \frac{P\ t}{V\ TS}$	kJ (kg TS)$^{-1}$ or kW s (kg TS)$^{-1}$
Dose	$Dose = \frac{P\ t}{V}$	J L^{-1} or W s L^{-1}
Density	$\rho_u = \frac{P}{V}$	W L^{-1}
Intensity	$I = \frac{P}{A}$	W cm^{-2}

Yan et al. (2010) showed that the soluble chemical oxygen demand (sCOD) increased linearly with specific energy in the range of 0 - 90000 kJ kg DS^{-1}. Similarly, the disintegration degree of particulate COD also increased linearly with specific energy. According to Tiehm et al. (2001) raising the ultrasonication time, increased the sCOD, indicating not only sonication power but also ultrasound application time changes the degree of disintegration. When the sonication time was raised to 30, 60, and 150 min, the degrees of disintegration (DD_{COD}) were augmented to 4.7, 13.1, 23.7 % respectively. Another study of the same team with 6 kW energy and 31 kHz frequency showed that 96 seconds of sonication releases more than 6 g COD L^{-1} whereas 64 seconds of sonication released 4 g COD L^{-1} (Tiehm et al., 1997).

These results showed that at short ultrasound application times, sludge floc agglomerates are dispersed while no cell destruction occurs whereas at longer treatment times or higher ultrasound intensity, the microbial cell walls are broken and intracellular material is released to the liquid phase.

Research conducted by Grönroos et al. (2004) illustrated that ultrasound administered up to 300 W L^{-1} with a frequency of 20 kHz for up to 30 minutes increased sCOD of the WAS, and generally improved methane production during anaerobic digestion. It was observed that ultrasonic pretreatment is more efficient at high power intensities for short durations compared to lower intensities for longer durations.

2.6. Fenton Pretreatment

2.6.1. Mechanisms of Action in Fenton's treatment of organics

Hydrogen peroxide is a strong oxidant (Standard potential 1.80 and 0.87 V at pH 0 and 14, respectively) and its application in the treatment of various inorganic and organic pollutants is well established. However, since hydroxyl radicals are stronger oxidants than H_2O_2 (oxidation potential 2.8 V and 1.95 at pH 0 and 14, respectively), transition metal salts (e.g. iron salts), ozone and UV-light can be used to activate H_2O_2 to form hydroxyl radicals. This increases the reaction rate at reasonable H_2O_2 concentrations (Neyens and Baeyens, 2003; Deng and Englehardt, 2006).

The oxidation processes utilizing Fe^{+2} salts to activate H_2O_2 are referred to as classical Fenton's reactions (Dewil et al., 2004). In classical Fenton process, reaction between dissolved Fe^{2+} and H_2O_2 in acidic aqueous solution leads to oxidation of Fe^{2+} to Fe^{3+} and formation of the highly reactive •OH.

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$	(chain initiation)	(2.5)
$k_5 \approx 70\ M^{-1}\ s^{-1}$	(Rigg et al., 1954)	
$\bullet OH + Fe^{2+} \rightarrow OH^- + Fe^{+3}$	(chain termination)	(2.6)
$k_6 \approx 3.2x10^8\ M^{-1}\ s^{-1}$	(Buxton and Greenstock, 1988)	

Moreover, the newly formed ferric ions may catalyse hydrogen peroxide, causing it to be decomposed into water and oxygen. Ferrous ions and radicals are also formed in the reactions. The reactions are shown in Eqs (7) - (11).

$Fe^{3+} + H_2O_2 \leftrightarrow Fe^{2+} + HO_2\bullet + H^+$		(2.7)
$k_7 \approx 0.001\text{-}0.01\ M^{-1}\ s^{-1}$	(Walling and Goosen, 1973)	
$Fe\text{-}OOH^{2+} \rightarrow HO_2\bullet + Fe^{2+}$		(2.8)

The reaction of hydrogen peroxide with ferric ions [reactions (7) and (8)] is referred to as a Fenton-like reaction.

$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2^-$ (2.9)

$k_9 \approx 1.3x10^6$ $M^{-1} s^{-1}$ (at pH=3) (Bielski et al., 1985)

$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+$ (2.10)

$k_{10} \approx 1.2x10^6$ $M^{-1} s^{-1}$ (at pH=3) (Bielski et al., 1985)

$\bullet OH + H_2O_2 \rightarrow H_2O + HO_2\bullet$ (2.11)

$k_{11} \approx 3.3x10^7$ $M^{-1} s^{-1}$ (Buxton and Greenstock, 1988)

As seen in reaction (11), H_2O_2 is both an initiator and an •OH scavenger, particularly when its concentration is high. The generated •OH radical can react effectively with a variety of organic compound (RH) as follows:

$RH + \bullet OH \rightarrow H_2O + R\bullet$ (chain propagation) (2.12)

$R\bullet + H_2O_2 \rightarrow ROH + \bullet OH$ (2.13)

$R\bullet + O_2 \rightarrow ROO\bullet$ (2.14)

The organic free radicals produced in reaction 12 may then be oxidised by Fe^{3+}, reduced by Fe^{2+}, or dimerised according to the following reactions:

$R\bullet + Fe^{3+}$- oxidation$\rightarrow R^+ + Fe^{2+}$ (2.15)

$R\bullet + Fe^{2+}$- reduction$\rightarrow R^- + Fe^{3+}$ (216)

The sequence of reactions (5), (6), (12) and (15) constitute the present accepted scheme for the Fenton’s reagent chain (Neyens and Baeyens, 2003). According to Deng and Englehardt (2006), although Fe^{3+} can be reduced to Fe^{2+} through reaction (7), the rate is several orders of magnitude slower than that of Fe^{2+} - Fe^{3+} conversion through reaction (5). And the formed Fe^{3+} may precipitate to iron oxyhydroxides, particularly as pH is increased.

Fenton’s reagent has different effects depending on the molar $H_2O_2/FeSO_4$ ratio. When the amount of Fe^{2+} employed exceeds that of H_2O_2, the treatment tends to behave like chemical coagulation. When the amount of H_2O_2 exceeds that of Fe^{2+}, the treatment behaves like chemical oxidation (Neyens and Baeyens, 2003).

The application of the classical Fenton process is limited by the amount of ferrous ion in the solution and the ability of the system to regenerate ferrous ions. Advanced Fenton process is a novel system for the generation of highly reactive hydroxyl radicals from a zero-valent iron/Fe^{2+} recycling method and hence gives rise to potent Fenton type reactions (Devi et al., 2009).

Zero-valent iron (ZVI) is a solid form of iron. When zero-valent iron is used as the catalytic source of iron, the surface of the metal iron corrodes producing insitu ferrous ions. The produced ferrous ions react with hydrogen peroxide to generate hydroxyl radicals. Catalytic activity of ZVI is based on the reactivity of iron to initiate surface chemistry and Fenton-like reactions in water. The reactions occur when the reactant molecules reach the iron solid surface. They then associate with the surface at sites that may be either reactive or nonreactive (Güyer and Ince, 2010).

A simplified reaction scheme occuring in water during advanced Fenton oxidation is the following (Güyer and Ince, 2010):

$$Fe^0_{(s)} + 2H_2O_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2OH^-_{(aq)} + H_{2(g)} \quad (2.17)$$

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2OH^- \quad (2.18)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (2.19)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \quad (2.20)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \bullet OOH + H^+ \quad (2.21)$$

The implementation of iron powder instead of iron salts results in the avoidance of unnecessary loading of aquatic system with counter anions. In addition, according to Lücking et al. (1998) the concentration of ferrous and ferric ions in wastewater treated by advanced Fenton process is significantly lower in comparison to the classical Fenton process. Furthermore, the faster recycling of ferric iron at the iron surface occurs through the following reaction:

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \quad (2.22)$$

Since acoustic cavitation is known to increase the surface area of reactive solids by causing particles to rupture, when the solution is sonicated the reactivity of ZVI increases dramatically. Application of ZVI together with ultrasonic irradiation leads to enhanced mass transport of reactants to the metal surface, where ultrasound increases the defects and the number of active sites while continuously cleaning it (Güyer and Ince, 2010). A simplified reaction scheme occurring in water during sonolysis in the presence of ZVI is the following:

$$Fe^0 \text{ (surface) +))) } \rightarrow Fe^{2+} + 2e^- \quad (2.23)$$

$$Fe^0 \text{ (surface) } + 2\, Fe^{3+} \rightarrow 3Fe^{2+} \quad (2.24)$$

$$Fe^0 \text{ (surface) } + H_2O_2 \rightarrow Fe^{2+} + \bullet OH + OH^- \quad (2.25)$$

2.6.2. Effects of Fenton pretreatment on the properties of sludge.

Fenton's peroxidation can effectively be used in WAS treatment. The hydroxyl radicals easily pass through the microbial cell membrane in the sludge, leading to oxidative decomposition of the cell wall. Consequently, organic substances are discharged from the microbial cell into the liquid phase. Moreover, the hydroxyl radicals oxidize the recalcitrant compounds in sludge into biodegradable ones which are further subject to biological treatment (Pham et al., 2010).

The application of the Fenton process for disintegration of WAS may cause two phenomena: solubilization and mineralization of sludge solids. Part of activated sludge is mineralized to carbon dioxide and water while part of sludge is solubilized to biodegradable organics, which are easily accessible and can be digested much faster in later biological process than sludge in a particular phase (Erden and Filibeli, 2010).

Solubilization of excess sludge is carried out in two steps. In the first step, some microorganisms are mainly killed and oxidized to dissolved organic substances by the Fenton oxidation process. Disruption of the cell walls cause the release of plasm from the cells, thus increasing the content of soluble organics and soluble nitrogen in the supernatant. With the increase of soluble organics, the amount of soluble organics to be oxidized increases as well resulting in a decrease in the soluble organics content. Thus, the oxidation of dissolved organic substances by the Fenton oxidation process is dominant in the second step (He Ming-he et al., 2010).

He Ming-he et al. (2010) applied Fenton process to evaluate the influence of sludge Fenton oxidation on the sludge yield and water quality. The initial concentrations of Fe^{2+} and H_2O_2 were 200 and 8000 mg L^{-1}, respectively, and the initial solution pH was 3. Treatment resulted in color change from the dark brown color to pale gray and the number and size of activated sludge flocs were decreased by the Fenton oxidation process. sCOD increased from 38 to 2213 mg L^{-1} during the initial 60 min of the Fenton oxidation process, and decreased at a slow rate to 1832 mg L^{-1} during the following hour. The BOD/sCOD ratio increased from 0.11 to 0.45 after 40 min of oxidation and thereafter decreased to around 0.31. It appears that the Fenton oxidation converted the sludge into various forms of easily biodegradable organic matter such as volatile fatty acids and low molecular weight compounds (He Ming-he et al., 2010).

Takumura et al. (2009) applied photo-Fenton reaction to WAS for disintegration purpose in the presence of 4 g H_2O_2 L^{-1}, 40 mg Fe^{2+} L^{-1} and 3000 mg MLSS L^{-1} (pH = 3, 6 h reaction time). They showed that the photo-Fenton process is one of the feasible processes for disintegration of excess WAS. The solubilization of excess sludge was carried out in two steps. The first step is that •OH radicals produced by photo-Fenton reaction attacked the excess sludge and broke up the cell wall. Cell lysis released cell contents into the sludge slurry and as a result the dissolved COD concentration in the slurry increased. In the second step, the photo-Fenton reaction also oxidized the cytoplasm eluted from the decomposed microorganism in the slurry and then the dissolved COD in the sludge slurry decreased. At longer than 6 h reaction time COD was decreased and mineralization occurred.

Lu et al. (2003) used four ratios of Fe^{2+}/ H_2O_2 to investigate the effect of Fe^{2+} concentrations on the reduction of specific resistance (SR). When the sludge was treated with 6000 mg L^{-1} of Fe^{2+} and 3000 mg L^{-1} H_2O_2, 90% reduction on the SR of the treated sludge was observed. Neyens and co-workers tested the effects of temperature, hydrogen peroxide concentration, pH and reaction time on the dewaterability of the sludge (Neyens et al., 2002; Neyens et al., 2003; Neyens et al., 2004a). Results of their studies showed that

Fenton's peroxidation can be considered as a useful sludge treatment, yielding (i) a considerable reduction of dry solids (DS) and organic dry solids (ODS) in the filter cake of approximately 20% and (ii) an improved dewaterability with a 30% reduction of the sludge volume, and a 30% increase of the cake DS-content when compared with the untreated sludge sample. These results show that the Fenton technology can be used to improve the dewatering of activated sludge. Promotion of the filterability and dewaterability could be due to the destruction of cells leading to the release of intracellular material.

3. MATERIALS AND METHODS

This chapter discusses the materials, experimental/analytical methods and the measurement parameters utilized during laboratory experiments. The first part of this laboratory work was completed in the Technical University of Hamburg Harburg (TUHH) Institute of Wastewater Management and Water Protection. The second or Fenton and US/Fenton part and data evaluation were completed in Boğaziçi University (BU) Institute of Environmental Sciences. The aim of the experiments conducted in TUHH was to determine the operating parameters of ultrasonic pretreatment of WAS. The aim of the experiments in BU was to apply US, classical Fenton, advanced Fenton and combinations of US/classical-Fenton and US/advanced-Fenton processes to observe synergistic effects and to set the operation parameters.

3.1. Materials

3.1.1. Waste Activated Sludge

3.1.1.1. Sludge 1 (TUHH). Sludge samples were taken from the aeration tank of Seevetal Local Municipal Wastewater Treatment Facility in Hamburg and chemically/physically analyzed for characterization. The results of analyses are presented in Table 3.1.

Table 3.1. The characteristics of the waste activated sludge

Parameters	Value
sCOD (mg L^{-1})	398
DOC (mg L^{-1})	136
TS (g L^{-1})	11.458
VS (g L^{-1})	7.66
Protein (mg L^{-1})	115
Total Dissolved Nitrogen (mg L^{-1})	24.5

<u>3.1.1.2. Sludge 2</u> (BU). The sludge in these experiments was obtained from a lab-reactor seeded with municipal AS, and analyzed chemically/physically for characterization. The reactor was fed twice a week by a synthetic feed solution, the nutrients of which are listed in Table 3.2. The reactor was maintained at room temperature (20-25 ^oC) and continuously aerated to maintain aerobic conditions and adequate mixing. The chemical/physical characterization of the sludge is presented in Table 3.3.

Table 3.2. The composition of the synthetic feed solution

Nutrient	**Amount (g)**
Anhydrous Glucose (Sigma-Aldrich)	28
Sodium Acetate Trihydrate (Riedel-de Häen)	40
Sodium Bicarbonate (Carlo Erba)	15
Ammonium Sulphate (J.T. Baker)	25
Dipotassium Hydrogen Phosphate (J.T. Baker)	10
Potassium Dihydrogen Phosphate (Reaktif)	10
Magnesium Sulphate (Fisher)	5
Calcium Sulphate Dihyrate	2.5
Iron (III) chloride (Merck)	1
Peptone Water (Merck)	10

Table 3.3. The characteristics of sludge in BU

Parameters	**Value**
TS (g L^{-1})	8.95
VS (g L^{-1})	3.95
sCOD (mg L^{-1})	131.3
DOC (mg L^{-1})	33.35
pH	6.24
CST (s)	55.8

3.1.2. Other Materials

3.1.2.1. Syringe Filters. Supernatant of the sludge samples in TUHH and BU were filtered through 0.45 μm disposable cellulose acetate syringe filters obtained from VWR International and Minisart, respectively.

3.1.2.2. Kits/Reagents of COD.

Test Kits (TUHH)
Lange LCK014 (1000-10000 mg L^{-1} O_2) and LCK514 (100-2000 mg L^{-1} O_2) COD cuvette tests obtained from Hach were used for sCOD determination.

Reagents (BU)
$K_2Cr_2O_7$, $HgSO_4$, Ag_2SO_4, H_2SO_4 (Merck) were used as COD reagents (digestion and sulfuric acid). Potassium Hydrogen Phthalate (KHP) was used to prepare KHP Standard for COD analysis.

3.1.2.3. Capillary Suction Time (CST) Tissues. CST papers (7x9, Triton) were used in TUHH and BU for CST analysis.

3.1.2.4. Agar, Petri Dishes, Filter Papers (BU). Standard methods agar (Acumedia), sterile petri dishes (single use) and 0.45 μm membrane filters (nitrocellulose) were obtained from Millipore.

3.1.2.5. Fenton Reagents and pH adjusters (BU). Reagent grade hydrogen peroxide (35%, w/v), and $FeSO_4.7H_2O$ were obtained from Merck and used as Fenton's reagents. Zero-valent Iron (ZVI) was obtained from Hepure. Reagent grade NaOH and H_2SO_4 (1N) were used for pH adjustment.

3.1.2.6. Catalase (BU). Catalase from *micrococcus Iysodeikticus* was obtained from Fluka to remove residual hydrogen peroxide in samples before analysis of COD and DOC. Catalase had 226170 U mL^{-1} activity (1 U corresponds to the amount of enzyme which decomposes 1 μ mol H_2O_2).

<u>3.1.2.7. Reagents in Nitrite & Nitrate analyses (TUHH).</u> Lange LCK339 (1-60 mg L^{-1} NO_3), LCK340 (22-155 mg L^{-1} NO_3) and LCK341 (0.05-2 mg L^{-1} NO_2) cuvette tests were obtained from Hach.

<u>3.1.2.8. INT-Dehydrogenase Solution, Formaldehyde (37%), Acetone, Na_2CO_3 (TUHH).</u> 3.95 mM INT solution was prepared by dissolving 200 mg of INT in 100 mL distilled water and adjusting the pH to 7.6 using 10% (w/v) Na_2CO_3. INT dye was obtained from Amresco. Acetone was used as the solvent for extracting INTF. Formaldehyde (37%) was used to stop the reaction.

<u>3.1.2.9. Lowry Reagent Solution, Folin's reagent, BSA Standard Protein Solution (TUHH).</u> Lowry Solution was prepared as the combination of Solution A:Solution B: Solution C with a ratio of (vol/vol) 100:1:1. Sodium tartrate was used for the preapartion of Solution C, Copper sulfate was used for the preparation of Solution B, NaOH and Na2CO3 was used for the preparation of Solution A. Folin and Ciocalteu's Phenol Reagent, 2 N, was used for the preparation of Folin's reagent. Bovine Serum Albumine was used for the preparation of BSA standard protein solution.

3.2. Instrumental Equipment

The following equipment were used in experiments:

1. pH Meter: Metler Toledo (BU)

2. Chemical Oxygen Demand (COD) analyzers:
   Hach reactor and DR/2010 model spectrophotometer (BU)
   CADAS 200 DR Lange Spektral Photometer (TUHH)

3. Nitrite/Nitrate Analyzer: CADAS 200 DR Lange Spektral Photometer (TUHH).

4. Dissolved Organic Carbon (DOC) Analyzers:
   Shimadzu TOC-V CSH Analyzer (BU).
   Multi N/C 3000 TOC/TN analyzer (TUHH).

5. Nephelometers: Hach 2100P (TUHH&BU).

6. Capilary Suction Time (CST) Instruments:

CST instrument supplied by Venture Innovations, Inc. (BU)

Triton Electronics Ltd. CST Filtrability tester model 200 (TUHH).

7. Total and Volatile Solids Equipments

Nüve FN 500 drying oven and a Protherm PLF 110/B muffle furnace (BU).

Memmert drying oven and a Heraeus M 104 muffle furnace (TUHH).

8. Microscope: Axiostar Plus microscope and a Canon PowerShot A640 digital camera (TUHH).

9. Particle size Analyzer: Galai, model CIS 100 automatic laser scanner (TUHH).

10. Colony Counter and Incubator: Fisher Dark-field Quebec colony counter, Fisher isotemp incubator.

11. Other devices: Centrifugators (Nüve NF 615, Sorvall Super, Hettich EBA 3S), analytical balances (Scaltec SBA 31, Sartorius MC1 AC 210S), mixers (A Vibrofix VF1, Nüve SL 350, Agimax).

3.3. Methods

3.3.1. Experimental Set-up

<u>3.3.1.1. Ultrasonication Experiments.</u> 20 kHz probe-type ultrasonic reactors were used in both laboratories.

<u>Ultrasonic Reactor 1</u> (TUHH)

A laboratory scale sonication unit that emitted a frequency of 20 kHz at an intensity of 20 W cm^{-2} was used at Ultrawaves GmbH laboratory. The energy for the oscillating unit was produced in the generator module of the type KS1000/2000.

The supply voltage of 230 V/50-60 Hz was transformed into an electrical sinusoidal oscillation of 20 kHz and applied via the HF-line to an oscillating unit of 1 kW. 1 kW oscillation unit is shown in Figure 3.1.

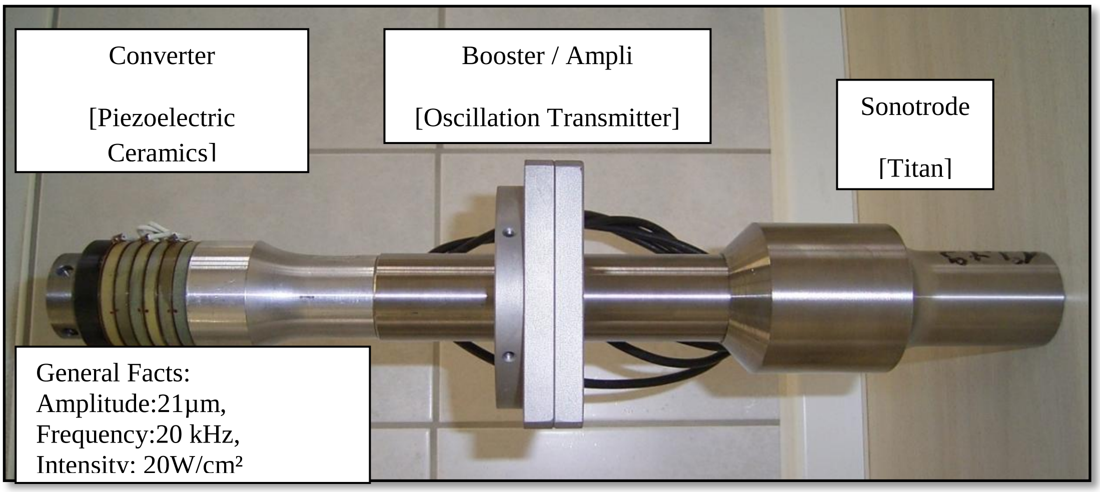
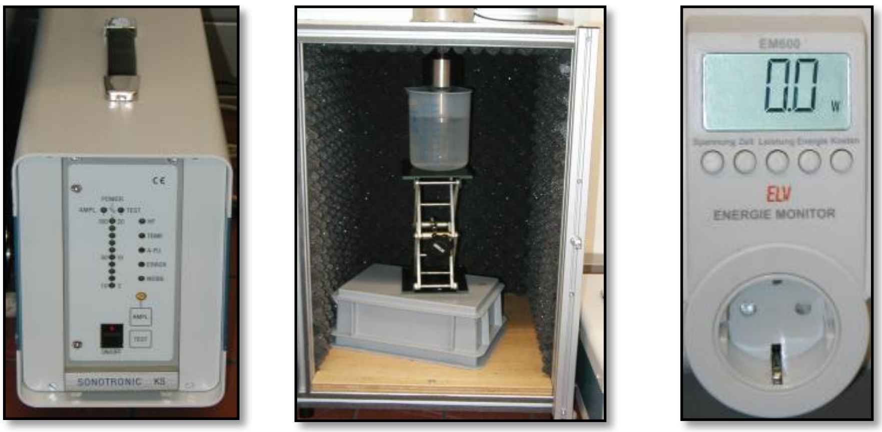


Figure 3.1. 1 kW Oscillating Unit

The energy input during sonication period was measured using an energy monitor ELV EM600. The data were recorded within 15 second intervals, and the average represented the energy input of the process. Equipment used for sonication is shown in Figure 3.2.



(a) (b) (c)

Figure 3.2. Sonication Equipment (TUHH). (a) Generator, (b) Horn Sonotrode Inside Protective Case, (c) Energy Monitor

Ultrasonic Reactor 2 (BU)

The system consisted of a 100 mL glass cell surrounded by a water-cooling jacket to keep the reactor at constant temperature (25 ± 0.5 °C), a probe type transducer with tip area of 1.13 cm^2, and emitting ultrasonic waves at 20 kHz, and a 180 W generator (Bandelin Sonoplus HD2200). The power was adjusted to 30%. The system was mounted in a polyurethane isolating material to prevent excessive noise. A photographic view of the reactor is presented in Figure 3.3.

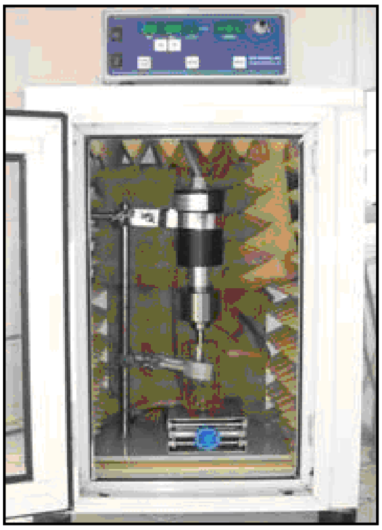


Figure 3.3. Ultrasonic reactor (BU)

3.3.2. Experimental Procedures

3.3.2.1. Sonication

Sonication-TUHH

750 mL of sludge samples were sonicated for different time intervals between 1 and 15 minutes, which correspond to an effective ultrasound energy input of 5.88 and 78.08 W h L^{-1}, respectively. Samples from the mixture were analysed for total solids (TS), volatile solids (VS), capillary suction time (CST), turbidity, microscopic image and particle size before and after sonication. The supernatant was separated by centrifugation (18500 rpm for 10 minutes) followed by filtration through 0.45 µm-pore opening size syringe filters. It was then analyzed for sCOD, dissolved organic carbon, total dissolved nitrogen, nitrate, nitrite, protein and INT-Dehydrogenase before and after sonication.

Sonication-BU

80 mL of sludge samples were sonicated for different time intervals between 1 and 55 minutes, which correspond to an effective ultrasound energy input between 2.83 and 155.65 W h L^{-1}, respectively. Samples from the mixture were analysed for CST, turbidity and microbial count before and after sonication. The supernatant was separated by centrifugation (4000 rpm for 30 minutes) followed by filtration through 0.45 µm-pore opening size syringe filters, and analyzed for sCOD and dissolved organic carbon.

3.3.2.2. Oxidation by Classical/Advanced Fenton Reaction (BU).

Classical Fenton Reaction

A series of batch experiments were carried out to determine the optimum operating conditions for WAS disintegration. Fifty milliliters of sludge samples were acidified to pH 3 by 1 N H_2SO_4. In order to initiate Fenton oxidation reaction, various mixtures of H_2O_2:$FeSO_4$ were added to the sludge according to the operating scheme given in Table 3.4, and allowed to react for one hour. The reactions were carried out at ambient temperature and the sludge samples were mixed at all times (mixing rate 125 rpm). At the end of reaction the mixture was analyzed for turbidity, CST and microbial count. The next step was separation of the supernatant, precipitation of iron at pH 10 and elimination of the residual H_2O_2 at pH 7.0. The remaining solution (supernatant) was then analyzed for sCOD and DOC.

Table 3.4. Chemical reagent doses used in the experiments

Doses	$[Fe^{2+}]$ (M)	$[H_2O_2]$ (M)	$[Fe^{2+}/H_2O_2]$	g Fe^{2+} (kg TS)$^{-1}$	g H_2O_2(kg TS)$^{-1}$
1	0.0044	0.0294	0.150	27.93	111.73
2	0.0044	0.0588	0.075	27.93	223.46
3	0.0089	0.0588	0.151	55.86	223.46
4	0.0089	0.1176	0.076	55.86	446.92
5	0.0133	0.0882	0.151	83.79	335.19
6	0.0133	0.1764	0.075	83.79	670.39
7	0.0178	0.1176	0.151	111.73	446.92
8	0.0178	0.2352	0.076	111.73	893.85

Advanced Fenton Reaction with Zero-Valent Iron (ZVI)

ZVI in powder form was used as the catalytic source of ferrous iron. Two different doses of Fe^0 and H_2O_2 were used to determine the best mixture. The test doses are listed in Table 3.5. At the end of one hour reaction the mixture was analyzed for turbidity, CST and microbial count. Then the supernatant was analyzed for sCOD and DOC following removal of iron and H_2O_2 as in the classical Fenton process.

Table 3.5. Chemical reagent doses used in the experiments

Doses	**[Fe^0] (M)**	**[H_2O_2] (M)**	**[Fe^0/H_2O_2]**	**g Fe^0 (kg TS)$^{-1}$**	**g H_2O_2(kg TS)$^{-1}$**
1	0.0018	0.0117	0.15	11.17	44.69
2	0.0089	0.0588	0.15	55.85	223.46

3.3.2.3. Sono-Oxidation.

Sono-Classical Fenton Oxidation

Sono- classical Fenton experiments were carried out with 0.0089 M Fe^{2+} and 0.1176 M H_2O_2 that corresponded to a molar Fe^{2+}/H_2O_2 ratio of 0.075. The sludge was sonicated between 1 and 55 minutes and samples were withdrawn from the reactor for the analysis of CST, turbidity and microbial count. The supernatant was separated by centrifugation (4000 rpm for 30 minutes) followed by filtration through 0.45 µm-pore opening size syringe filters, treated to remove the residual iron and H_2O_2, and analyzed for sCOD and dissolved organic carbon. The tests were run first at pH 3 and than at pH 6.24 (natural pH of the sludge), because sono-Fenton disintegration of the sludge at pH 3 was poor.

Sono-Advanced Fenton Oxidation

Sono-advanced Fenton experiments were carried out with 0.0089 M ZVI and 0.0588 M H_2O_2 correponding to a molar Fe^0/H_2O_2 ratio of 0.15. The sludge was sonicated between 1 and 55 minutes and samples from the mixture were analyzed for CST, turbidity and microbial count before and after sonication. The rest of the experimental procedure was exactly the same as described previously in sono-Fenton oxidation.

3.3.3. Analytical Methods

3.3.3.1. Chemical Oxygen Demand (COD). Standard Methods of Water and Wastewater Analysis (APHA, 1998) and Hach's USEPA approved dichromate methods were used in BU and TUHH respectively. To determine soluble COD (sCOD) samples were first centrifuged and then filtered through 0.45 µm-pore opening size filters and analyzed.

The sCOD values were also used to estimate the degree of sludge disintegration by using the following formula.

$$DD_{COD}=(sCOD-sCOD_0)/(sCOD_{NaOH}-sCOD_0)x100 \quad (3.1)$$

where;
DD_{COD}: Degree of Disintegration, %
sCOD: COD in the supernatant of the pretreated sludge, mg L^{-1}
$sCOD_0$: COD in the supernatant of the untreated sludge, mg L^{-1}
$sCOD_{NaOH}$: COD in the supernatant of the chemically disintegrated sludge in one mol L^{-1} NaOH, g L^{-1}.

3.3.3.2. Total and Volatile Solids. TS and VS were determined respectively by the methods 2540 B and 2540 E described in Standard Methods of Water and Wastewater Analysis (APHA,1998).

3.3.3.3. Capillary Suction Time. CST was analyzed according to the method 2710 G described in Standard Methods of Water and Wastewater analysis (APHA, 1998). The method involves placing of the CST paper between two plastic blocks and pouring of five mililiters of sludge into the stainless steel collar. The time elapsed to move a volume of the filtrate over a specified distance as a result of the capillary suction pressure of dry filter paper gives the value of CST.

3.3.3.4. Turbidity. Turbidity of the supernatants gathered via centrifugation (4000 rpm, 15 min) were measured by nephelometric method following Standard Methods 2130B (APHA, 1998).

3.3.3.5. Dissolved Organic Carbon (DOC) & Total Dissolved Nitrogen (TDN). DOC and TDN in TUHH and BU were determined instrumentally using the equipments described is Section 3.2. DOC analyzer was operated in the non-purgeable organic carbon (NPOC) mode in BU. The instrument was calibrated by standard solutions of KHP (5-40 mg L^{-1}). All samples were measured in triplicate.

3.3.3.6. Protein. The Folin-phenol method (Lowry et al., 1951) was used for protein determination. Bovine serum albumine (BSA) standard solution was used for obtaining the calibration curves. Spectrophotometric measurements were done at 750 nm. The procedure is outlined as:

i. 1 milliliter of samples was placed in test tubes.
ii. 1.4 milliliter of Lowry Reagent Solution (49 mL Solution A, 0.5 mL Solution B, 0.5 mL Solution C) was added to each test tube. The test tubes were mixed well and allowed to stand at room temperature in dark for 20 minutes.
iii. After 20 min of incubation, 0.2 mL of Folin's reagent was added into each test tube with rapid and immediate mixing.
iv. The tubes were allowed to stand at room temperature in dark for 30 minutes, for the color development.
v. The absorbance values of the prepared samples were measured at 750 nm. These values were compared to the data obtained from calibration curve.

3.3.3.7. Microscopic Image Analysis. The effects of sonication on the sludge microorganisms was evaluated by microscopic examination and a digital camera.

3.3.3.8. Particle Size Distribution. Particle size analysis was conducted with an automatic laser scanner. The samples were suspended by magnetic stirring.

3.3.3.9. INT-Dehydrogenase Test. Dehydrogenase activity was evaluated by the method proposed by Lopez et al., (1986). This method is based on measurement of the color production by reduction of the original substrate, INT [2-(p nitrophenyl)-5-phenyltetrazoliumchloride], to INT-formazan, by the oxidative effect of the dehydrogenase enzymes. The following is a simple outline of the procedure:

i. 5 mililiters of samples were placed in test tubes.
ii. 0.5 mililiters of INT Solution (3.95 mM) was added to each test tube. The test tubes were mixed well and allowed to stand at room temperature in dark for 20 minutes.
iii. After 20 minutes of incubation, reaction is stopped by adding 1 mililiter of formaldehyde (37%) into each test tube.
iv. 2 mililiters of samples was centrifuged at 4000 r min^{-1} for 10 minutes
v. The supernatant was seperated and the INT-formazan was extracted by adding 5 mililiters of acetone.
vi. The test tubes were mixed well and allowed to stand at room temperature in dark for 30 minutes.
vii. After 30 minutes of incubation samples were centrifugated as before
viii. The concentration of dye was measured by absorbance values of the prepared samples at 490 nm.

INT-DHA was estimated by using the following equation (Sanchez et al., 2006):

$$INT-DHA(mgO_2/gTS.day)=\frac{1024.D_{490}.v}{C_b.V.t.F} \tag{3.2}$$

where;

D_{490}: Absorbance at 490 nm,
v: Final volume of the solvent used to extract formazan, (mL)
V: Volume of the sample, (mL)
C: Concentration of MLSS, (g L^{-1})

t: Incubation time, (min)

F: Dilution factor

1024: Conversion factor (Lopez et al., 1986)

3.3.3.10. Microbial Count Analysis. Membrane filter technique described in Standard Methods of Water and Wastewater Analysis (APHA, 1998) was followed. Total heterotrophic bacteria were quantified in terms of colony forming units (CFU) that become visible on growth plates after incubation.

4. RESULTS AND DISCUSSION

4.1. Pretreatability of WAS by Ultrasound Alone

The efficiency of ultrasonic pretreatment of WAS is closely related to factors such as the ultrasonic dose or the energy given to the system, the contact time, the characteristics of the sludge and the type of ultrasound equipment. The following section describes how the ultrasonic power or dose was optimized in the two laboratories

4.1.1. Determination of the Ultrasonic Power Deposited in the Reactors

Ultrasonic systems transform electrical power into mechanical energy, which is then transmitted into the reaction media. Part of it is lost to produce heat, and another part produces cavitation, but not all of the cavitational energy produces chemical and physical effects. Some energy is reflected and some is consumed in sound re-emission (Mason, 1999). Hence, there can be significant differences between the power supplied from the generator and that delivered into the reactor. In this study ultrasonic power in the reaction media were determined by using either an energy monitor (TUHH), or the calorimetric method (BU).

4.1.1.1. Power Determination-TUHH. As described previously in Section 3.3.1., the energy input during sonication period was measured using an energy monitor. Table 4.1 represents the data recorded within 15 second intervals and Figure 4.1 shows the variation of power with sonication time. The data were fitted to a polynomial, the linear coefficient of which gives the change in power per the increase in contact time. Thus, it was found that the energy input to the system was 0.071 W s^{-1}.

Table 4.1. The energy input as measured within 15 s intervals during 15 min sonication.

Sonication time (s)	**Power (W)**	**Sonication time (s)**	**Power (W)**
15	275.12	465	244.09
30	274.33	480	243.05
45	273.11	495	242.01
60	272.07	510	240.98
75	271.06	525	239.94
90	270.03	540	238.90
105	268.99	555	237.86
120	267.95	570	236.83
135	266.91	585	235.79
150	265.88	600	234.75
165	264.84	615	233.71
180	263.80	630	232.68
195	262.76	645	231.64
210	261.73	660	230.60
225	260.69	675	229.71
240	259.65	690	228.80
255	258.61	705	227.93
270	257.58	720	227.03
285	256.54	735	226.20
300	255.50	750	225.16
315	254.46	765	224.12
330	253.43	780	223.08
345	252.39	795	222.05
360	251.35	810	221.01
375	250.31	825	219.97
390	249.28	840	218.93
405	248.24	855	217.90
420	247.20	870	216.86
435	246.16	885	215.82
450	245.13	900	214.78

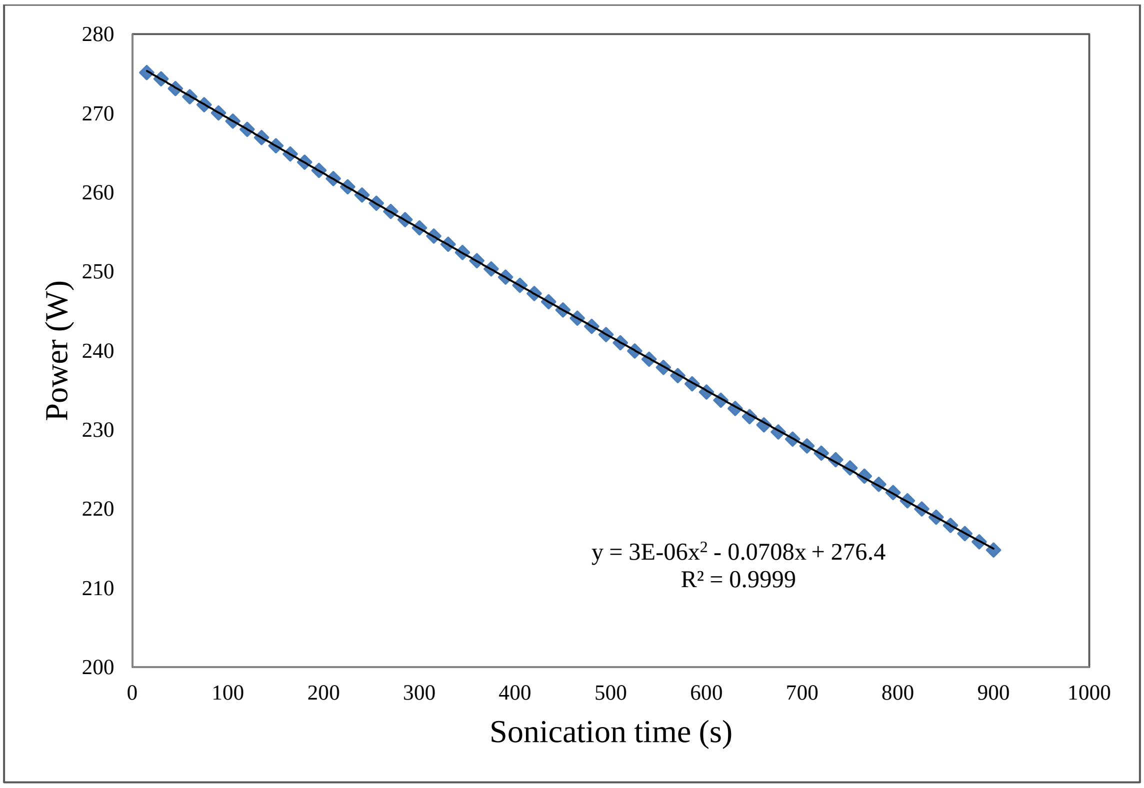


Figure 4.1. Energy input of the process with increasing sonication time.

4.1.1.2. Power Determination-BU. Among available methods to measure the amount of ultrasonic power entering a sonochemical reaction medium, the most common and easiest is calorimetry (Mason, 1999). The method involves measurement of the temperature increase against time during a fixed time period. From temperature versus time data, the temperature rise at zero time, dT/dt, can be estimated by curve-fitting of the data to a polynomial in t. The ultrasonic power (P) actually entering the system can then be estimated by substituting the value of dT/dt into equation 4.1. (Mason,1999; Mason and Cordemans, 1998; Mason et al., 1992):

$$\text{Power}=(dT/dt).C_p.M \qquad (4.1)$$

where;

C_p: heat capacity of water, (4.179 J $g^{-1}.^{o}C$)

dT/dt: the temperature rise at zero time

M: total mass of water in the reaction vessel, (g)

In this study, the temperature rise against time within 5-second intervals for 20 min was recorded to estimate the energy deposition in distilled water (DW) and WAS. The polynomial fits to the data provided the information about the power deposited in the two media by using the following constants and Eq. 4.1.:

C_p= 4.179 J g^{-1} $^oC^{-1}$,

M = 80 g

The linear coefficients of the polynomials also provided the necessary information on dT/dt of DW and WAS which are:

$(dT/dt)_{DW}$= 0.0487 ^oC s^{-1},

$(dT/dt)_{WAS}$=0.0465 ^oC s^{-1}.

Accordingly the powers deposited were estimated as:

P_{DW} = 0.0487 (^oC s^{-1}). 4.179 (J g^{-1} $^oC^{-1}$). 80 (g) = 16.281 W

P_{WAS} = 0.0465 (^oC s^{-1}). 4.179 (J g^{-1} $^oC^{-1}$). 80 (g) = 15.54 W

Power density$_{DW}$ = 16.281 W / 80ml =0.2 W mL^{-1}

Power density$_{WAS}$ = 15.54 W / 80ml =0.19 W mL^{-1}

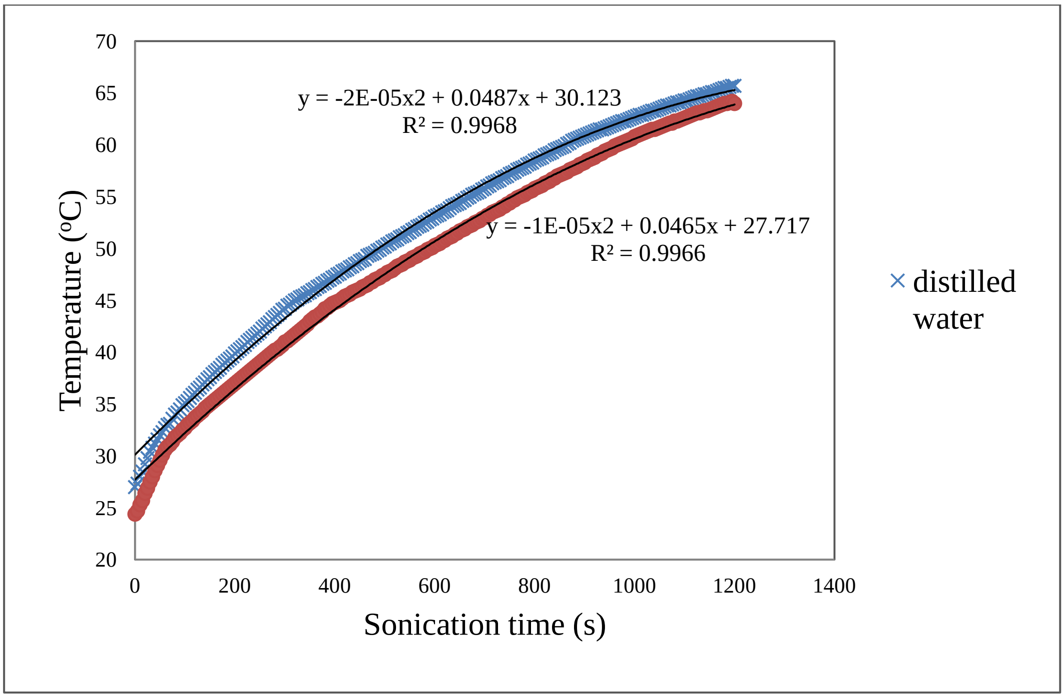


Figure 4.2. Estimation of the Power input by Calorimetric Experiments

4.1.2. Assesment of WAS Quality upon Ultrasonic Pretreatment

4.1.2.1.Ultrasonic Pretreatment-TUHH. Parameters employed to evaluate sludge disintegration efficiency can be collectively classified into three categories namely, chemical (such as increase in sCOD concentration, DOC, TDN, NO_x-N concentrations and release of protein), physical (such as change in particle size distribution, CST, turbidity and microscopic examination), and biological (INT-DHA activity test). Detailed discussion of each category is presented in the following section.

Chemical Parameters

Ultrasound Dose, sCOD, DD_{COD}

As described in Chapter 3, the ultrasonic dose was estimated by monitoring the energy input into the sludge solution. The data were used to determine the ultrasonic dose in W h L^{-1}. It is also possible to express the energy input in terms of “specific energy”, which is described as the quantity of energy deposited per unit weight of solids in WAS. Table 4.2 summarizes the impact of ultrasound dose/specific energy/time on sCOD and DD_{COD} of WAS.

Table 4.2. Effect of ultrasound dose/specific energy/time on solubilization of COD

Sonication Time (min)	**Ultrasound Dose ($W\ h\ L^{-1}$)**	**Specific Energy [$kJ\ (g\ TS)^{-1}$]**	**sCOD ($mg\ L^{-1}$)**	**DD_{COD} (%)**
0	0.0	0.0	398.5	0.00
1	6.1	1.9	695.1	7.11
3	17.8	5.6	1289.5	20.20
5	28.7	9.0	1809.3	31.89
7	38.9	12.2	2094.0	38.72
9	48.5	15.2	2503.0	48.89
11	57.3	18.0	2834.6	58.08
15	74.2	23.3	3444.6	73.10

The data in Table 4.2 are shown graphically in Figure 4.3. It was found that the relation between sCOD and the applied ultrasound dose or specific energy was linear and maximum COD solubilization was achieved at a dose of 74.2 $W\ h\ L^{-1}$ or 23.3 $kJ\ (kg\ TS)^{-1}$. Disintegration of the sludge was calculated from sCOD data and listed in Table 4.2. it was found that the ultrasound dose that yielded maximum sCOD also provided maximum disintegration.

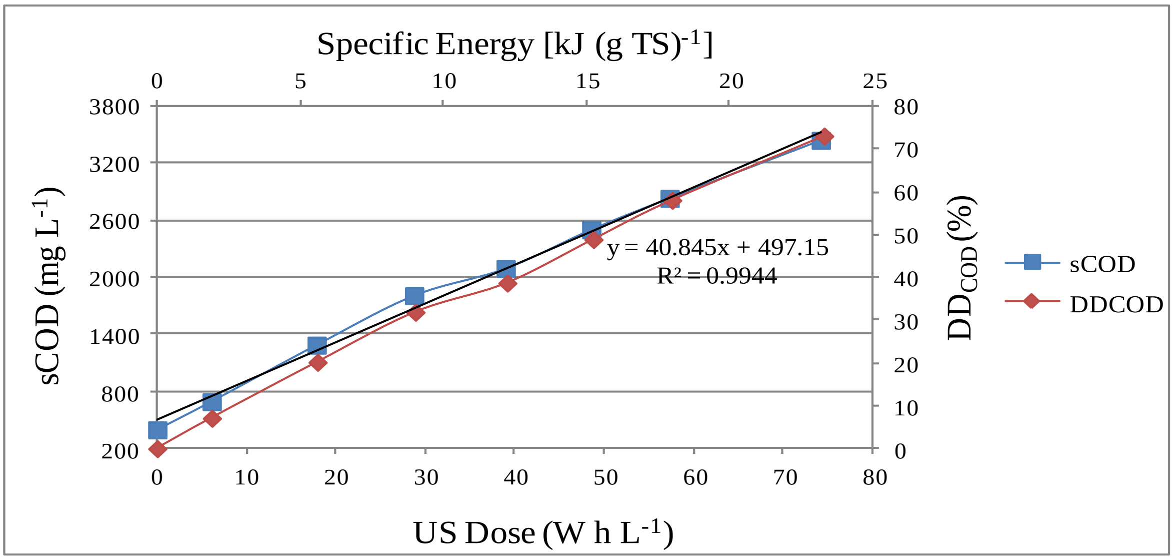


Figure 4.3. Effect of ultrasound dose and specific energy on sCOD increase

Similarly, Yan et al. (2010) conducted ultrasonic tests with an operating frequency of 20 kHz for an initial sCOD of 150 mg L^{-1}. They found that the sCOD dramatically and linearly increased to 3752.2 mg L^{-1} with an increase of the specific energy to 90000 kJ kg^{-1} TS.

DOC

The efficiency of pretreatment was further assessed by monitoring the DOC of the WAS samples. The changes in DOC at each ultrasound dose and specific energy are given in Table 4.3 for 15 min sonication. The data are presented graphically in Figure 4.4.

Table 4.3. Effect of ultrasound dose/specific energy/sonication time on DOC of sludge samples

Sonication Time (min)	**Ultrasound Dose (W h L^{-1})**	**Specific Energy [kJ (g TS)$^{-1}$]**	**DOC (mg L^{-1})**
0	0.0	0.0	135.6
1	6.1	1.9	233.3
3	17.8	5.6	406.8
5	28.7	9.0	520.9
7	38.9	12.2	629.8
9	48.5	15.2	751.2
11	57.3	18.0	841.0
15	74.2	23.3	995.1

The relation of DOC with ultrasound dose/energy/sonication time is closely the same as that of sCOD as shown in Figure 4.3. We found that DOC also increased linearly with US dose and energy.

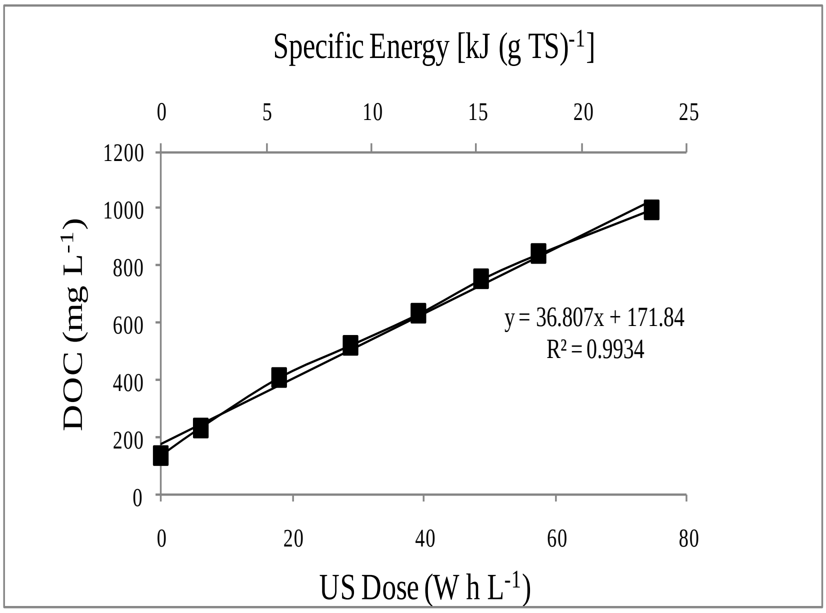


Figure 4.4. Effect of ultrasound dose and specific energy on DOC concentration

Total Dissolved Nitrogen (TDN)

The effect of ultrasonic pretreatment was also assessed in terms of the increase in total dissolved nitrogen concentration of the sludge. The data are given in Table 4.4 and plotted in Figure 4.5.

Table 4.4. Increase in TDN concentration with ultrasound dose and specific energy

Sonication Time (min)	**Ultrasound Dose (W h L^{-1})**	**Specific Energy [kJ (g TS)$^{-1}$]**	**TDN (mg L^{-1})**
0	0.0	0.0	24.55
1	6.1	1.9	31.92
3	17.8	5.6	77.40
5	28.7	9.0	117.17
7	38.9	12.2	170.10
9	48.5	15.2	213.49
11	57.3	18.0	257.03
15	74.2	23.3	359.33

As shown in Fig 4.5. the TDN concentration of the liquid phase increased exponentially with increasing ultrasound dose/energy. These result showed that along with the release of organic compounds, many nitrogen species were released during sonication of WAS samples. Zhang et al. (2008) also observed that ultrasound led to nitrogen release into the liquid phase because of cell disruption. They reported that liquid phase TN concentrations of all sonicated samples were in the range of 200-300 mg L^{-1} relative to the initial TN of <31 mg L^{-1}.

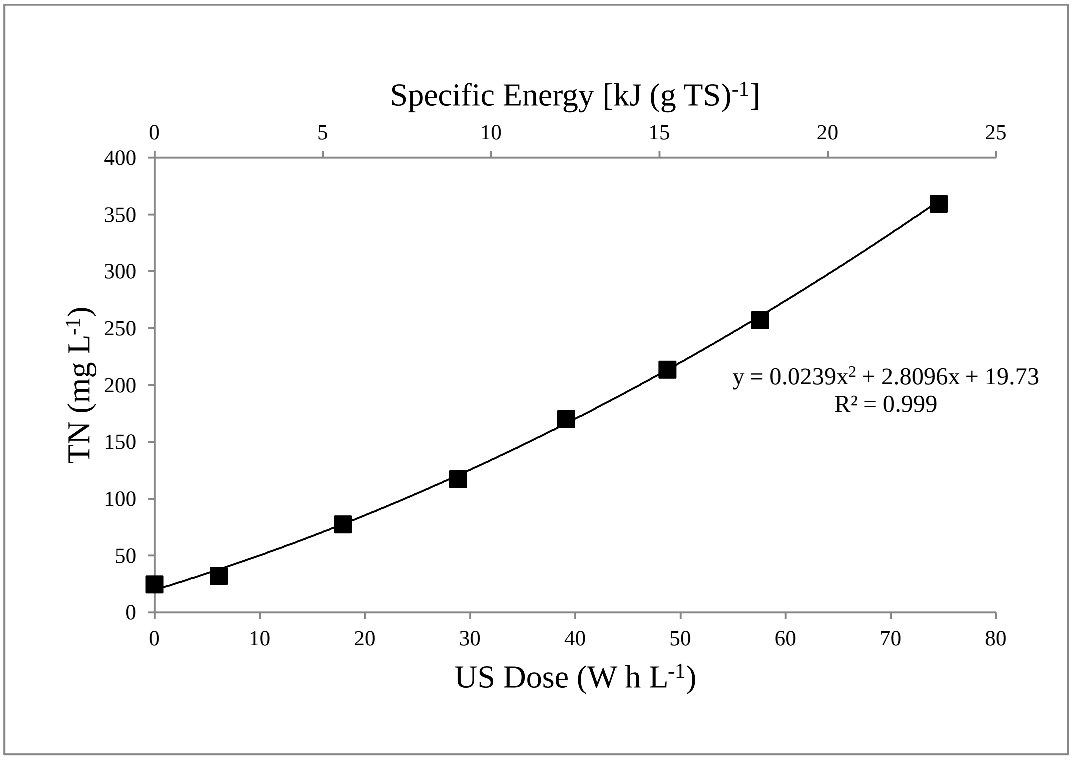


Figure 4.5. Effect of ultrasound dose and specific energy on TDN concentration

Assessment of Nitrogen Species

Nitrogen components were monitored to estimate the oxidation of NH_3-N to NO_2-N and NO_3-N. The data are presented in Table 4.5 and plotted in Figure 4.6. It was found that NH_3-N was significantly converted to NO_2 and NO_3-N. The oxidation is partly due to the presence of O_2 in solution, but more significantly to the chemical effects of ultrasound.

Table 4.5. Increase in NOx-N concentrations with ultrasound dose/specific energy/sonication time

Sonication Time (min)	**Ultrasound Dose (W h L^{-1})**	**Specific Energy [kJ (g TS)$^{-1}$]**	**NO_2-N (mg L^{-1})**	**NO_3-N (mg L^{-1})**
0	0.0	0.0	2.05	0.31
1	6.1	1.9	2.88	0.26
3	17.8	5.6	3.39	0.37
5	28.7	9.0	4.50	0.33
7	38.9	12.2	6.10	0.41
9	48.5	15.2	7.44	0.47
11	57.3	18.0	7.88	0.51
15	74.2	23.3	9.70	0.57

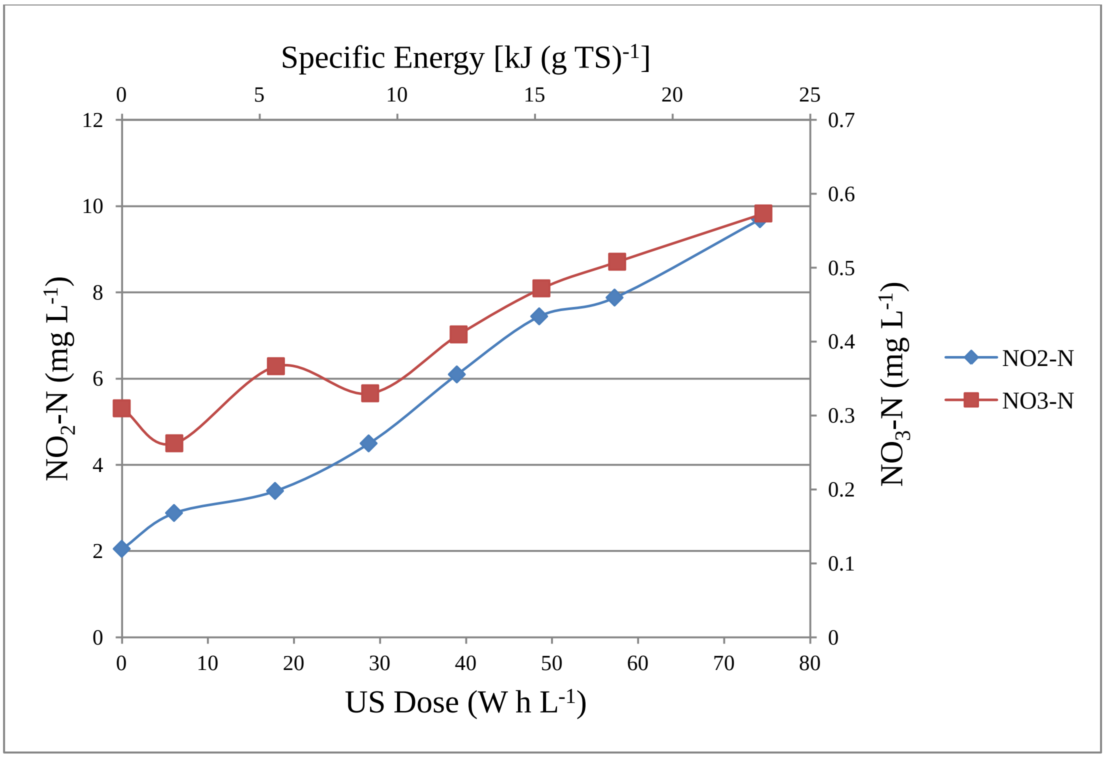


Figure 4.6. Increase in NO_2-N and NO_3-N concentrations with ultrasound dose/specific energy

Proteins

Proteins are important building blocks of all microbial cells. Wang et al. (2006) reported protein contents of 698 and 11338 mg L^{-1}, respectively in EPS and inside the microbial cells with 3% TS content. Therefore, it was anticipated that through the break-up of biosolids, sonication would cause an increase in the protein concentration of the supernatant. Table 4.6 summarizes the applied ultrasound doses, specific energies and their effect on the protein concentration in the supernatant.

Table 4.6. Increase in soluble protein concentration with ultrasound dose/specific energy/sonication time

Sonication Time (min)	**Ultrasound Dose (W h L^{-1})**	**Specific Energy [kJ (g TS)$^{-1}$]**	**Protein (mg L^{-1})**
0	0.0	0.0	115.0
1	6.1	1.9	208.8
3	17.9	5.6	353.0
5	28.8	9.0	422.6
7	39.0	12.2	540.8
9	48.6	15.2	657.5
11	57.3	18.0	808.8
15	74.1	23.3	968.8

Figure 4.7 shows the effect of ultrasound dose on the concentration of soluble proteins during ultrasonic treatment of WAS. The data show that soluble proteins in the liquid phase increased from 115 mg L^{-1} to 968.8 mg L^{-1}, to be attributed to the disruption of released intracellular polysaccharides and proteins into the extracellular matrix. These results agree with those of Zhang et al. (2008), Wang et al. (2006) and Feng et al. (2009) who similarly concluded that ultrasonic sludge disintegration significantly increases the concentration of soluble proteins.

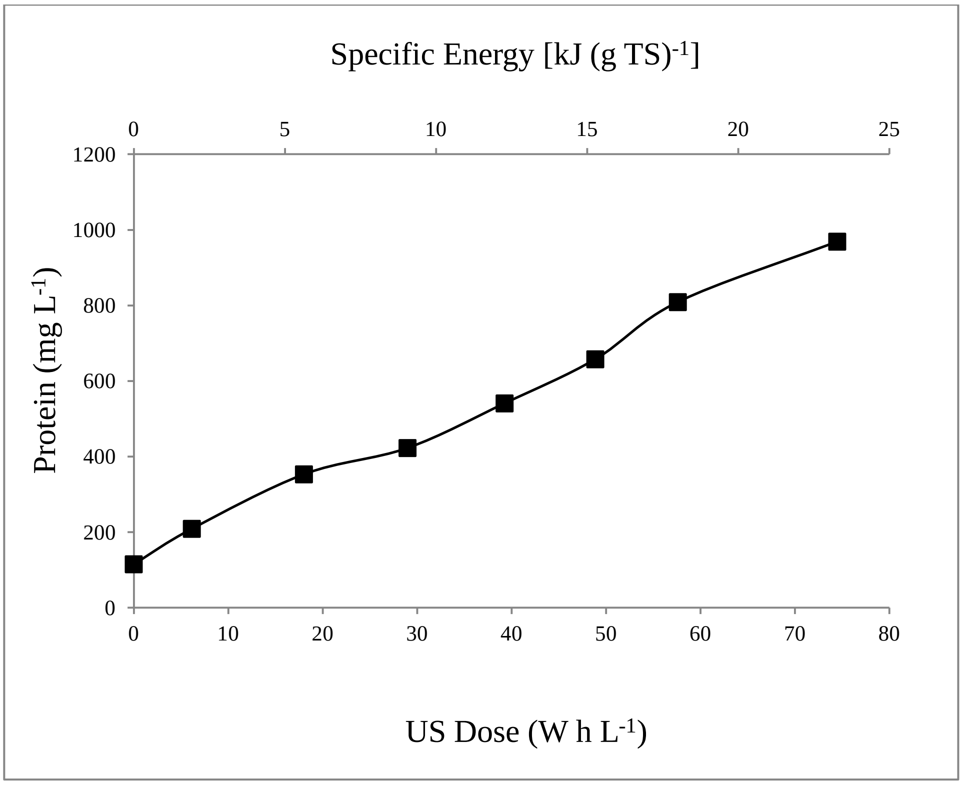


Figure 4.7. Effect of ultrasound dose/specific energy on protein concentration

Summary of Results on Solubilization of WAS (TUHH)

Table 4.7 summarizes the relative increase in the value of chemical parameters after 15-min sonication of WAS at the specified conditions. It was found that maximum enhancement was in total dissolved nitrogen as a consequence of cellular disruption.

Table 4.7. The increase in chemical WAS quality parameters after 15 min sonication

Parameter ($mg\ L^{-1}$)	**Increase (%)**
sCOD	764
DOC	633
TDN	1363
NO_2-N	375
NO_3-N	91
Soluble Protein	742

Physical Parameters

Particle Size

In order to investigate the influence of ultrasound on particle solubilization, particle size analyses were carried out. Table 4.8 summarizes the effect of applied ultrasound dose and specific energy on the average particle size of the sludge samples. The average particle size d_{50} denotes the 50^{th} percentile i.e. 50% of the particles by volume with diameter equal or lower than d_{50}. We found that sonication at 75.8 W h L^{-1} resulted in a decrease in d_{50} of 75.7%.

Table 4.8. Effect of applied ultrasound doses and specific energies and on the average particle size

Sonication Time (min)	**Ultrasound Dose (W h L^{-1})**	**Specific Energy [kJ (g TS)$^{-1}$]**	**d_{50} (µm)**	**Size Reduction (%)**
0	0.0	0.0	187.4	0.0
1	6.2	1.95	103.4	44.8
3	18.2	5.72	92.7	50.3
5	29.0	9.11	89.6	52.1
7	39.3	12.35	81.9	56.3
9	49.6	15.59	70.5	62.3
11	58.6	18.41	61.7	67.0
15	75.8	23.82	45.4	75.7

The results are illustrated in Figure 4.8, which confirms that ultrasound de-agglomerates biological flocs and disrupts large organic particles into smaller size particles. Hence, the applied ultrasonic pretreatment was very effective in reducing the particle size of the sludge. Bougrier et al. (2005) also examined particle size distribution at different specific energy inputs (kJ $kgTS^{-1}$) at 20 kHz frequency and found 38.5%, 42.18%, 45% and 60% d_{50} reduction at specific energy inputs of 660, 1350, 6950 and 14550 kj $kgTS^{-1}$, respectively.

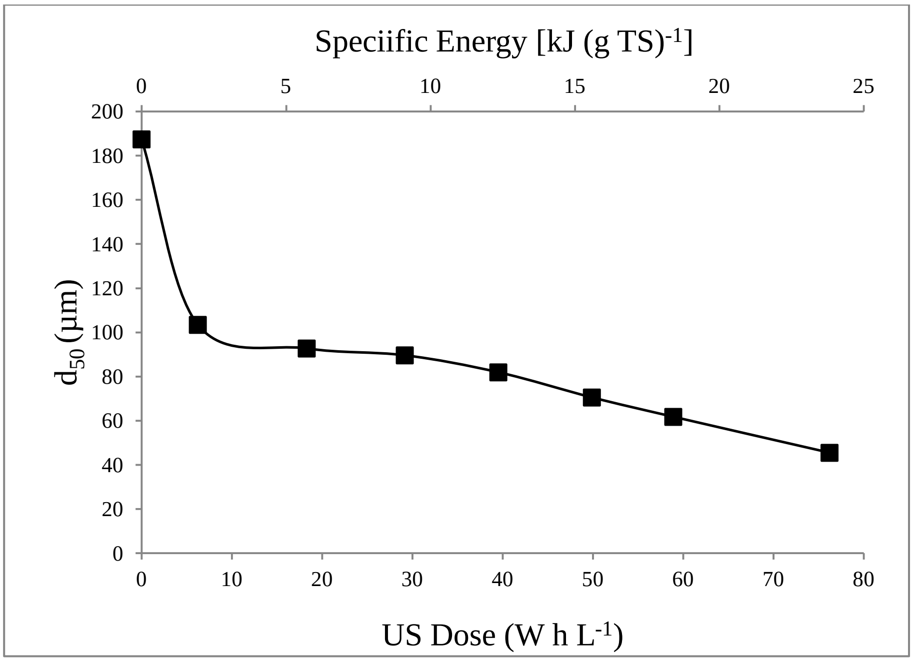


Figure 4.8. Effect of ultrasound dose/specific energy on average particle size

Turbidity

Another parameter to assess the efficiency of ultrasonic pretreatment is turbidity. Table 4.9 summarizes the impact of ultrasound dose/energy/sonication time on the turbidity of sludge supernatants. The data as plotted in Figure 4.9 shows that ultrasound (74.5 W h L^{-1}) rendered considerable increase in the turbidity of the sludge supernatant (1246%).

Table 4.9. Effect of applied ultrasound doses and specific energies and on the turbidity of sludge supernatants

Sonication Time (min)	**Ultrasound Dose (W h L^{-1})**	**Specific Energy [kJ (g TS)$^{-1}$]**	**Turbidity (NTU)**
0	0.0	0.0	28.75
1	6.1	1.9	108.75
3	18.0	5.6	171.25
5	28.9	9.1	229.00
7	39.2	12.3	262.25
9	48.9	15.3	300.75
11	57.7	18.1	339.50
15	74.5	23.4	387.25

Nearly in all literature published on ultrasonic sludge disintegration, turbidity of the sludge increases with the increase in ultrasound dose/energy/sonication time, as a consequence of the release of microparticles into the supernatant.

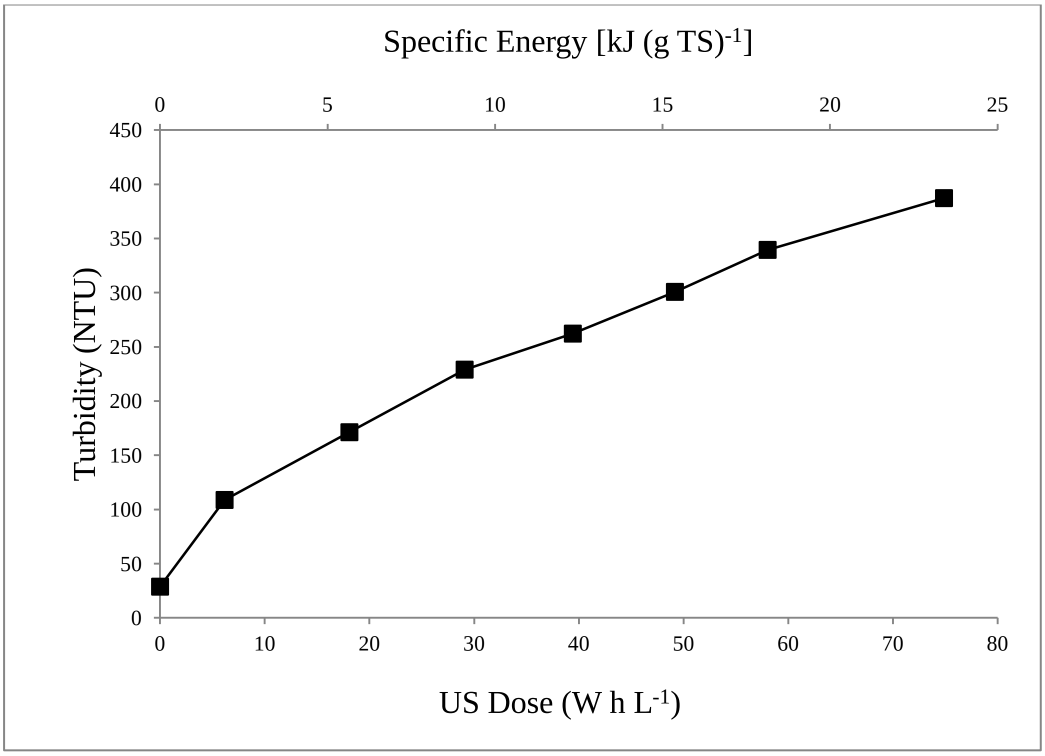


Figure 4.9. Effect of ultrasound dose and specific energy on turbidity

CST

Dewaterability of treated WAS is one of the most important parameters reflecting the efficiency of the pretreatment method. Dewaterability is generally expressed in terms of capillary suction time (CST). The higher the CST, the harder the sludge will be to dewater. The CST data are given in Table 4.10 and plotted in Figure 4.10.

Table 4.10. Effect of applied ultrasound doses and specific energies and on the CST

Sonication Time (min)	**Ultrasound Dose (W h L^{-1})**	**Specific Energy [kJ (g TS)$^{-1}$]**	**CST (s)**
0	0.0	0	14
1	6.1	1.9	152
3	17.9	5.6	235
5	28.8	9.0	272
7	39.0	12.2	314
9	48.6	15.3	331
11	57.3	18.0	358
15	74.1	23.3	383

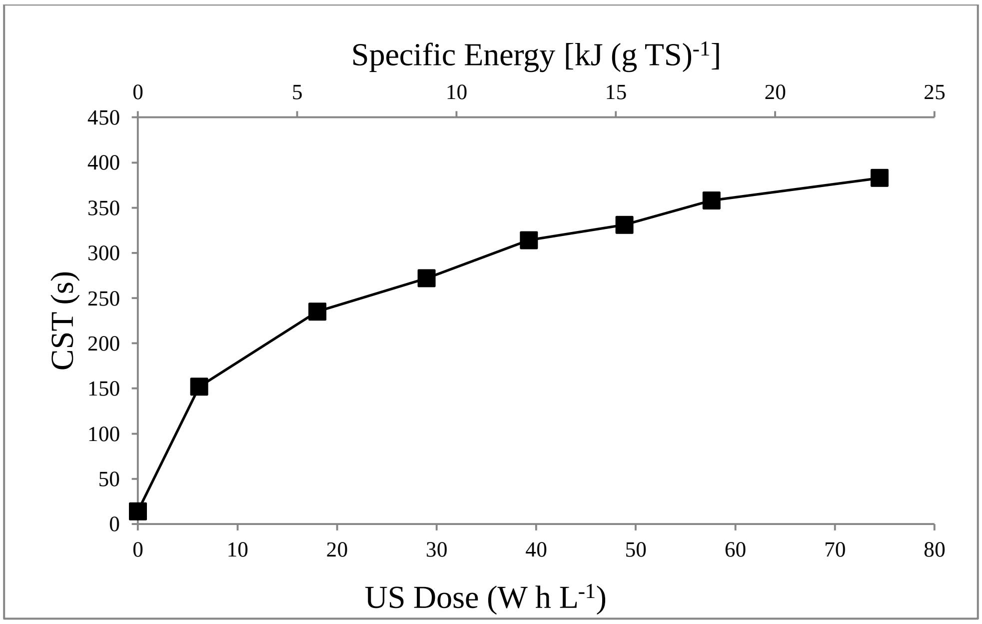


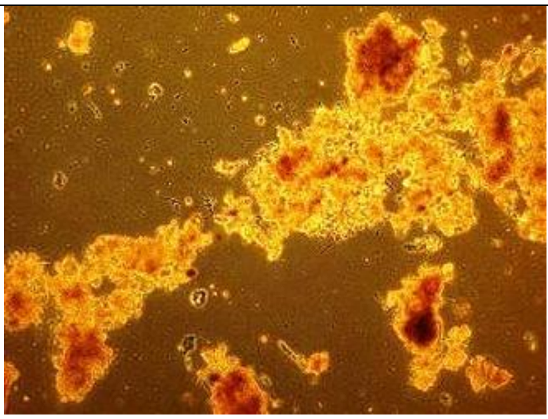
Figure 4.10. Effect of ultrasound dose and specific energy on CST

Hence, it seems that by increasing the CST, sonication reduces the dewaterability of WAS. Wang et al, (2006) reported also that CST increased from 82 s to 344 s using an ultrasonic density of 0.528 W mL^{-1} for 5 min. Increased CST during sonication can be explained by the release of biopolymers from the flocs to the aqueous phase. Thus when sludge cells release biopolymers into the aqueous phase, dewaterability becomes more difficult, because a large fraction of biopolymers consist of water.

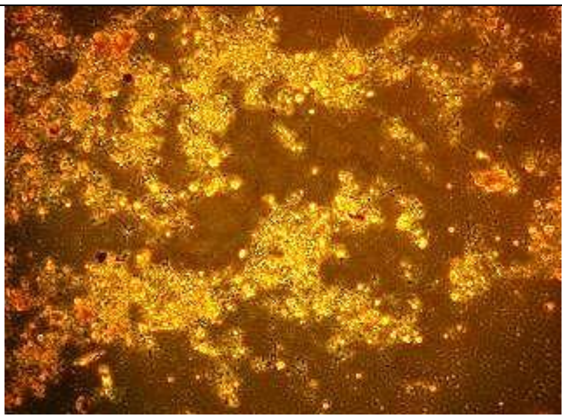
The observed increase in the previous two parameters, turbidity and CST during sonication shows that ultrasonication at the employed conditions does not improve the dewaterability of WAS.

Microscopic Image Analysis

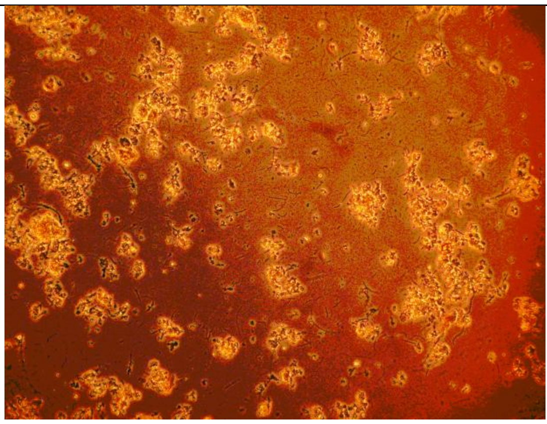
The sludge was further examined by microscopic analysis as shown by the photographic images in Figure 4.11. It was found that the images varied with respect to the applied ultrasound dose. There was a considerable change in particle or sludge structure upon 6.1 W h L^{-1} ultrasound application and a further change upon 18.2 W h L^{-1}, but little change was observed after 29.5 W h L^{-1} or higher doses. This is reasonable, because the particle size reduction was also largest at a change from 6.1 to 18.2 W h L^{-1}.



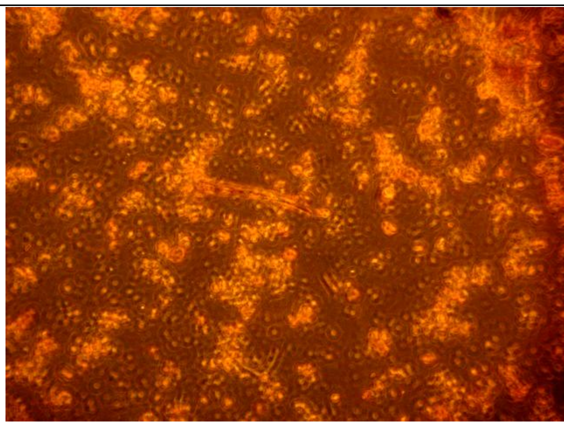
a) Unsonicated WAS



b) 6.1 W h L^{-1} US



c) 18.2 W h L^{-1} US



d) 29.5 W h L^{-1} US

Figure 4.11. Microscopic Images

Biological Parameters

INT-Dehydrogenase Activity

Solubilization of organic mater during ultrasonic disintegration of WAS leads to variations in enzymes activities. Thus, in this study the activity of dehydrogenase was investigated at various specific energy inputs as given in Table 4.11 and Figure 4.12. It was found that ultrasonic pretreatment has a positive influence on the dehydrogenase enzyme activity, which in turn reflects increased intracellular material release.

Table 4.11. Effect of applied ultrasound doses and specific energies on INT-Dehydrogenase activity

Sonication Time (min)	**Ultrasound Dose (W h L^{-1})**	**Specific Energy [kJ (g TS)$^{-1}$]**	**INT-DHA [mgO_2(gTS.day)$^{-1}$]**
0	0.0	0.0	4.25
1	6.1	1.9	5.11
3	17.9	5.6	5.65
5	28.8	9.1	6.32
7	39.0	12.3	7.39
9	48.6	15.3	8.34
11	57.3	18.0	9.20
15	74.1	23.3	10.05

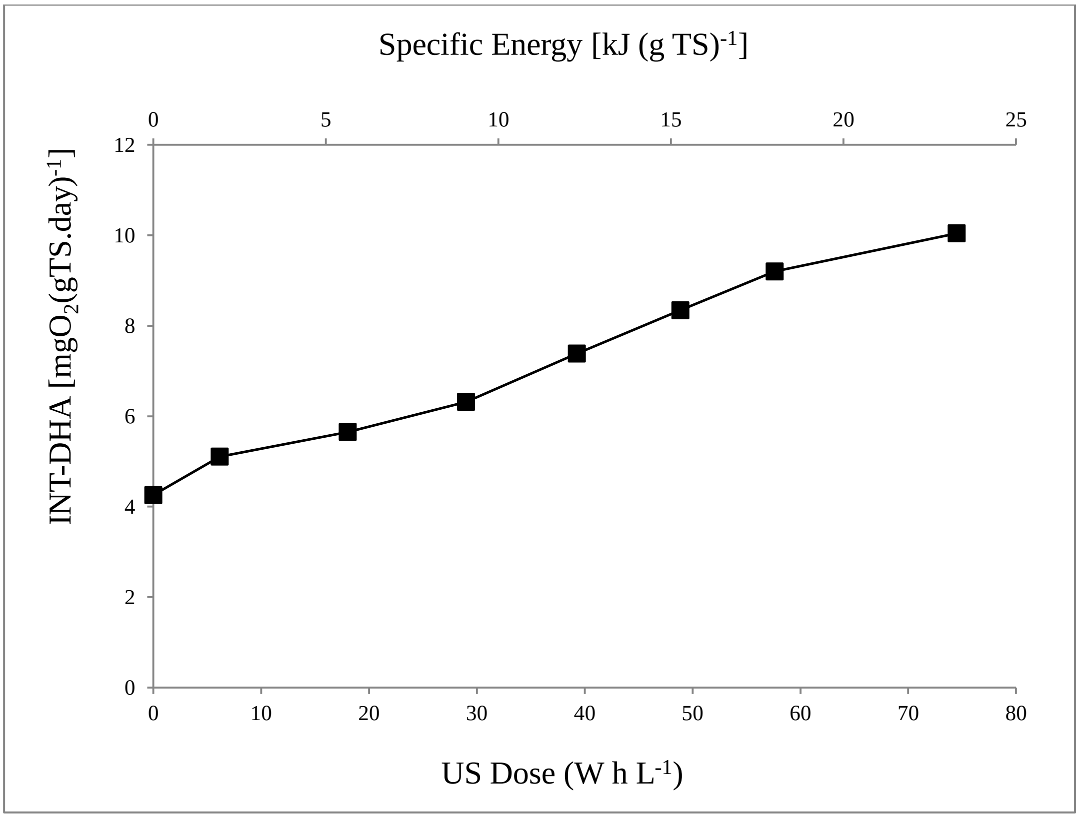


Figure 4.12. Effect of applied ultrasound doses and specific energies on INT-Dehydrogenase activity

Figure 4.12 shows that the activity of dehydrogenase increased from 4.25 to 10.05 mg O_2 $(gTS.day)^{-1}$ with the application of 74.1 W h L^{-1} ultrasound dose (23280.86 kJ kg TS^{-1} specific energy). Yan et al. (2010) with a specific energy range of 0 - 90000 kJ kg TS^{-1} found that maximum activities of four hydrolytic enzymes occurred at a specific energy of 30000 kJ kg TS^{-1}. They explained the increase in the activity by the dependencies of the activities of enzymes on the concentrations of soluble proteins and carbohydrates in WAS treatment system.

<u>4.1.2.2. Ultrasonic Pretreatment</u>-BU. The study at BU mainly aimed to investigate the effect of classical Fenton (Fe^{2+}/H_2O_2) and advanced Fenton (Fe^0/H_2O_2) reaction on ultrasonic disintegration of WAS. Before these experiments, preliminary sonication of WAS was carried out to confirm the increase in sCOD, DOC, solubilization, CST and turbidity. In the following sections the results of chemical, physical and biological analysis in BU are discussed.

Chemical Parameters

Table 4.12 gives the results of preliminary chemical experiments. The data are also shown graphically in Figures 4.13, 4.14, 4.15.

Table 4.12. Results of the chemical analyses on the preliminary ultrasound experiments

US Dose (W h L^{-1})	**sCOD (mg L^{-1})**	**sCOD/TCOD (%)**	**DOC (mg L^{-1})**
0.0	131.3	2.8	33.3
15.8	513.9	11.0	115.3
31.6	876.4	18.9	217.0
47.5	1252.2	27.0	280.9
63.3	1250.8	27.0	304.6
79.1	1615.0	34.8	361.8
95.0	2014.8	43.5	435.1
126.6	2869.0	61.9	726.7
174.1	2737.0	59.1	693.5

It was found that, at low doses of US, the disintegration of WAS showed similar behaviour to that in TUHH. However, at higher doses and contact times the increase in sCOD, solubilization, DOC slowed down and even decreased at excess doses. This is due to the fact that at high power inputs and sonication times, the excess water inside the cavitation bubbles lead to the cushion effect or a reduction in the violance of implosion. As such, the impact on cell disruption fades away.

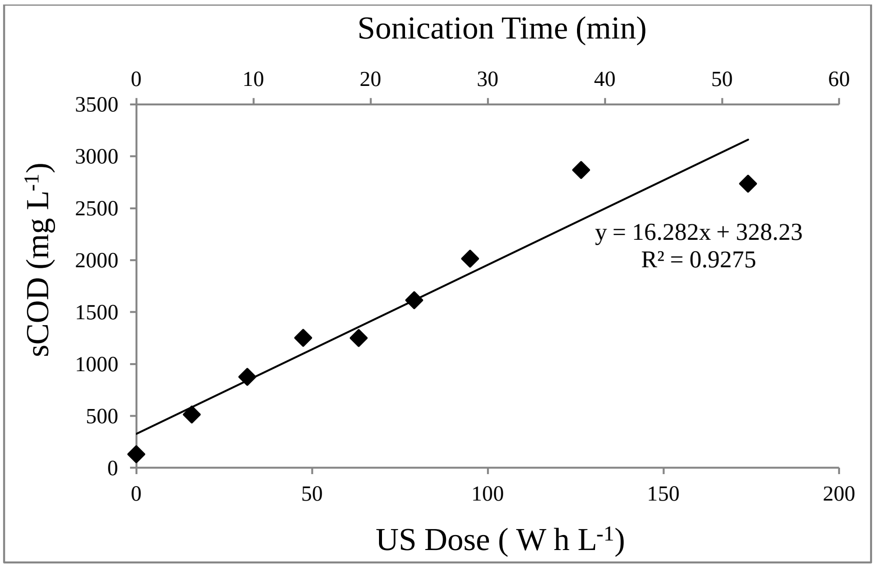


Figure 4.13. Effect of ultrasound dose and contact time on sCOD concentration

Soluble COD (sCOD) and Total COD (TCOD) display the quantity of organic matter in the liquid phase and the mixture, respectively. It is important to note that TCOD remain stable for the same sludge sample. Then, the increase in sCOD/TCOD ratio demonstrates the release of organic materials from solid to the liquid phase upon ultrasonic pretreatment. The plots of sCOD/TCOD and DOC against US dose or contact time are presented in Figure 4.14 and Figure 4.15.

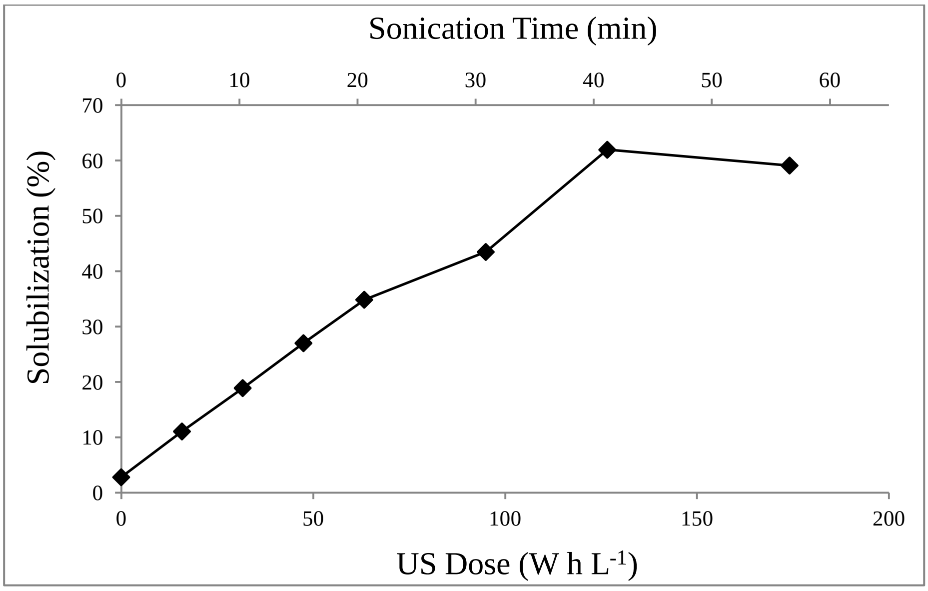


Figure 4.14. Effect of ultrasound dose and contact time on solubilisation of WAS

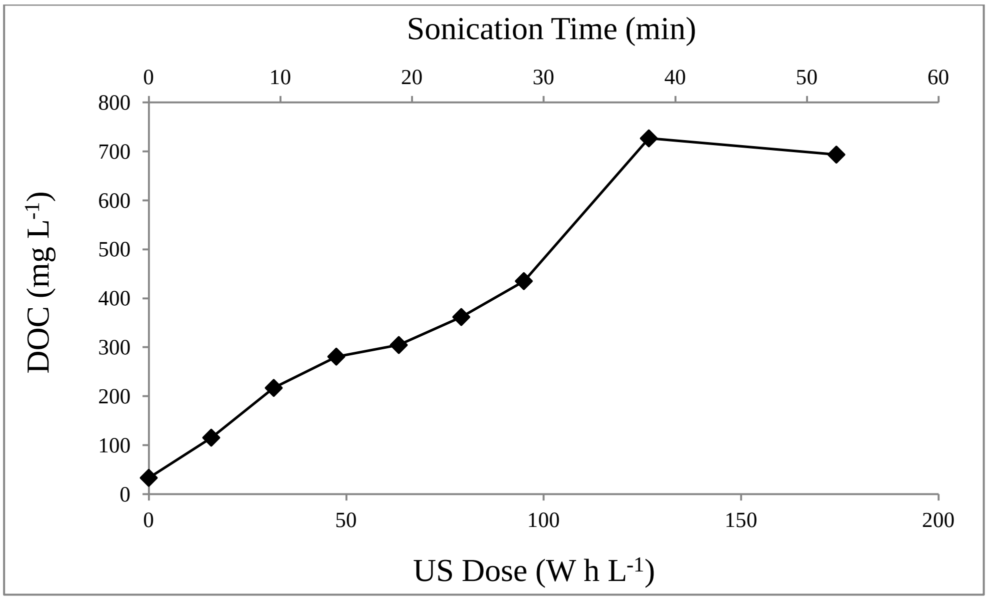


Figure 4.15. Effect of applied ultrasound dose and contact time on DOC concentration

Note that the increasing trend in DOC with increasing US dose is very similar to that of sCOD as both parameters represent the organic content of the sludge.

Physical Parameters

Table 4.13 gives the results of the preliminary physical experiments. The data are also shown graphically in Figures 4.16 and Figure 4.17.

Table 4.13. Results of the physical analyses on the preliminary ultrasound experiments

US Dose (W h L^{-1})	**Turbidity (NTU)**	**CST (s)**
0.0	41	56
15.8	164	291
31.6	216	404
47.5	382	456
63.3	453	583
79.1	578	645
95.0	747	730
126.6	1476	1064
158.3	2232	1345
174.1	-	1520

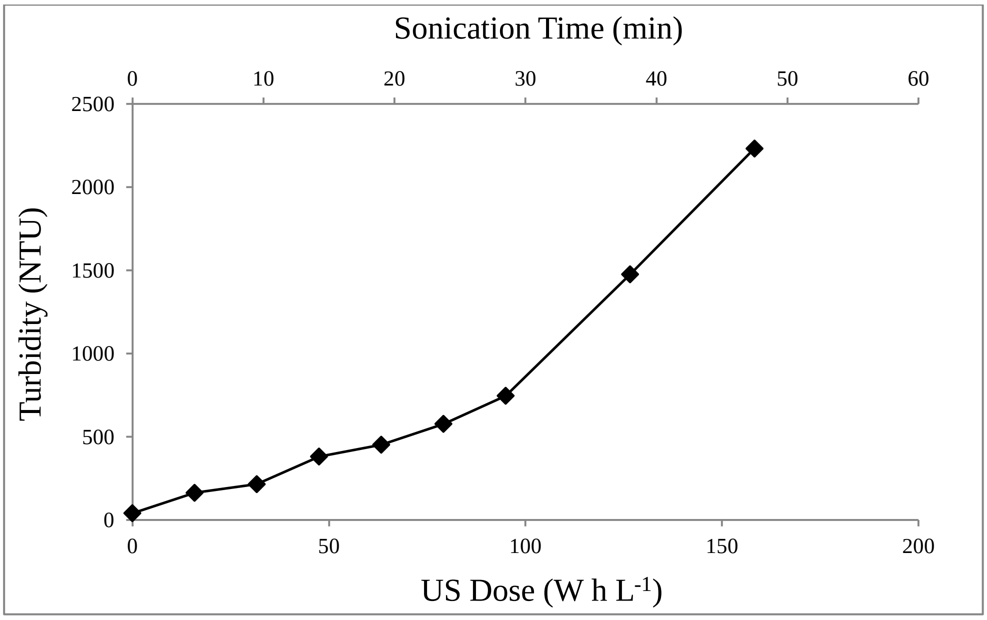


Figure 4.16. Effect of ultrasound dose/contact time on turbidity

Figure 4.16 shows that the turbidity increased from 41 NTU to 2232 NTU with an increase of US dose from 0 to 158.3 W h L^{-1}. As previously explained in section 4.1.2.1 nearly in all literature published on ultrasonic sludge disintegration, turbidity of sludge increases with increasing ultrasound dose as a consequence of the release of intracellular material.

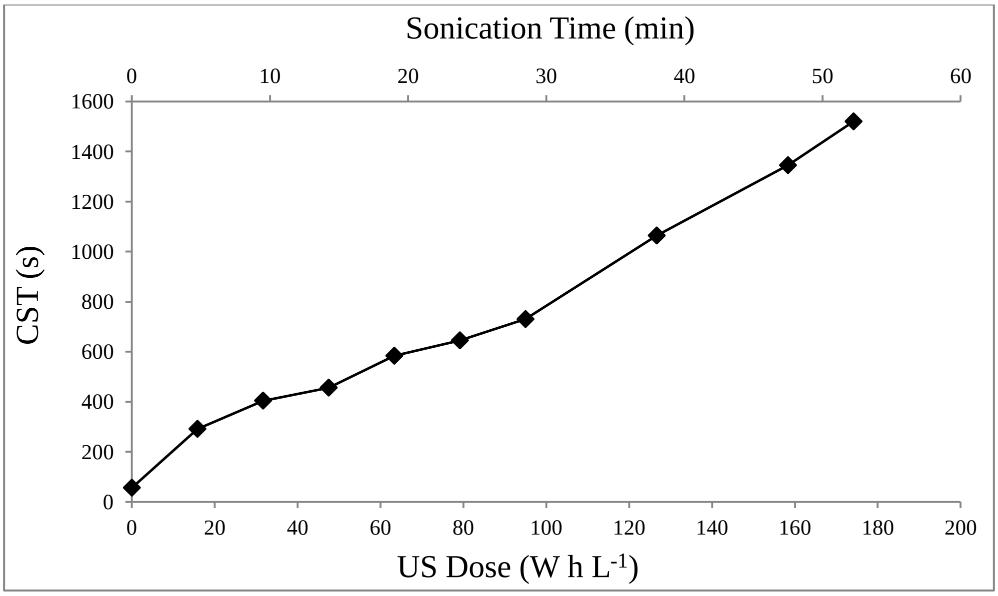


Figure 4.17. Effect of ultrasound dose/contact time on CST

Figure 4.17 shows that CST of WAS increases again (as in TUHH) with increasing doses and sonication times. Application of ultrasound at 174.1 W h L^{-1} dose increased CST from 56 s to 1520 s. Hence, dewaterability of WAS is negatively effected by sonication as in TUHH.

The increasing trends of CST and turbidity are compared in Figure 4.18 and Figure 4.19 for the data generated in TUHH and BU. Hence, in both laboratories regardless of the US equipment and applied doses the dewaterability of the sludge decreased with increasing US doses.

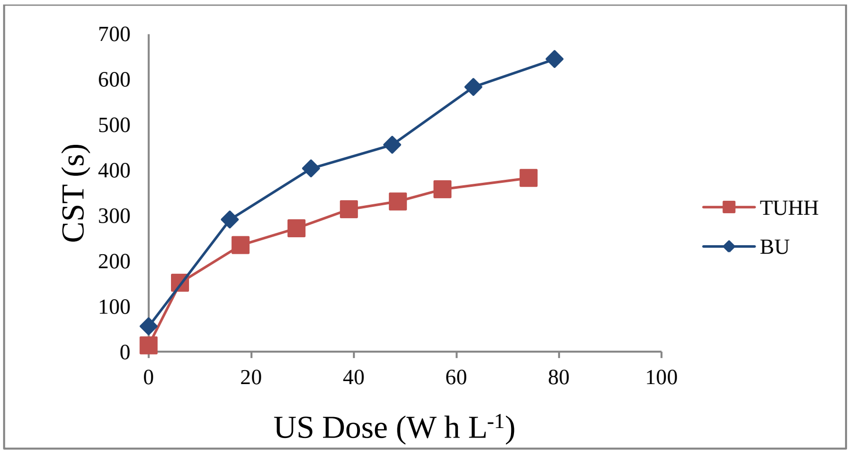


Figure 4.18. Comparative increase in CST by increasing ultrasound doses in TUHH & BU

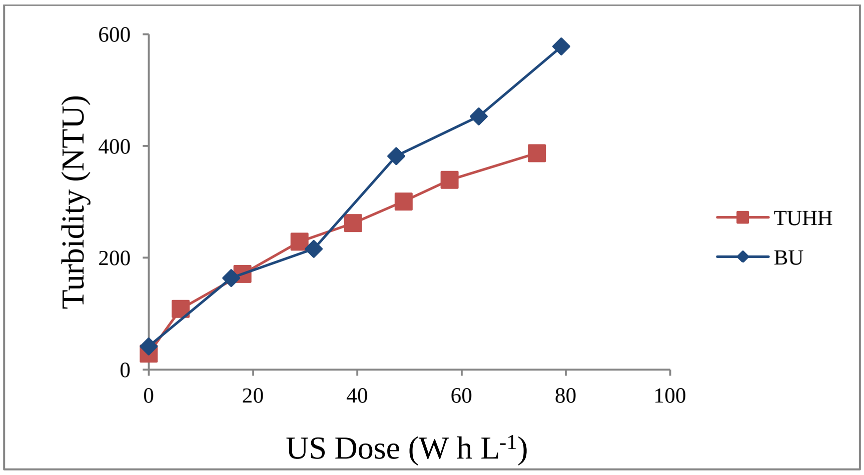


Figure 4.19.Comparative increase in turbidity by increasing ultrasound doses in TUHH & BU

The effect can be explained by the fact that the US energy reduces the average floc size, thus enhancing the particle surface area. As such, the capacity to adsorp water increases with an increase in cake clogging and a decrease in the filterability (Dewil et al., 2006).

Biological Parameters

In addition to the chemical and physical parameters, the sludge was analyzed for the microbial count to confirm the impact of ultrasound on deactivation of viable microorganisms. The data are presented in Table 4.14 and Figure 4.20 in terms of a survival curve, defined as the logarithm of the relative population size [ln (N/N_0)] as a function of time.

Table 4.14. Effect of ultrasound dose/specific energy/time on number of bacterial colonies

Sonication time	**US dose ($W\ h\ L^{-1}$)**	**N ($CFU\ mL^{-1}$)**	**Survival Ratio N/N_0**	**ln(N/No)**
0	0.0	$2.48x10^7$	1	0
5	15.8	$2.1\ x10^4$	$8.46x10^{-4}$	-7.07408
15	47.5	$5.5\ x10^3$	$2.21\ x10^{-4}$	-8.41385
25	79.1	$4.4\ x10^3$	$1.77\ x10^{-4}$	-8.63699
40	126.6	$3.2\ x10^3$	$1.29\ x10^{-4}$	-8.95545

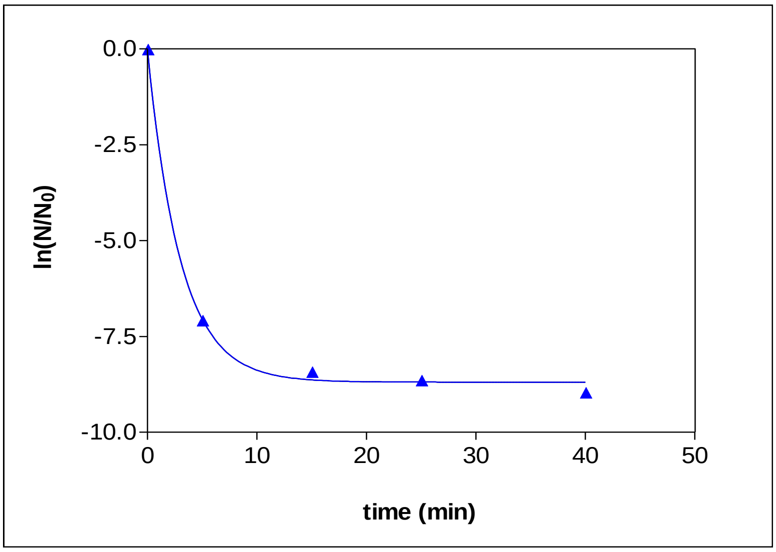


Figure 4.20. Effect of contact time on deactivation

The shape of the survival curve shows that the density of heterotrophic bacteria decreased sharply during the initial stages of sonication, but much slower after 15 minutes. Survival ratio after 40 minutes of ultrasonication was reduced to 0.01%.

4.2. Pretreatability of WAS by Classical and Advanced Fenton Oxidation

As mentioned previously in section 4.1.2.2 the study at BU mainly aimed to investigate the effect of Fe^{2+}/H_2O_2 and Fe^0/H_2O_2 on ultrasonic disintegration of WAS. Before application of the hybrid process, (US/Fenton) preliminary silent tests were carried out with Fe^{2+} and Fe^0 to select the optimum operating concentrations.

4.2.1. Assessment of Classical Fenton Oxidation Parameters

The reagent doses applied were previously given in Table 3.4. It was observed that the classical Fenton pretreatment of WAS resulted in a color change from brown to gray in almost all doses applied. Figure 4.21 shows the observed color change after classical Fenton pretreatment of the sludge.

a) Raw sludge	b) $[Fe^{2+}]$=0.0044 M, $[H_2O_2]$=0.0588 M	c) $[Fe^{2+}]$=0.0089 M, $[H_2O_2]$=0.1176 M	d) $[Fe^{2+}]$=0.0133 M, $[H_2O_2]$=0.176 M

Figure 4.21. Change in sludge color after 1 h silent classical Fenton reaction at pH=3 (mixing rate 125 rpm, $[Fe^{2+}/H_2O_2]$=0.075).

Table 4.15 gives the changes in chemical parameters of the WAS upon 1 hour exposure to the classical Fenton process (Fe^{2+}/H_2O_2). The "Dose" of the reagent as defined previously refers to specific molar concentrations of Fe^{2+} and H_2O_2. The data are plotted in Figure 4.22 and 4.23 as bars.

Table 4.15. Changes in the chemical parameters of WAS after 1 hour exposure to varying doses of Fenton's reagent.

Dose	$[Fe^{2+}]$ (M)	$[H_2O_2]$ (M)	sCOD (mg L^{-1})	DOC (mg L^{-1})	sCOD/TOC (%)
0	0.0000	0.0000	152.21	30.23	3.29
1	0.0044	0.0294	178.02	39.37	3.84
2	0.0044	0.0588	238.90	45.07	5.16
3	0.0089	0.0588	276.17	54.05	5.96
4	0.0089	0.1176	710.57	103.64	15.34
5	0.0133	0.0882	267.04	52.35	5.77
6	0.0133	0.1764	442.33	79.26	9.55
7	0.0178	0.1176	228.89	51.70	4.94
8	0.0178	0.2352	218.66	38.61	4.72

The data show that the solubilization of COD and release of intracellular material into the aqueous phase was maximum at Dose 4. Therefore, Dose 4 was selected as the optimum dose and used in combination with ultrasound during sono-classcal Fenton oxidation experiments.

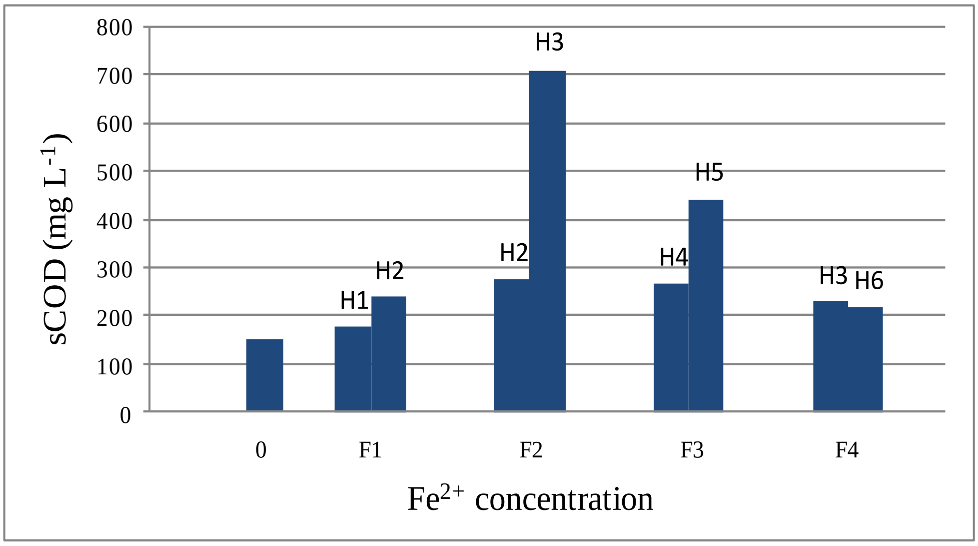


Figure 4.22. Effect of reagent dose on solubilization of COD by silent classical Fenton oxidation (0= Raw Sludge, F1= 0.0044 M Fe^{2+}, F2=0.0089 M Fe^{2+}, F3= 0.0133 M Fe^{2+}, F4= 0.0178 MFe^{2+}, H1= 0.0294 M H_2O_2, H2= 0.0588 M H_2O_2, H3= 0.1176 M H_2O_2, H4= 0.0882 M H_2O_2, H5= 0.1764 M H_2O_2, H6= 0.2352 M H_2O_2)

Figure 4.22 and Figure 4.23 demonstrate that increasing Fe^{2+} and H_2O_2 concentrations positively affected sludge solubilization up to Dose 4 (Fe2=0.0089 M Fe^{2+}, H3= 0.1176 M H_2O_2). At higher concentrations, a decreasing trend in solubilization was observed. Therefore, optimum molar Fe^{2+}/H_2O_2 ratio was set as 0.075.

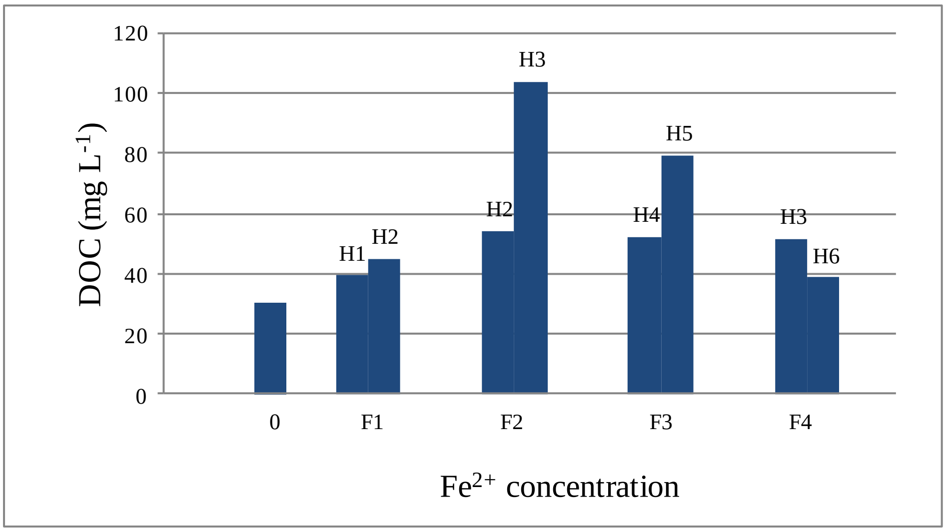


Figure 4.23. Effect of reagent dose on DOC increase by silent classical Fenton oxidation (F1= 0.0044 M Fe^{2+}, F2=0.0089 M Fe^{2+}, F3= 0.0133 M Fe^{2+}, F4= 0.0178 MFe^{2+}, H1= 0.0294 M H_2O_2, H2= 0.0588 M H_2O_2, H3= 0.1176 M H_2O_2, H4= 0.0882 M H_2O_2, H5= 0.1764 M H_2O_2, H6= 0.2352 M H_2O_2)

Lower efficiency of WAS solubilization at doses higher than Dose 4 can be attributed to two phenomena: i) the competition between organic cell material and H_2O_2 for •OH radicals, ii) oxidation of DOC/sCOD exerting compounds in the presence of excess •OH. Similar findings were reported in the literature for WAS pretreatment by classical Fenton process (Bougrier et al., 2006, Tokumura et al.,2008, He Ming-he et al., 2009, Tokumura et al., 2006).

CST and turbidity measurements of Fenton-processed WAS samples for evaluation of dewatering characteristics are given in Table 4.16. It was found that dewaterability was also improved by the applied Fenton pretreatment. The data are also presented graphically in Figure 4.24 and 4.25.

Table 4.16. Changes in the physical parameters of WAS after 1 hour exposure to varying doses of Fenton's reagent.

Dose	**[Fe^{2+}] (M)**	**[H_2O_2] (M)**	**CST (s)**	**Turbidity (NTU)**
0	0.0000	0.0000	55	51
1	0.0044	0.0294	44	42
2	0.0044	0.0588	37	46
3	0.0089	0.0588	32	52
4	0.0089	0.1176	23	35
5	0.0133	0.0882	30	31
6	0.0133	0.1764	25	38
7	0.0178	0.1176	26	38
8	0.0178	0.2352	21	28

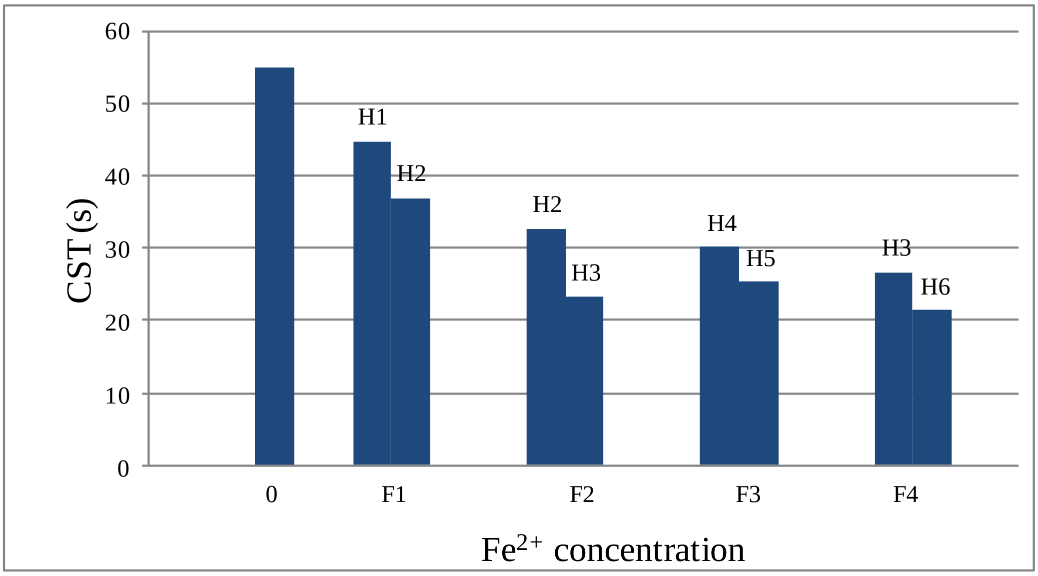


Figure 4.24. Effect of reagent dose on CST reduction by silent classical Fenton oxidation (F1= 0.0044 M Fe^{2+} , F2=0.0089 M Fe^{2+}, F3= 0.0133 M Fe^{2+}, F4= 0.0178 MFe^{2+}, H1= 0.0294 M H_2O_2, H2= 0.0588 M H_2O_2, H3= 0.1176 M H_2O_2, H4= 0.0882 M H_2O_2, H5= 0.1764 M H_2O_2, H6= 0.2352 M H_2O_2)

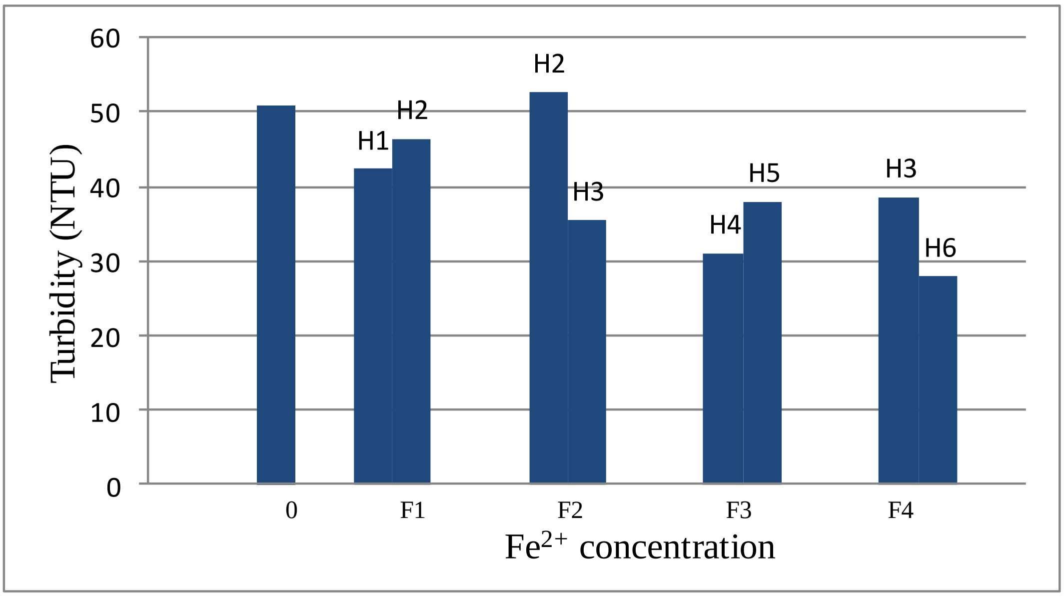


Figure 4.25. Effect of reagent dose on turbidity reduction by silent classical Fenton oxidation (F1= 0.0044 M Fe^{2+} , F2=0.0089 M Fe^{2+}, F3= 0.0133 M Fe^{2+}, F4= 0.0178 M Fe^{2+}, H1= 0.0294 M H_2O_2, H2= 0.0588 M H_2O_2, H3= 0.1176 M H_2O_2, H4= 0.0882 M H_2O_2, H5= 0.1764 M H_2O_2, H6= 0.2352 M H_2O_2).

Fig 4.24 shows that higher Fe^{2+} and H_2O_2 concentrations caused larger reduction in CST. This results show that in addition to increased solubilization, Fenton process improved the filtration characteristics of the sludge. Minimum CST value achieved at a molar [Fe^{2+}/H_2O_2] ratio of 0.075 ([Fe^{2+}]=0.0178 M). In agreement with this observation, Pere et al. (1993) also stated that Fenton pretreatment of sludge enhances dewaterability. Neyens et al. (2004) applied Fenton’s oxidation to thickened sludge taken from a municipal sewage treatment plant at different conditions and achieved a reduced CST-value by approximately 20 s when compared with the ‘blank’ sample. They explained that Fenton’s oxidation enhances cake dewaterability in two ways: (i) Fenton oxidation degrades EPS (extracellular polymeric substances) proteins and polysaccharides reducing the EPS water retention properties (ii) it promotes flocculation which reduces the amount of fine flocs.

The CST data observed were closely verified by the turbidity data plotted in Figure 4.25.

4.2.2. Analysis of Advanced Fenton Oxidation Parameters

The applied reagent doses were previously given in Table 3.5. In this process also the color of the sludge changed from brown to light brown after 1 hour silent contact.

	
a) Raw sludge	b) $[Fe^0]$=0.0089 M, $[H_2O_2]$=0.0588 M

Figure 4.26. The change in sludge color after 1 h silent advanced Fenton reaction at pH=3 (mixing rate 125 rpm, $[Fe^0/H_2O_2]$=0.15).

Table 4.17 gives the changes in chemical parameters of the WAS upon 1 hour exposure to the advanced Fenton process (Fe^0/H_2O_2). The data are plotted in Figure 4.27 and 4.28 as bars.

Table 4.17. Changes in the chemical and physical parameters of WAS after 1 hour exposure to varying doses of Fenton's reagent.

Dose	**$[Fe^0]$ (M)**	**$[H_2O_2]$ (M)**	**sCOD ($mg\ L^{-1}$)**	**sCOD/TCOD (%)**	**DOC ($mg\ L^{-1}$)**	**CST (se)**	**Turbidity (NTU)**
0	0.0000	0.0000	152.2	3.2	30.2	55	51
1	0.0018	0.0117	159.8	3.4	32.5	-	-
2	0.0089	0.0588	535.0	11.5	84.8	32	41

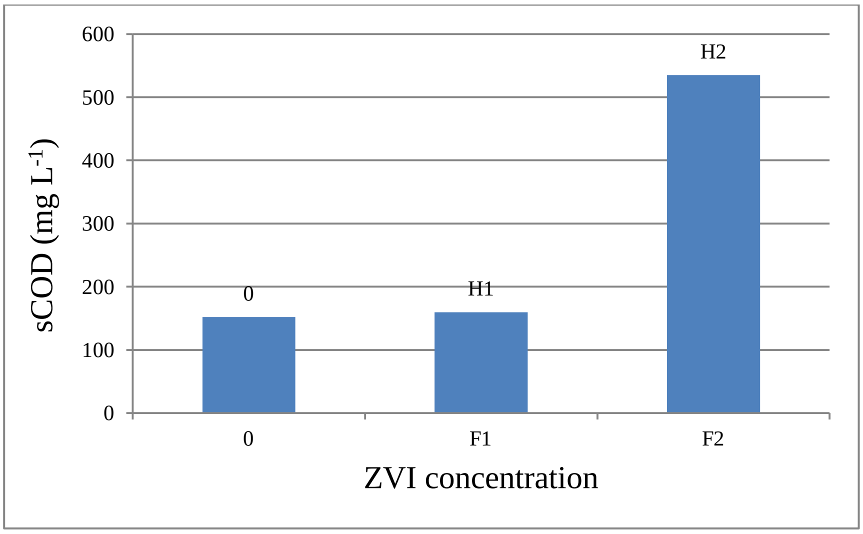


Figure 4.27. Increase of sCOD with Advanced Fenton's Reagent Doses
(F1= 0.0018 M Fe^0 , F2=0.0089 M Fe^0, H1=0.0117 M H_2O_2, H2=0.0588 M H_2O_2).

Figure 4.27 shows that solubilization of COD and the release of intracellular material into the aqueous phase was maximum at F2/H2 which corresponds to Dose3. Note that when the same dose was applied in the classical Fenton's process (Figure 4.22, Dose3) the sCOD was increased to half of that achieved by advanced Fenton's. Concentration of H_2O_2 in advanced Fenton process was half of that used in the classical Fenton process, but maximum solubilization in terms of sCOD/TCOD was 11.5% and 15%, respectively.

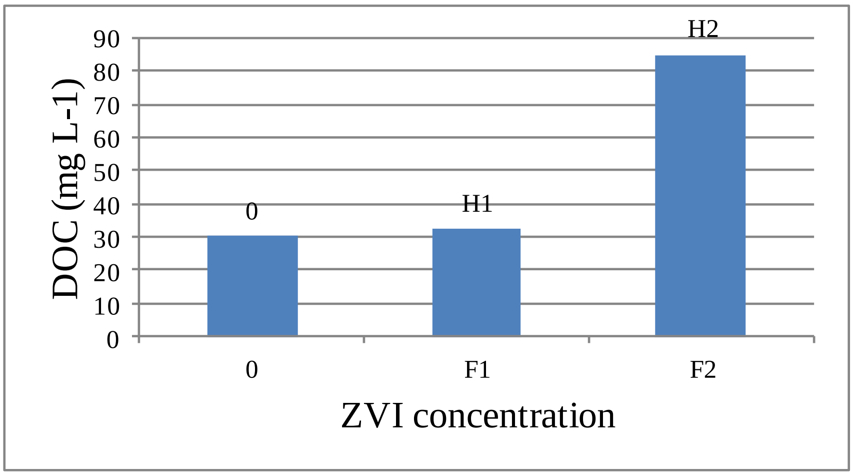


Figure 4.28. Increase of DOC with Advanced Fenton's Reagent Doses
(F1= 0.0018 M Fe^0 , F2=0.0089 M Fe^0, H1=0.0117 M H_2O_2, H2=0.0588 M H_2O_2).

In addition, CST and turbidity of WAS was reduced upon the Advanced Fenton reaction, indicating the improvement on the dewaterability of the sludge. Application of F2 and H2 resulted in 42% CST and 20% turbidity reduction.

The efficiency of advanced Fenton processes on solubilization and dewaterability despite the two-fold lower dose of hydrogen peroxide can be attributed to the faster recycling of ferric iron at the iron surface through Reaction (22) given in Section 2.6, and the heterogenous surface reactions (Bremner et al.,2006).

The efficiency of classical and advanced Fenton processes at the natural pH of the sludge (pH=6.24) was also tested. It was found that both processes were ineffective for solubilization at the natural pH of the sludge. Previous Fenton studies have also shown that acidic pH levels near 3 are usually optimum for Fenton oxidations (Hickey et al. 1995). The poor efficiency at pH 6.2 is due to catalyst precipitation above pH 3 in the form of relatively inactive hydrous oxyhydroxides (Pignatello, 2006).

4.3. Pretreatability of WAS by Combined US/Classical-Fenton and US/Advanced-Fenton Oxidation Processes

The following sections contain the results of the two hybrid processes tested, namely US/Fe^{2+}-Fenton and US/ZVI-Fenton.

4.3.1. Chemical Parameters

4.3.1.1. sCOD & Solubilization. The efficiency of US/Fe^{2+}-Fenton process was first tested at two distinct pH levels: i) pH=3, ii) pH=6.24 (natural). The results are plotted in Figure 4.29. The data for US alone are also included for comparison.

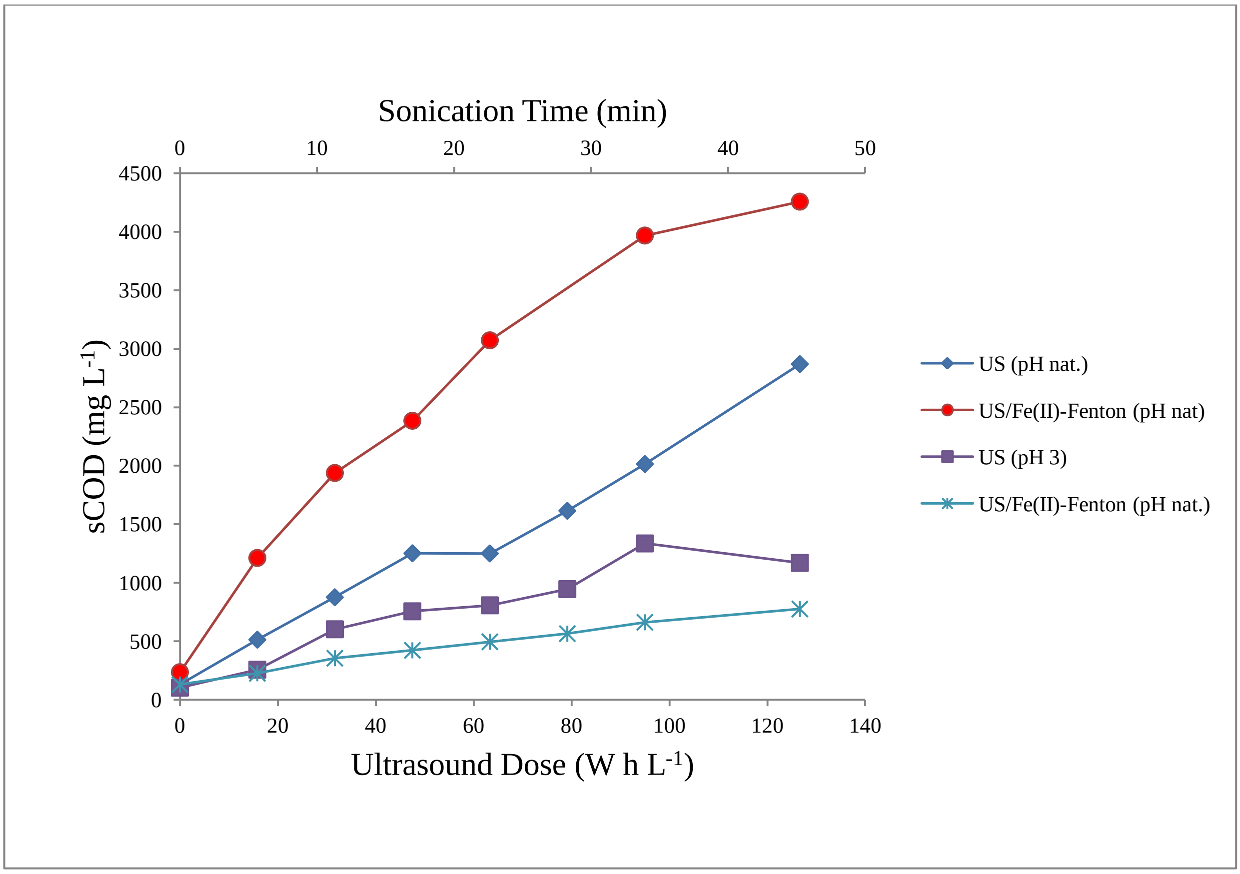


Figure 4.29. Effect of pH on COD solubilization by US/Fe^{2+}-Fenton process during 40-min sonication of raw sludge at pH 3 and pH 6.2.

Figure 4.29 shows that solubilization of WAS was poor at pH 3 with US alone and US/Fe^{2+}-Fenton reagent. The degree of solubilization increased sharply in both the US and US-Fenton combined processes when pH was raised to 6.2.

Poor solubilization at acidic pH by US can be explained by the following phenomenon: the isoelectric or “zero-point charge” of WAS lies between pH 1-3, meaning that at pH 3, the surface of the colloidal particles carry practically no electric charge (Forster, 1971). As such, particles are stationary and tend to agglomerate when surrounded by a metallic salt such as H_2SO_4 (Neyens et al., 2003; Chen et al., 2001). In that case, the probability of hiting by a microjet stream is fairly low.

In the case of US/Fe^{2+}-Fenton, solubilization seems to be even poorer (than US alone), but we're not sure at this point whether lower sCOD values are due to poorer solubilization or to the oxidation of some solubilized COD by •OH radicals formed by Reaction (5). In addition, the "zero-point charge" condition is a drawback for the adsorption of Fe^{2+}/H_2O_2 pair on colloid surfaces for cell disruption or oxidation.

At pH 6.24, solubilization by US is much faster because of the charge separation between the ends of long extracellular material chains (Jin et al., 2003). The more hydrophobic positive end bends toward the cavity bubbles, while the less hydrophobic negative end pulls towards the bulk solution. Hence, the destruction cleavage and thermal fragmentation of the molecules may take place.

It was also found that solubilization or sCOD release was very fast in the US/Fe^{2+}-Fenton hybrid process at pH 6.24. This is due to a variety of factors such as

i) the existence of excess heterogenous surfaces at this pH [($Fe(OH)_3$], which leads to excess cavity formation and excess surface reactions (between microbial cells and H_2O_2) that disrupt the cell wall and release extracellular material.

ii) the lack of •OH radical reactions at this pH to oxidize the sCOD causing organic compounds, as was the case at pH 3.

In accordance with these findings, we carried out the rest of the experiments at the natural pH of the sludge. Figure 4.30 shows the impact of ultrasound dose/sonication time on sCOD of WAS in US, US/Fe^{2+}-Fenton and US/ZVI-Fenton systems at pH 6.2.

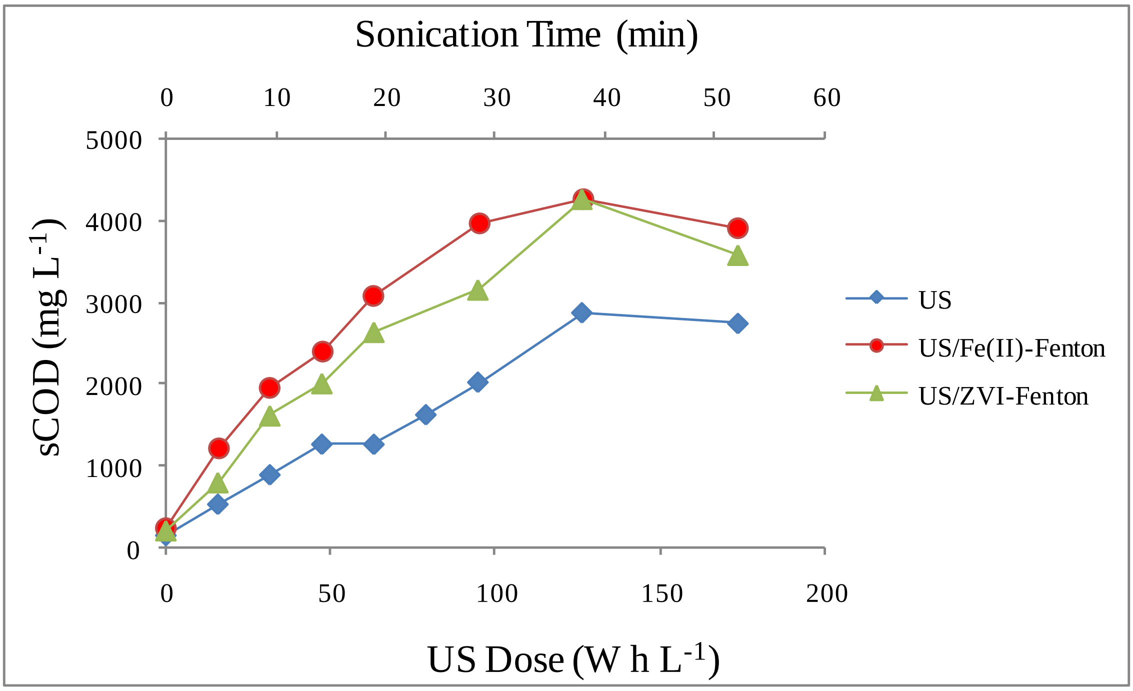


Figure 4.30. Effect of US dose on sCOD in the slurry by US alone, US/Fe^{2+}-Fenton, US/ZVI-Fenton systems at pH 6.2.

The results obtained demontrated that application of ultrasound in the presence of classical or advanced Fenton's reagents at pH 6.2 led to a significant increase in COD solubilization. The sCOD concentration of the untreated sludge (131.3 mg L^{-1}) was increased to 2737, 3912.6, 3586.6 mg L^{-1} after 40-min. pretreatment with US, US/Fe^{2+} and US/ZVI, respectively. At longer treatment duration, the value of sCOD was found to decline as a consequence of simultaneous oxidation of the soluble organic matter. The degree of solubilization, i.e. the ratio of sCOD to TCOD is given in Figure 4.31 for the same data.

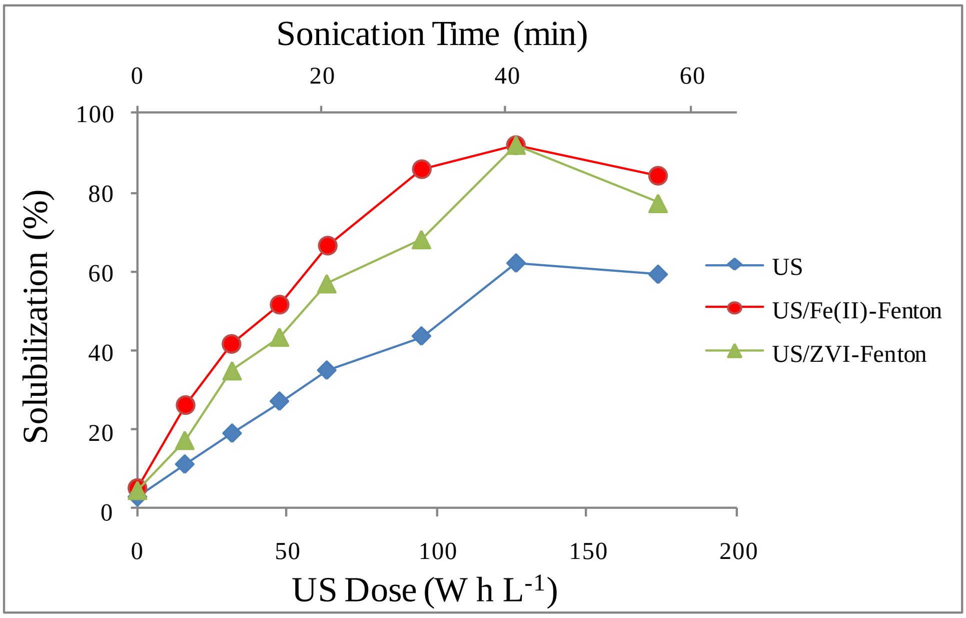


Figure 4.31. Comparative profiles of organic matter solubilization by ultrasound, US/Fe^{2+}-Fenton and US/ZVI-Fenton hybrid processes at pH 6.2.

It is important to keep in mind that a slightly better solubilization in the presence of US/Fe^{2+}-Fenton than US/ZVI-Fenton process is due to a two-fold larger hydrogen peroxide dose in the former. Closely equivalent yields obtained in sono-Fenton and sono-advanced Fenton processes despite the two-fold lower dose of hydrogen peroxide in the latter is due to the power of ultrasound for disintegrating heterogenous surfaces, thus increasing surface defects and the number of active sites while inducing a continuous cleaning action (Eren and Ince, 2010).

To our knowledge, there is no report on disintegration of WAS by US/Fe^{2+}-Fenton or US/ZVI-Fenton hybrid processes. However, Liang and co-workers observed that combination of ultrasonic irradiation with ZVI resulted in a significant enhancement in the degradation of 4-chlorophenol (Liang et al., 2007). Chand and co-workers also reported that phenol degradation performance by low frequency US was remarkably improved in the presence of CCl_4, nano-sized TiO_2 and zero-valent copper (Chand et al., 2009). Tezcanlı and Ince (2011) studied degradation of diclofenac by high frequency ultrasound and reported improved efficiency by the addition of iron species, which they explained by the synergy of nanotechnology and ultrasound; i.e. massive surface areas, excess cavitation nuclei, enhanced mass transfer and continuous cleaning of the metal surface. Zhang et al. (2009) also reported that the combination of ultrasound and advanced Fenton process could decolorize C.I Acid Orange 7 effectively.

Ultrasonic irradiation could lead to a faster dissolution of iron due to the removal or destruction of passivation films on the metal surface by cavitation effects and the increased mass transfer caused by microjetting (Suslick, 1994). As previously explained in Section 2.5, microjetting is formed when cavitation bubbles implode asymetrically. In the meantime, the high speed microjets can break up iron particles resulting in a larger contact area and accordingly higher mass transfer rates. Therefore, the corrosion of ZVI was enhanced with increasing US energy.

4.3.1.2. DOC. The impact of US dose/sonication time on DOC release by the US alone, US/Fe^{2+}-Fenton and US/ZVI-Fenton systems at pH 6.2. are presented in Figure 4.32.

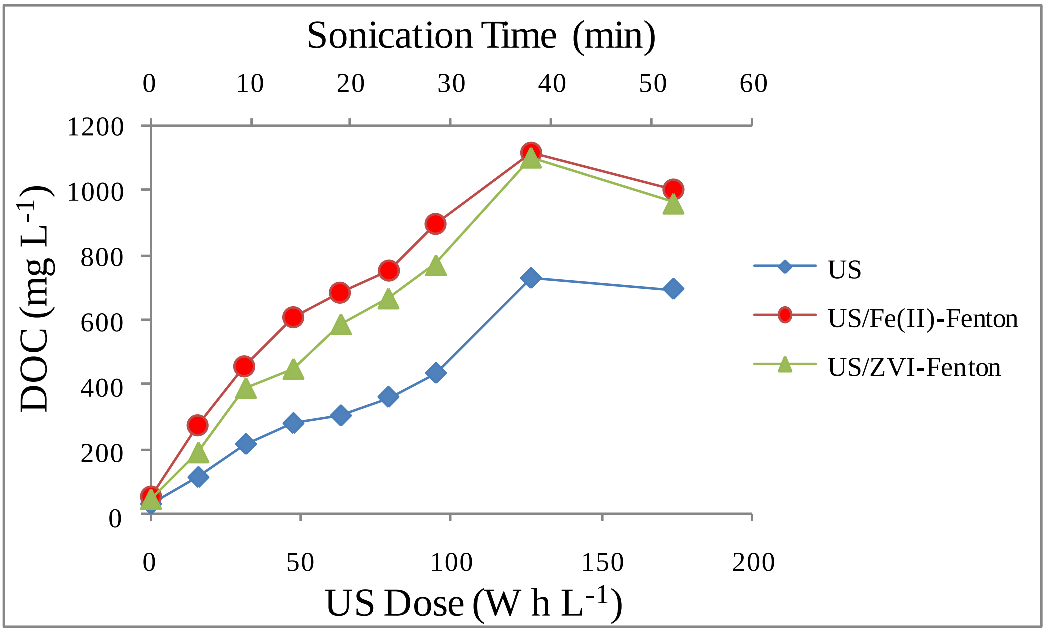


Figure 4. 32. Effect of US, US/Fe^{2+}-Fenton and US/ZVI-Fenton systems on DOC increase during sonication of raw sludge at its natural pH.

Figure 4.32 shows that the tendency of DOC increase is very similar to that observed in sCOD. The DOC concentration of the untreated sludge (33.35 mg L^{-1}) was increased to 726.7,1113,1104.5 mg L^{-1} after 50-min. pretreatment with US, US/Fe^{2+} and US/ZVI, respectively. It was found that at DOC_0= 33.35 mg L^{-1}, maximum DOC was 726.7, 1113, 1104.5 mg L^{-1}, with US, US/Fe^{2+}-Fenton and US/ZVI-Fenton processes respectively. The reduction in DOC after reaching the maximum is the result of mineralization of dissolved organic substances.

4.3.2. Physical Parameters

4.3.2.1. Turbidity. Figure 4.33 shows the impact of US dose/sonication time on the turbidity of sludge supernatants during US and US-combined pretreatments.

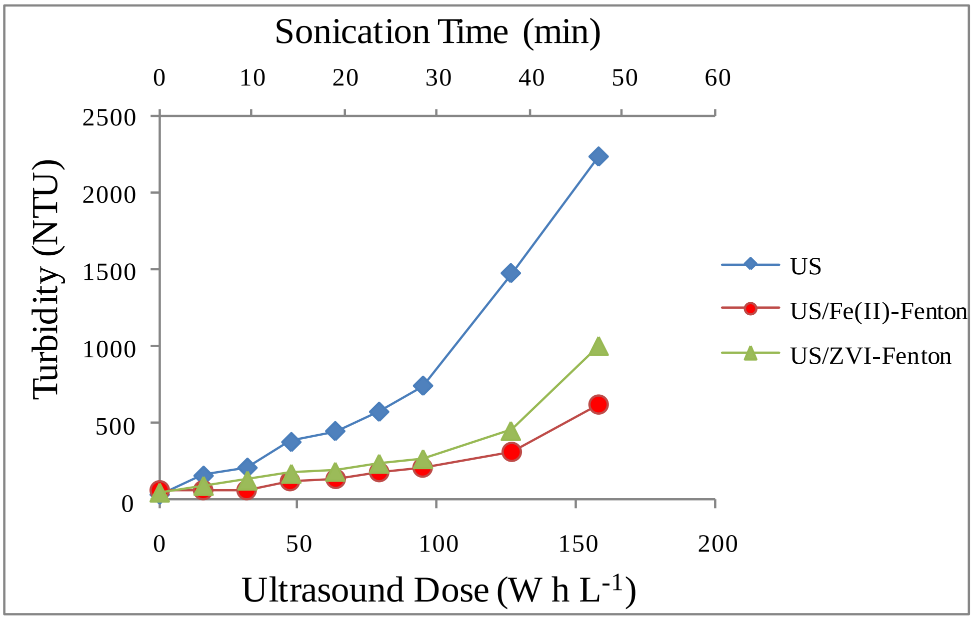


Figure 4.33. Comparative profiles of turbidity increase by US, US/Fe^{2+}-Fenton and US/ZVI-Fenton processes

The data show that at pH 6.2 turbidity of the supernatant is lower in US-combined Fenton processes than in US alone. On the other hand, the combined processes were found to increase the degree of solubilization, which in turn is expected to enhance turbidity of the supernatant. The contradiction of lower turbidity in the presence of classical/advanced Fenton reagent can be explained by two phenomenon: i) at pH 6.2 some of iron species exist as the insoluble $Fe(OH)_3$, which precipitates during centrifugation; ii) simultaneous mineralization of soluble organics.

4.3.2.2. CST. Figure 4.34 shows the impact of US dose/sonication time on sludge dewaterability by ultrasound alone and the hybrid processes. Dewaterability was analyzed by measuring the CST.

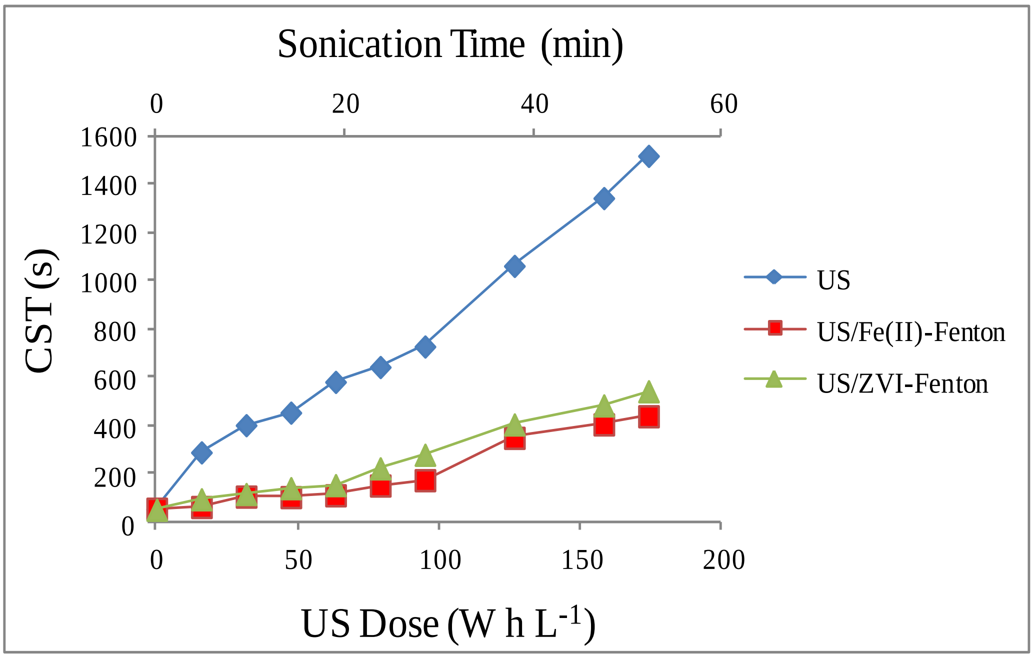


Figure 4.34. Increase in CST during exposure to US, US/Fe^{2+}-Fenton and US/ZVI-Fenton systems at increasing ultrasound dose

The overall dewaterability was found to decrease when the irradiation time or the US dose was increased, as a consequence of the water-retaining effect of released biopolymers from the flocs to the aqueous phase. In any case, the data show that combined US-Fenton processes are more effective than US alone for dewaterability. The reason for better dewaterability in hybrid processes than in ultrasound alone can be explained by the potential degradation of EPS (extracellular polymeric substances) proteins and polysaccharides. In addition Fenton oxidation is known to improve sludge flocculation such that Fenton's reagent act as a conditioning agent for sludge settleability. Furthermore, formation of ferric hydroxo- complexes accounts for the coagulation capability of Fenton's reagent.

4.3.3. Biological Parameters

4.3.3.1. Microbial Count. Classical Fenton (Fe^{2+}-Fenton) and US/Fe^{2+}-Fenton processes were applied to sludge samples with an initial cell concentration of N_0 = 2.48x10^7 CFU mL^{-1}. The survival ratio was reduced to 0.57% after 1 hour silent classical Fenton reaction. The appearance of the colonies after US and US/Fe^{2+}-Fenton processes are given in Table 4.18.

Table 4.18. Microbial count results after varying contacts with US alone and US/classical Fenton processes.

Sonication Time	**Survival %**	
	US	**US/Fe^{2+}-Fenton**
0	100	100
5	0.085	0.044
10	-	0.023
15	0.022	-
20	0.020	0.013
25	0.018	-
30	-	0.008
40	0.013	-

It was found that 99.56% of bacteria were inactivated in 5-min sonolysis alone. The degree of inactivation was 99.91% in 5-min sonication with Fenton's reagent. Almost complete inactivation was accomplished after 20 minutes by sonication with or without Fenton's reagent. The survival ratio after 20 minutes sonolysis with and without Fenton's reagent is presented as bars in Figure 4.35.

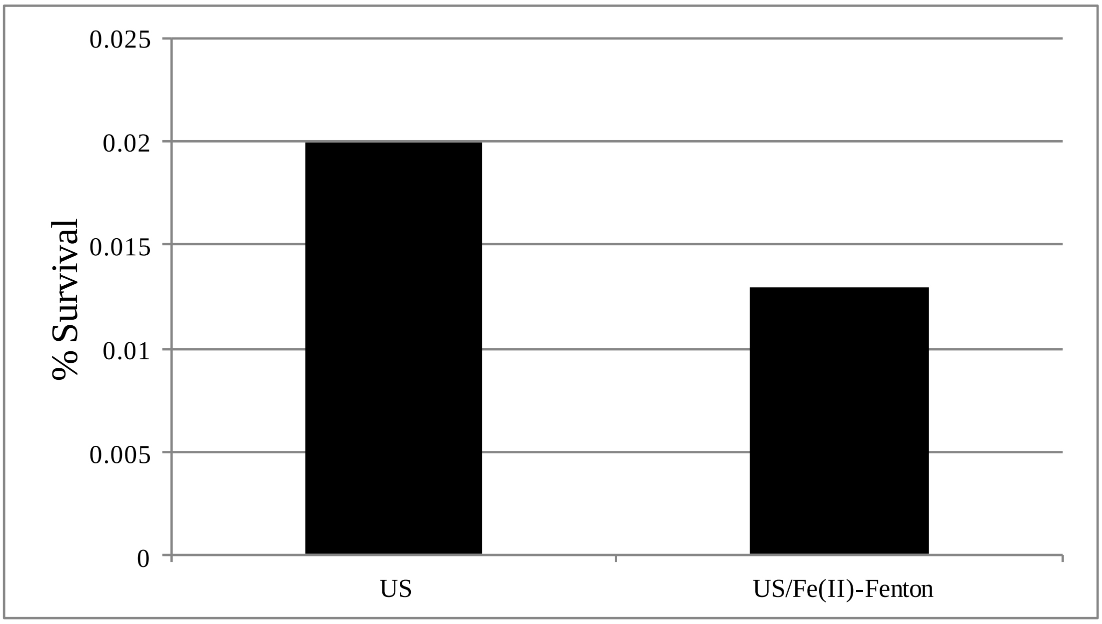


Figure 4.35. The microbial survival ratio after 20-min sonolysis with and without Fenton's reagent.

5. CONCLUSIONS AND RECOMMENDATIONS

The study presented herein was about a research on the individual and combined effects of short-wave ultrasound (US) and two different Fenton processes on solubilization and disintegration of waste activated sludge. The following conclusions were derived:

- The pretreatment of waste activated sludge (WAS) by short wave ultrasonication is a suitable method for rendering disintegration and organic solutes transfer from solids into the aqueous phase to enhance the biodegradability of the sludge. The degree of disintegration is directly proportional to the energy input, the applied US dose or the contact time.

- Individual application of US showed that solubilization of WAS was very sensitive to the ambient pH: i) poor solubilization at acidic level (pH 3) was attributed to the low "isoelectric" or "zero-point charge" of waste activated sludge (pH 2-3), at which particles have a net zero electrical charge and remain stationary in solution. When surrounded by a mineral acid such as H_2SO_4, they tend to agglomerate and form flocs, which are harder to break-up by ultrasound than the particulate forms; ii) much better solubilization at pH 6.24 is therefore the result of destabilization and charge separation between different moities of long extracellular compounds. At such, the hydrophobic moities approach the bubble-liquid interface, where they are readily disrupted by microjet streams following cavitational collapse. In addition, application of US alone reduced the dewaterability of WAS at pH 6.24, to be attributed to the release of biopolymers into the aqueous phase.

- Individual classical and advanced Fenton applications showed that both were effective for solubilization and dewaterability at pH 3, but relatively ineffective at pH 6.2. High efficiency at acidic pH is the result of excessive •OH production by the cyclic Fe^{2+}/Fe^{3+} oxidation/reduction mechanism. It was also found that the "advanced" Fenton process was nearly twice more effective than the classical Fenton, due to the presence of excess reaction sites (surfaces).

- Combined US/Fenton applications at pH 6.2 using either Fe^{2+} or solid Fe^0 were found to increase the solubilization efficiency of ultrasonic treatment via the existence of excess heterogenous surfaces at this pH level that led to excess cavity formation and additional reaction sites. The microjet streams formed by cavitational collapse facilitated mass transfer of solutes onto solid surfaces and the release of the cell contents into the sludge slurry. At pH 3, both of combined US/Fenton processes were found less effective (than single US) in terms of the magnitude of sCOD observed, which, however might be due to simultaneous solubilization and oxidation/mineralization processes.

- Finally, combined US-Fenton processes were also effective for improving the dewaterability of the sludge, which was not the case in single US application. The finding was attributed to the potential mineralization of extracellular material and the formation of ferric hydroxo-complexes, which act as coagulating agents.

APPENDIX A: CALIBRATION CURVE

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

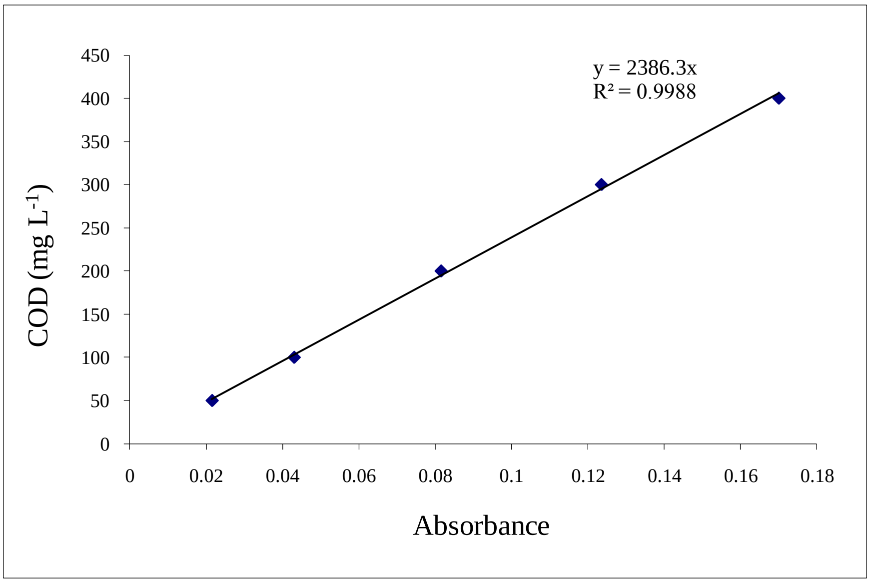


Figure A.1. Calibration curve prepared for COD analysis.

APPENDIX B: Raw data of US dose determination by calorimetric method

The raw data of temperature rise with sonication is given in Table A. 1.

Table B.1. Temperature rise with sonication

Sonication time (s)	Temperature (^oC)		Sonication time (s)	Temperature (^oC)	
	Distilled Water	Sludge		Distilled Water	Sludge
0	27.0	24.4	155	37.9	35.2
5	27.3	24.7	160	38.1	35.4
10	28.0	25.3	165	38.3	35.6
15	28.5	25.7	170	38.5	35.8
20	29.2	26.4	175	38.8	36.0
25	29.8	26.9	180	39.0	36.2
30	30.4	27.5	185	39.2	36.4
35	30.8	28.0	190	39.4	36.6
40	31.2	28.6	195	39.6	36.8
45	31.6	29.1	200	39.9	37.0
50	32.0	29.6	205	40.1	37.2
55	32.3	30.1	210	40.3	37.4
60	32.7	30.6	215	40.5	37.6
65	33.0	30.9	220	40.7	37.8
70	33.1	31.1	225	41.0	38.0
75	33.6	31.4	230	41.2	38.2
80	34.0	31.8	235	41.4	38.4
85	34.2	32.0	240	41.6	38.6
90	34.5	32.2	245	41.8	38.8
95	34.9	32.5	250	42.0	39.0
100	35.1	32.7	255	42.3	39.2
105	35.3	33.0	260	42.5	39.4
110	35.6	33.2	265	42.7	39.6
115	35.9	33.4	270	42.9	39.8
120	36.1	33.7	275	43.2	40.0
125	36.4	33.9	280	43.4	40.2
130	36.6	34.1	285	43.6	40.3
135	36.9	34.3	290	43.8	40.5
140	37.1	34.6	295	44.1	40.7
145	37.4	34.8	300	44.2	41.0
150	37.6	35.0	305	44.5	41.1

Table B.1. Temperature rise with sonication (continued)

Sonication time (s)	**Temperature (°C)**		**Sonication time (s)**	**Temperature (°C)**	
	Distilled Water	**Sludge**		**Distilled Water**	**Sludge**
310	44.6	41.3	485	49.8	47.1
315	44.8	41.5	490	49.9	47.2
320	45.0	41.7	495	50.1	47.4
325	45.1	41.9	500	50.2	47.5
330	45.3	42.1	505	50.4	47.7
335	45.4	42.3	510	50.5	47.8
340	45.5	42.5	515	50.7	47.9
345	45.7	42.7	520	50.8	48.1
350	45.8	43.0	525	50.9	48.3
355	46.0	43.2	530	51.1	48.4
360	46.1	43.4	535	51.2	48.5
365	46.3	43.5	540	51.3	48.7
370	46.4	43.7	545	51.5	48.8
375	46.6	43.9	550	51.6	48.9
380	46.7	44.2	555	51.8	49.1
385	46.9	44.3	560	51.9	49.2
390	47.0	44.5	565	52.1	49.3
395	47.2	44.7	570	52.2	49.5
400	47.3	44.8	575	52.3	49.6
405	47.5	44.9	580	52.5	49.7
410	47.6	45.0	585	52.6	49.9
415	47.8	45.2	590	52.8	50.0
420	47.9	45.4	595	52.9	50.1
425	48.0	45.5	600	53.1	50.3
430	48.2	45.6	605	53.2	50.4
435	48.3	45.8	610	53.3	50.5
440	48.5	45.9	615	53.5	50.7
445	48.6	46.0	620	53.6	50.8
450	48.8	46.1	625	53.7	51.0
455	48.9	46.3	630	53.9	51.1
460	49.0	46.4	635	54.1	51.2
465	49.3	46.5	640	54.2	51.4
470	49.4	46.7	645	54.3	51.5
475	49.5	46.8	650	54.4	51.7
480	49.6	47.0	655	54.6	51.8

Table B.1. Temperature rise with sonication (continued)

Sonication time (s)	Temperature (^oC)		Sonication time (s)	Temperature (^oC)	
	Distilled Water	Sludge		Distilled Water	Sludge
660	54.7	51.9	830	59.2	56.5
665	54.9	52.1	835	59.3	56.7
670	55.0	52.2	840	59.5	56.8
675	55.2	52.3	845	59.6	57.0
680	55.3	52.5	850	59.7	57.1
685	55.4	52.6	855	59.8	57.2
690	55.5	52.7	860	59.9	57.3
695	55.7	52.9	865	60.1	57.4
700	55.8	53.0	870	60.2	57.6
705	56.0	53.2	875	60.4	57.7
710	56.1	53.3	880	60.5	57.8
715	56.3	53.5	885	60.6	57.9
720	56.4	53.6	890	60.7	58.1
725	56.5	53.7	895	60.8	58.2
730	56.6	53.8	900	60.9	58.3
735	56.8	54.0	905	61.0	58.5
740	56.9	54.1	910	61.1	58.6
745	57.0	54.3	915	61.2	58.7
750	57.2	54.4	920	61.3	58.8
755	57.3	54.6	925	61.4	59.0
760	57.4	54.7	930	61.5	59.1
765	57.6	54.9	935	61.5	59.2
770	57.7	55.0	940	61.6	59.4
775	57.8	55.1	945	61.7	59.5
780	57.9	55.2	950	61.8	59.6
785	58.1	55.4	955	61.9	59.7
790	58.2	55.5	960	62.0	59.9
795	58.3	55.6	965	62.1	60.0
800	58.5	55.8	970	62.2	60.1
805	58.6	55.9	975	62.3	60.2
810	58.7	56.0	980	62.3	60.3
815	58.8	56.1	985	62.4	60.4
820	59.0	56.3	990	62.5	60.5
825	59.1	56.4	995	62.6	60.6

Table B.1. Temperature rise with sonication (continued)

Sonication time (s)	Temperature (°C)	
	Distilled Water	Sludge
1000	62.7	60.8
1005	62.8	60.9
1010	62.9	61.0
1015	62.9	61.1
1020	63.0	61.2
1025	63.1	61.3
1030	63.2	61.4
1035	63.3	61.5
1040	63.3	61.5
1045	63.4	61.6
1050	63.5	61.7
1055	63.6	61.8
1060	63.7	61.9
1065	63.8	62.0
1070	63.8	62.1
1075	63.9	62.1
1080	64.0	62.3
1085	64.1	62.3
1090	64.1	62.4
1095	64.2	62.5
1100	64.3	62.6
1105	64.3	62.7
1110	64.4	62.8
1115	64.5	62.9
1120	64.6	63.0
1125	64.7	63.1
1130	64.7	63.1
1135	64.8	63.2
1140	64.9	63.3
1145	64.9	63.3
1150	65.0	63.4
1155	65.1	63.5
1160	65.1	63.6
1165	65.2	63.7
1170	65.3	63.8
1175	65.4	63.9
1180	65.5	64.0
1185	65.5	64.0
1190	65.6	64.1
1195	65.7	64.2
1200	65.7	64.0

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