EFFECT OF ULTRASOUND ON THE ENHANCEMENT OF BIODEGRADABILITY: A STUDY WITH OLIVE MILL WASTEWATERS

by

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BS in Environment Eng., Istanbul Technical University, 2003

Submitted to the Institute of Environmental Science in partial fulfillment of the requirements for the degree of

Master of Science

In

Environmental Technology

Boğaziçi University

2009

ACKNOWLEDGEMENT

I would like to express my deepest gratitude to my thesis supervisor Prof. Dr. Nilsun H. İnce for her support, continuous guidance and patience.

I am grateful to my co-advisor Prof. Dr. Beyza Üstün for the time dedicated and observations she made throughout this work.

I would also thank to Prof. Dr. Orhan Yenigün, Prof. Dr. Orhan İnce and Assoc. Prof. Başak Güven for accepting to participate in the examining committee of this thesis.

I would recall Midas Olive Oil Plant and their employees for providing the material support for the realisation of this work.

I am also appreciated to Mrs. Gülhan Özkösemen, Asu Ziylan, Gül Geyik, Aslin Erdinç and Derya Aydın for their friendship, collaboration and kindness during my laboratory work.

I am thankful to Sema Çelebi on behalf of the Aksem Kimya Co. for her financial support and endless tolerance throughout this project. I would also recall my workmates for their kindness and moments we shared.

Last but not least, I would like to thank my dear parents Meral and Mehmet Çoker, my brother Tarık Çoker and my girlfriend Naz Çiloğlu for their support and unconditional love not only during this project, but also in my life.

ABSTRACT

Olive mill wastes are a significant source of potential or existing environmental pollution in the Mediterranean region. Olive mill wastewaters can be characterized high degree of organic pollution, dark colored, foul-smelling and hard to biodegrade due to existing non-biodegradable structure. The environmental impacts of olive mill wastewaters are considerable with the dangerous effects such as colouring of natural waters, threat to the aquatic life, causing surface and groundwater pollution, changing soil quality and plant growth. Therefore, it must be treated before discharged into the environment.

There are conventional methods existing in the treatment of olive mill wastewaters, however scientists have been still investigating alternative treatment technologies and methods. Advanced oxidation process (AOP), which are recognized with their capabilities to destroy pollutants by powerful hydroxyl radicals, are considered as a promising alternative in the treatment of these hardly wastewaters.

In this research, the removal efficiencies of organic matter and the biodegradability enhancement in the treatment of olive mill wastewaters via applying Ultrasound, UV irradiation, Fenton, photo-Fenton and combinations of them were investigated. The aim of the study was to determine the most appropriate process and its operating conditions for the treatment of olive mill wastewaters using advanced oxidation methods.

It was found that ultrasonic bath used in this study was ineffective to produce sufficient hydroxyl radicals for degradation of organic matter. However, the effectiveness of the bath increased when the system was combined with AOP processes like Fenton and UV irradiation either sequentially or simultaneously. The sequential processes of US/UV followed Fenton Process was determined the most effective method for treating olive mill wastewater in terms of COD, BOD_5 removal and biodegradibility enhancement.

ÖZET

Zeytinyağı atıksuları, Akdeniz Bölgesinde varolan veya oluşabilecek olan çevresel kirliliğin en önemli kaynakları arasında bulunmaktadır. Zeytinyağı atıksuları, yüksek miktarda organik kirlilik içeren, koyu renkli, rahatsız edici kokuya sahip, biyolojik olarak ayrışabilirliği zor yapısından kolay arıtılamayan karakterde sular olarak tanımlanmaktadır. Zeytinyağı atıksularının çevreye olan tehlikeli etkileri arasında doğal kaynak sularının renklenmesi, su yaşamına tehdit oluşturması, yüzey ve yeraltı su kirliliğine neden olması ile bitki gelişimi ve toprak kalitesini değiştirilmesi sayılabilir. Bu nedenlerden dolayı, bu tarz atıksuların arıtılarak doğaya deşarj edilmeleri gerekli olmaktadır.

Zeytinyağı atıksuları, konvansiyonel arıtma teknikleri ile arıtılabilinmesine karşın, bilim adamları ve araştırmacılar, hala alternatif arıtma teknolojileri ve metotları üzerinde çalışmaktadır. Güçlü hidroksil radikalleri ile kirlilik yaratan maddeleri yok etmeleriyle bilinen ileri oksidasyon prosesleri bu tarz atıksuların bertaraf edilmesinde alternatif olarak ümit vericidir.

Bu çalışmada, zeytinyağı atıksularının ultrases, UV ışıması, Fenton, Foto-fenton ve bunların çeşitli kombinasyonlarının organik maddelerin arıtma verimliliğine ve biyolojik olarak ayrışabilirliği incelenmiştir. Bu çalışmanın amacı, farklı ileri oksidasyon prosesleri ve bu prosesleri kontrol eden işletme şartlarının belirlenerek, zeytinyağı atıksularının arıtılmasında en uygun ve verimli metot veya kombinasyonların ortaya konulmasıdır.

Çalışmada kullanılan ultrases banyosunun, organik maddelerin parçalanması için gerekli hidroksil radikali üretiminde yetersiz kaldığı ve verimsiz olduğu tespit edilmiştir. Bununla beraber, banyonun zeytinyağı atıksularının arıtımında Fenton ve UV gibi diğer oksidasyon prosesleriyle eşzamanlı veya sıralı uygulanmasının verimliliği arttırdığı görülmüştür. Ultrases/UV prosesini takip eden Fenton sıralı proses kombinasyonun zeytinyağı atıksuları için KOİ, BOİ gideriminde ve biyolojik ayrışabilirliğin arttırılmasında en etkili metot olduğu görülmektedir.

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1. INTRODUCTION

Olive oil production as one of the oldest processes in the world has rapidly increased in recent years due to enhanced consumption of olive products and market demand. Although worldwide olive oil production is variable and subjected to a multitude of factors such as the pattern of annual rainfalls and regional soil properties, olive oil industry is of fundamental economic importance for many Mediterranean countries that account approximately 95% of the worldwide production (2 million m^3/year) (RAC/CP, 2003). As a Mediterranean country and the fifth biggest producer in the world, Turkey is believed to benefit from the present trend.

Discharging olive mill wastewaters without proper treatment leads to environmental, ecological and toxicological problems. Environmental impacts of olive mill wastewaters must be seriously considered, since they have the potential to induce hazards on aquatic life, to enhance surface and ground water pollution, to alter the soil quality and plant growth. Containing high degree of organic pollution, and hardly biodegradable characteristics due to existing non-biodegradable structure such as polyphenols and long-fatty acids are primary difficulties in the treatment of olive mill wastewaters with conventional methods. Therefore, alternative methods, such as advanced oxidation processes (AOP's) should be considered in the pre-or post-treatment of olive mill wastewaters and their applicability with conventional treatment methods.

In this research, the removal efficiencies of organic matter and the biodegradability enhancement in the treatment of olive mill wastewaters via applying Ultrasound, UV irradiation, Fenton, photo-Fenton and combinations of them were investigated. The aim of the study was to determine the effectiveness of advanced oxidation methods and improve its biodegradability enhancement for the integration with biological systems. COD, BOD_5, biodegradability ratio and its operating conditions are important control parameters to monitor the process effectiveness during laboratory experiments.

2. THEORETICAL BACKGROUND

2.1 Olive Oil Industry

Olive oil industry which is known one of the oldest one in the world, has rapidly grown in recent years due to increasing consumption rate and demand of the market. Although olive oil accounts for only about 3% of the global market in edible oil, it has traditionally played a major role in oil and fats supply in the areas of production. Since the 1990's, however, significant quantities of olive oil have also been consumed outside those areas. World consumption of olive oil has been progressing fairly steadily, without the fluctuations that are a feature of production. Since 1995/96 the average annual increase in consumption has been 6%, with even higher relative growth in new markets (Directorate-General for Agriculture, 1995).

Worldwide olive oil production is variable and subjected to a multitude factors such as meteorological conditions and regional properties. In addition to those, it is a seasonal production, taking place between September and November and in "on years" this period can extend to March (RAC/CP, 2003).

Olive oil industry is of fundamental economic importance for many Mediterranean countries. Almost 98% of olive trees are growing in this part of the world and this area provides 97% of the total oil production alone. It is estimated that worldwide olive oil production is reached to 2 million metric tons (RAC/CP, 2003, Alcaide et al., 1996).

There are currently several categories of olive oil on the market. Virgin oils, which are extracted mechanically, direct from the olives, comprise the "extra virgin" and "virgin" classes of olive oil - ready for consumption - and *lampante* olive oil, which has to be refined and used mostly for cooking and frying purposes. "Composed" olive oil is a blend of refined and "virgin" or "extra virgin" olive oil. Finally, olive pomace oil is obtained by extraction with solvents, typically hexane, from the olive pomace and contains large

amounts of free fatty acids which increase the acidity and lowers quality (Directorate-General for Agriculture, RAC/CP, 2003).

2.1.1. General Description and Basic Operations of Olive Oil Production

The general and comprehensive process of work at an olive mill is illustrated in Table.2.1 (RAC/CP, 2003).

Table 2.1 Basic Operations of the Olive Oil Production Process (RAC/CP, 2003)

AREA/ENTRY	OPERATIONS	EQUIPMENT	OUTPUT
1. RECEPTION AREA			
Harvested olive →	UNLOADING	Hoppers, belts	
	↓		
	CLEANING	Pneumatic, sieving	Leaves, Earth, Shoots...
	↓		
	CONTROL	Scales, laboratory	
	↓		
	STORAGE	Hoppers	
	↓		
	RINSING	Water, rinser	Rinsing water
	↓		
2. OIL EXTRACTION AREA	↓		
Water, system 1 →	MILLING	1. Mill stone	
	↓	2. Mill hammers	
	↓	3. Mixed types	
	BEATING	Beater	
	↓		
Water, systems 1 and 2 →	SEPARATION	1. Press	Oil + Veg. water
	↓	2. Decanter 3 F	+ spent olives
	↓	3. Decanter 2 F	Oil + moist spent olives
	↓		
Water →	CLEANING	Centrifuge and decantation well	Oil Veg. water
	↓		
3. CELLAR	↓		
	STORAGE	Stainless containers	
	↓		
4. BOTTLING AREA	FILTERING		
	↓		
Bottles, auxiliary material →	BOTTLING	Bottling line	Bottled oil
	↓		
	SHIPMENT		

As previously indicated, there are various divisions and sub-divisions through the process in which virgin olive oil is obtained from olive fruits. However, it should be noted that the operations except extraction are not directly concerning the scope of this thesis. Therefore, those processes will be mentioned briefly. The reception operations are common in all mills and they are varying in the degree of perfection and automatization with which they are carried out. They consist of cleaning and rinsing, control and storage processes and then the olive fruit is prepared for its later milling. The storage and bottling processes are carried out for marketing purposes (RAC/CP, 2003).

Oil extraction processes are the most important part of the whole process because olive oil is mainly obtained through these processes. Another feature is that except the rinsing process in reception operations, significant amount of water at different temperatures is only used through extraction processes. This is important in terms of environmental considerations because the output from the process is higher and consists of high amount of organic load. Extraction processes differs regionally and mainly depending on the method in extraction of the olive oil used. Generally, extraction processes consist of milling, beating or malaxation, separation and cleaning (RAC/CP, 2003).

Milling

Milling is carried out by stone mills or with hammers or disks at modern installations. The objective is to tear the flesh cells to let the oil run out of the vacuoles, thus permitting the formation of larger drops that then can be separated from the other phases. Figure 2.1 shows example for milling devices both traditional installations.

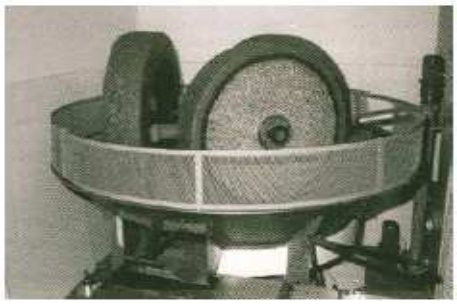


Figure 2.1 Milling device – Cylindrical stone mill (TDC-Olive Project, 2003)

Beating or Malaxation

The object of this stage is prepare at a suitable temperature the paste or mass to favour the separation of oil, increase the size of oil drops and break up the oil/ water emulsion. The process of the milling gives rise to the formation of emulsions between the oil and the water. Therefore, mixing is necessary to increase the oil droplet size. It is suitable to be done at above room temperatures, and lasts at least an hour. These plants are equipped with two or three mixing units, consisting of semi cylindrical, large capacity vats fitted with an outer chamber through which heated water circulates. Within malaxer, the olive paste is maintained in movement by means of a device (spades or other system) that turns around a shaft. The inner view of a malaxer is illustrated in Fig 2.2.

Figure 2.2 Inner view of a malaxer (TDC-Olive Project, 2003)

An increase in mixing temperature raises extraction yields, especially when the olive paste is not manageable. The most efficient temperature is about 30-35ºC. The increase in mixing time, however, results in the decrease of the phenolic substances contained in the oil (Masghouni et al., 1999).

Separation

In this process the liquid phase separated from the solid phase by applying centrifugal force, which increases the difference between the specific density of the oil, the vegetation water and the solid residue. Separation operations at continuous three-phase systems are

accomplished in horizontal centrifuges or decanters as they are also known. Figure 2.3 represents a diagram of a three-phase decanter.

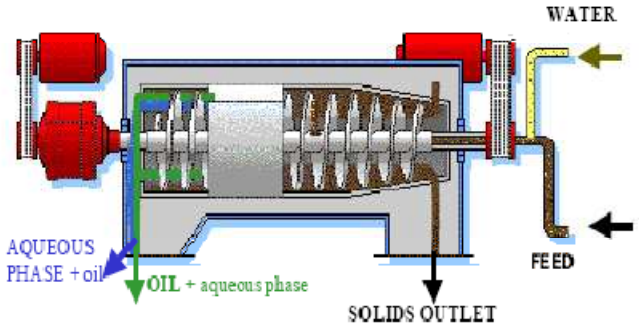


Figure 2.3 Diagram of a three-phase decanter (TDC-Olive Project, 2003)

Cleaning or Centrifugation

Cleaning of the oil or centrifugation is the separation of the leftovers of solid residue and watery residue proceeding from the extraction process. It carried out by filtering by mesh filter that enables partial separation of solids of greater size from particles, decantation in appropriate pots embedded in the ground or centrifuging in a vertical high-speed centrifuge. Figure 2.4 shows some examples of vertical centrifuges.

Figure 2.4 Examples of high-speed vertical centrifuges (TDC-Olive Project, 2003)

2.1.2 Olive Oil Production Systems

Generally, olive oil is obtained by three principal methods.

1. Pressing or traditional system,
2. Three-phase continuous system
3. Two-phase continuous system

2.1.2.1 Traditional System. Traditionally, until the appearance of the modern methods of extraction by centrifuge, the method of extraction by pressure has been the only existing procedure for obtaining olive oil. In this method, the olive, stored and rinsed in the yard of the oil mill, is milled in a stone mill. The resulting solid paste is laid out in fine layers upon the disks of filtering material (fabric, or more recently plastic fiber), called pressing mats. These pressing mats are piled up one on top of the other in a wagon and guided by a central needle. These ensembles formed by the wagon, the needle and the pressing mats piled up with the paste receive the name of charge (RAC/CP, 2003).

The latter is subjected to pressing by means of a hydraulic press. The pressure that the charge receives is generated by a group of hydraulic pumps housed in the so-called pump box.

The operation described is not continuous and is composed of three stages.

- The stage of charge formation
- Pressing
- Removal of pressing mats

When pressing is finished, the liquid phase is taken to deposits (pots embedded in the ground or small tanks), where the natural decantation is produced and the watery phase separating from the oily one, obtaining virgin olive oil and vegetable water (approximately 40-60 L of vegetable water per 100 kg of olive) (RAC/CP, 2003).

2.1.2.2 Continuous Three-Phase System. The continuous system was introduced in the seventies when the new technologies for the extraction of olive oil started to be applied.

The main reason behind this technological improvement is that low-quality olives yield better quality oil when processed with continuous systems (Giovacchio et al., 1980, RIRDC Project, 2001). Therefore, the modern conception of the extraction replaced the traditional pressing with horizontal centrifuges, called “decanters” which considerably improved the performance and productivity of oil mills.
The new method presented the following advantages over the traditional method:

- Mechanical simplification
- Elimination of the pressing mats
- Continuous production
- Less labour
- Smaller surface occupied by the installation

Continuous methods require, like the traditional one, a prior milling, which is carried out with hammers or disks. Once the milling has been performed, the paste is sent by means of a dosifying pump of variable speed to a horizontal centrifuge. In the centrifuge, three phases are separated; the spent olives, the oil and the vegetable water. The solid phase contains the greater part of the solids that are to be found in olives; skin, pulp, stone, and a small portion of oil. The watery residue called vegetable waterish initially dark liquid, of a reddish colour, which, due to a series of enzymatic processes, rapidly degraded and converts into vegetable water. The quantity and the quality of the vegetable water are variable, depending on the system, type of olive, amount of water used, etc. The watery phase contains a small amount of oil, which separates on subjecting the vegetable water to further centrifuging in a vertical centrifuge. The oily liquid phase, which contains a small quantity of vegetable water, must be purified by centrifuge, more vigorously, in a vertical centrifuge.

The consumption of water in the three-phase system is notably higher than the traditional system, amounting to an approximate total of 100-130 L per 100 kg of olives (RAC/CP, 2003). The distribution of water consumption in oil mills is generally as follows:

- Rinsing: is a closed cycle, the consumption is in the range of 10-12 L water per 100 kg olives (RAC/CP, 2003).
- Milling: on occasions, hot water must be added to avoid the adhesion of the paste to the surface, with an average consumption of approximately 25 L per kg of olives.
- Beating: hot water is used in closed circuit.
- Separation: usually done in decanters where the greatest amount of water is used, which must be hot to facilitate the transport. The expense is produced in two stages in a stage previous to the centrifuging with an expense of around 80-100 L/100 kg olives. For the actual centrifuging, approximately 20 L water/100 kg olives are added with the purpose of improving the separation.

2.1.2.3 Continuous Two-Phase System. The large amount of waste generated in the process of olive oil extraction by the three-phase method, together with the increasingly demanding legislation regarding the treatment and management of oil mill waste, in some countries encouraged the development of new technologies. The new system called “Ecologic” in two phases (RAC/CP, 2003).

The main innovation the two-phase system brings is that of permitting the elaboration of virgin olive oil without the need to add water in the separation phase, means, which there are practically no vegetable water produced. This extraction technology offers the advantage of saving of water, energy and reducing environmental impacts (RAC/CP, 2003).

The two-phase system modifies the operating conditions as it eliminates the need to add hot water in the process. Also, it is necessary to modify the decanter. In the process two currents are generated; one which contains the oil and another that contains the majority of the solids and nearly all the constituting water, which receives the name of moist spent olives (RAC/CP, 2003).

The oil directly obtained in the decanter needs to be subjected to a more energetic process of centrifuging in a vertical centrifuge to clean the oil. In two phase systems,

vegetable water is principally generated in the rinsing of the oil and in the drainage water of the storage hopers.

Some other advantages of two-phase continuous system over continuous three-phase system are described below (RAC/CP, 2003).

- The construction of the two-phase “decanter” is simpler than that of three-phase “decanter”, which means it can be acquired far more cheaply.
- The oil yield of the two-phase system is somewhat greater than that obtained with the three-phase system, due to fact that more oil is retained in the solid part.
- The processing capacity is higher than that of the three-phase centrifuges as they do not require additional water in the extraction process.
- The quality of the oil produced by two-phase system is superior particularly with regard to the resistance to oxidation and the more bitter character.
- The cost of the operation is less (Cabrera et al., 1996).

2.2 Environmental Aspects of Olive Oil Industry

Olive mill wastes are a significant source of potential or existing environmental pollution in the Mediterranean region. The environmental problems associated with mills relate mainly to water consumption in regions where supplies are limited and to the elimination or harnessing of the waste from the oil extraction process: solid residue and liquid extracts (mixture of the vegetable water from the rinsing of the olives and water added during the kneading of paste). Solid fraction of the olive mill effluents are valuable source of reusable materials serving different aims and their negative impacts to the environment can be reduced. However, liquid wastes must be treated before discharged into the environment.

The quantity of olive oil mill vegetation and washing effluents (commonly referred to as vegetable water) generated, and consequently the environmental impacts, depend on multitude factors such as, regional properties and climate conditions , but amongst them

the method of oil extraction process used is particularly important. The traditional cold press method typically generates about 40-50% of vegetable water relative to the initial weight of the olives, whereas the three-phase method generates 80-130% of wastewater due to rinsing and the continuous washing of the olive paste with warm water prior to oil separation from the paste. Although the least wastewater is produced in two-phase system, the mills are still being operated in many countries with the traditional method and three-phase olive extraction processes. It is estimated today that the annual olive mill wastewater production in the Mediterranean region exceeds $30x10^6$ m^3 (RAC/CP, 2003).

The environmental impacts of olive mill wastewaters are considerable with the dangerous effects such as colouring of natural waters, threat to the aquatic life, causing surface and groundwater pollution, changing soil quality, plant growth and source of odour production. Depending on the method of extraction used, olive mill wastewaters can be characterized high degree of organic pollution, dark coloured, foul-smelling and hard to biodegrade due to existing non-biodegradable structure. OMW may have COD values as high as about 220 g/L and the organic fraction contains a complex consortium of polysaccharides, sugars, lipids, polyalcohol's, phenols and phenolic acids, nitrogenous compounds (especially amino acids), organic acids (palmitic, oxalic, oleic acid), tannins, pectin's, carotenoids and oil residues (Parinos et al., 2007, Federici 2006). The inorganic fraction contains chloride, sulphate and phosphoric salts of potassium as well as calcium, iron, magnesium, sodium, copper and other trace elements in various chemical forms (Federici, 2006). Average composition of olive mill wastewaters is given in Table 2.2 below.

Table 2.2 Average composition of olive mill wastewaters (Federici, 2006).

Density	1.023-1.054
pH	4.6-6.7
Turbidity	11,000-65,000
Water (%)	82.4-96.0
Dry extract (%)	3.0-18.0
Suspended solids (%)	0.04-1.04
Mineral compounds (%)	0.4-7.2
Organic compounds (%)	3.9-16.5
Total sugars (%)	1.0-8.0
Total pectins (%)	0.05-0.15
Total polyphenols (%)	0.15-1.75
Total nitrogen (%)	0.1-7.2
BOD (mg/l)	9,600-110,000
COD (mg/l)	30,000-195,000

In addition to its high degree of organic pollution capacity, the effluent has the following characteristics;

- BOD_5/COD ratio varies between 0.2-0.4 (hardly biodegradable).
- High organic contents which contribute to the consumption of dissolved oxygen in natural waters.
- Acidic pH range, which is the main and direct cause of fish death when vegetation waters are discharged in riverbeds.
- High fat content which provokes the formation of a layer on the surface of the water that impedes its correct oxygenation and the passing of the sunlight preventing the normal development of the fauna and flora in surface waters.
- Contamination of waterbeds due to the associated biorecalcitrant characteristics in case of spreading onto the field (Miranda et al., 2000).
- Strong, unpleasant olive oil smell due to highly concentrated phenolic compounds up to 10,000 mg/L (Mantzavinos, 2005).

By its nature, several low-molecular-weight phenolic compounds are present such as, the phenolic derivatives of hydroxycinnamic, ferulic, and caffeic acids and, in larger amounts, tyrosol (4-hydroxyphenetyl alcohol) and hydroxytyrosol (3, 4 dihydroxyphenetil alcohol). Although to a different extent, all these compounds are characterized by high antioxidant activity, display sharp characteristic odour and inhibits seed germination

(Nianousakis et. al., 2004, Federici, 2006). Molecular structures of some phenols and phenolic acids existing in olive mill wastewaters are illustrated in Figure 2.5.

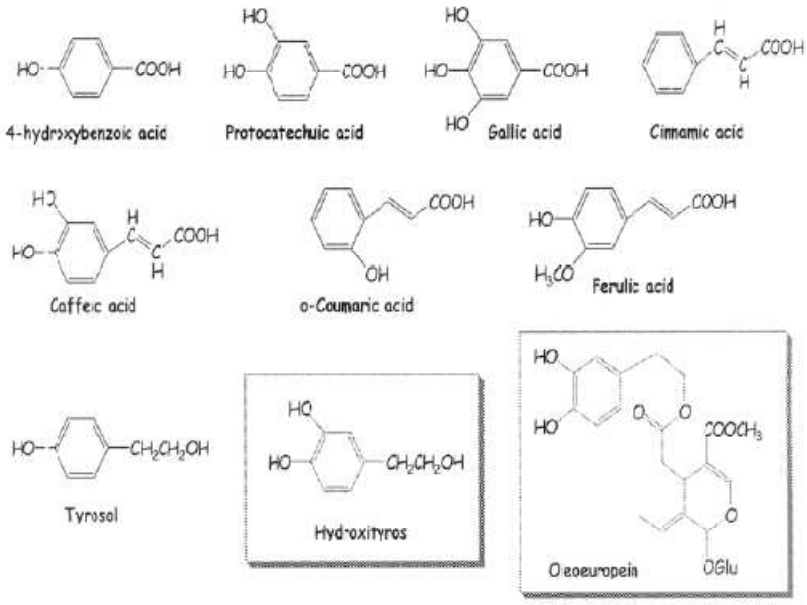


Figure 2.5 Phenols and phenolic acids existing in olive mill wastewaters (Federici, 2006)

2.3 Conventional Treatment Methods of Olive Mill Wastewaters

After high pollutant power and their potential negative impacts on the environment have been realized, from the seventies on, olive mill wastewaters have been the object of great attention on the part of scientific institutions, firms and public organizations with the object of studying and proposing the best strategies and technologies of minimization, valorization or elimination (Alcaide et al., 1996). However, specific properties of this effluent have revealed some difficulties about potential application of the possible strategies. The major concerns regarding olive mill wastewaters treatment are the following treatment processes:

- The intrinsic composition of the vegetable water and its high pollutant power compared to many various industries.

- Seasonal production throughout the milling campaign, which lasts no longer than 6 months between November and February, sometime becomes shorter from year to year due to the requirements of the oil quality.
- The variability of the problem or impact depending on the characteristics of the oil mills such as location, meteorological conditions and concentration in the territory
- Olive oil manufacturing industries are small plants with a daily flow rate between 10 and 100 m^3 and are distributed over large areas (Borja et al., 1998).

Many different technologies have been proposed so far either single or combined processes tested in laboratory scale or pilot scale. Olive mill wastewater treatment is mainly aiming at the removal of organic matter from the liquid phase. The predominant technologies for olive mill wastewater treatment are

1. Physico-chemical treatment methods,
2. Lagooning for natural evaporation,
3. Membrane processes (reverse osmosis, ultrafiltration) and
4. Anaerobic-aerobic biological purification (Fountoulakis et al., 2006).

These processes, however, suffer from serious drawbacks like high cost, low efficiency and sludge-disposal problems.

Among others, biological treatment methods are particularly important because all applications for olive mill wastewaters consisting either single or a series of combined processes must include at least one biological step eventually. Biological processes are the most environmentally compatible and least expensive wastewater treatment methods. Anaerobic digestion is usually the basic biological process for olive mill wastewaters treatment since it has many advantages compared to aerobic treatment. Anaerobic processes are less energy intensive and produce less waste sludge than aerobic processes, while they may also lead to energy generation in the form of biogas. They can also cope with seasonal olive mill wastewater production, since anaerobic digesters can be easily restarted even after several months of shutdown. On the other hand, both anaerobic and aerobic processes can not deal with the high organic load of olive mill wastewater that need to be diluted several times or employed further processes prior to biological

treatment, thus introducing serious cost implications. Moreover, in order to enhance the anaerobic degradation of olive mill wastewaters, an aerobic pretreatment stage is favorable in reducing the amount of inhibitory or toxic compounds such as polyphenols and lipids (Borja et al., 1998). Some microbiological cultures were used in studies in order to find out the effect of aerobic pretreatment on the subsequent anaerobic degradation (Wu et al., 2006). Besides reducing the COD and total phenol concentration, the results show that aerobic pretreatment is capable of reducing toxicity as well (Fountoulakis et al., 2006).

2.4 Advanced Oxidation Processes (AOP's)

Increasing variety of new industries and recent developments on the industrial scale have introduced new complex organic and inorganic compounds to wastewater treatment plants and most of them are discharged into the environment or aqueous media due to incapability of conventionally biological treatment methods. The studies have shown that conventional oxidizing agent is not generally effective and feasible due to long reaction times (Beccari et al., 1996). New technology considered in the treatment of this new kind of aqueous wastes is advanced oxidation processes (AOP) (Capasso et al., 1992). AOP's approach is particularly appropriate for effluents containing refractory, toxic and non-biodegradable materials (Ince et al., 2001). Therefore, scientists and engineers have been widely challenged in last decades with AOP's, which are highly promising and innovative techniques for the remediation of such contaminated water systems without generating any sludge or hazardous compounds (Alnaizy et al., 2000).

Advanced oxidation processes are defined as those processes in which hydroxyl radicals ($OH\cdot$) are the main oxidants involved. The hydroxyl radical is far more powerful as an oxidizing agent that commonly known strong oxidants like hydrogen peroxide (H_2O_2), ozone (O_3) and reacts one million to one billion times faster than others (Mason et al., 1998). The efficiency of AOP's are based on the presence and beneficial reaction capacity of hydroxyl radicals which are capable of complete mineralization of all pollutants to carbon dioxide (CO_2), water and mineral salts or for the selective removal of more bioresistant pollutants and their conversion to biodegradable intermediates (Borja et al., 1998). Direct oxidation of aqueous solutions containing organic contaminants can be performed under a variety of conditions ranging from ambient conditions to supercritical

water oxidation a very high temperatures and pressures. These processes include (1) homogenous ultraviolet irradiation- either direct irradiation of the contaminant or photolytic oxidation mediated by hydrogen peroxide (UV/H_2O_2), ozone and/or ($UV/O_3/H_2O_2$ or UV/O_3), (2) Fenton and Photo-Fenton processes, (3) heterogeneous photo catalysis using semiconductor catalysts (UV/TiO_2), (4) ultrasonic irradiation, (5) supercritical wet oxidation, (6) electrochemical water oxidation, (7) X-ray or gamma-ray radiolysis, (8) electron-beam irradiation and as well as various combination of the above (Borja et al., 1998, Legrini et al., 1993). The brief explanation of some of the common AOP's are given below.

2.4.1 Homogenous Processes

2.4.1.1 UV/H_2O_2 Process. Briefly, the H_2O_2/UV system involves the formation of ●OH radicals by hydrogen peroxide photolysis and subsequent propagation reactions. The mechanism most commonly accepted for H_2O_2 is the cleavage of the molecule into hydroxyl radicals:

$$H_2O_2 + h\upsilon \rightarrow 2\ \bullet OH \qquad (2.1)$$

Low pressure mercury vapor UV lamps with a 254 nm peak emission are typically used to produce UV radiation, but these lamps may not be the best choice for a UV/H_2O_2 process because the maximum absorbance of UV radiation by H_2O_2 occurs at about 220 nm and therefore the molar adsorption coefficient of H_2O_2 at 254 nm is low. If low pressure mercury lamps are used, a high concentration of H_2O_2 is needed in the medium to generate sufficient ●OH because of the low molar adsorption coefficient. However, high concentrations of H_2O_2 may scavenge the ●OH, making the process less effective. To overcome this limitation, some AOP technology vendors use high intensity, medium-pressure, broad band UV lamps; others use high intensity, xenon flash lamps whose spectral output can be adjusted to match the absorption characteristics of H_2O_2 or another photolytic target (U.S EPA, 1998)

2.4.1.2 Ozone. Ozone can react with substances in two different ways, either indirectly or directly. The indirect reaction pathway involves radicals. The first step is the

decomposition of ozone, accelerated by initiators, such as hydroxide ion (OH^-) to form secondary oxidants such as hydroxyl radicals which are non-selective in their reactions. The direct oxidation of organic compounds by ozone is a selective reaction with slow reaction rate constants, typically being in the range of 1 to 10^3 M^{-1} s^{-1}**.** Normally, under acidic conditions (pH<4) the direct pathway dominates, above pH 10 it changes to the indirect.

2.4.1.3 UV/O_3 and UV/O_3/H_2O_2 Processes. UV photolysis of O_3 in water yields H_2O_2, which in turn reacts with UV radiation or O_3 to form ●OH as shown below:

$$O_3 + h\upsilon + H_2O \rightarrow H_2O_2 + O_2 \quad (2.2)$$

$$H_2O_2 + h\upsilon \rightarrow 2\ \bullet OH \quad (2.3)$$

$$2O_3 + H_2O_2 \rightarrow 2\ \bullet OH + 3O_2 \quad (2.4)$$

Because the molar absorption coefficient of O_3 is 3300 M^{-1} cm^{-1} at 254 nm, UV photolysis of O_3 is not expected to have the same limitation as that of H_2O_2 when low pressure mercury vapor UV lamps are used (U.S EPA, 1998).

Addition of hydrogen peroxide to the UV/O_3 process results in a net enhancement due to the dominant production of $OH^{\bullet}$ radicals as shown in equations below:

$$H_2O_2 \rightarrow HOO^- + H^+ \quad (2.5)$$

$$O_3 + HOO^- \rightarrow \bullet OH + O_2^- + O_2 \quad (2.6)$$

$$O_3 + O_2^- \rightarrow O_3^- + O_2 \quad (2.7)$$

$$O_3^- + H_2O \rightarrow \bullet OH + HO^- + O_2 \quad (2.8)$$

2.4.1.4 Fenton and Photo-Fenton Processes. Fenton process is an advanced oxidation process (AOP) that can be used to treat non-biodegradable organic wastewater. The Fenton system uses ferrous ions to react with hydrogen peroxide at low pH producing hydroxyl radicals (•OH) for the destruction of the compounds. Although the idea of AOPs has been in existence since the mid 20th century, active research efforts in this field has only taken place in the last 20 years (Benatti et al., 2006).

Fenton process involve homogenous reaction have a stronger oxidation potential (2.8 V) than ozone (2.07 V). The classical Fenton reactions at acidic pH known as Fenton reaction, which led to the production of ferrous or ferric ion and of the hydroxyl radical (Eqn. 2.9) (Pignatello et al., 2006).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (2.9)$$

Both ferrous and ferric iron generates hydroxyl radicals (●OH) by reaction with hydrogen peroxide. Hydroxyl radical reacts rapidly and nonselectively with most organic compounds by H abstraction and addition to C-C unsaturated bonds (Equation 2.10). Carbon-centered radicals generated by oxyl radical attack and may react with O_2 to give organoperoxy radicals (ROO●), which can decompose to form $HO_2\bullet$, or ultimately non-radical oxygenated products (Equation 2.10, 2.11). Organoradicals may in some cases be reduced by Fe^{2+} or oxidized by Fe^{3+} (Equation 2.13) (Lindsey et al., 2000).

Hydroxyl radicals may react with organics starting a chain reaction:

$$\bullet OH + RH \rightarrow H_2O + R\bullet \quad \text{RH= Organic substrate} \quad (2.10)$$

$$R\bullet + O_2 \rightarrow ROO\bullet \quad \text{Products of degradation} \quad (2.11)$$

Hydroxyl radicals may be scavenged by reaction with another Fe^{2+} or with H_2O_2:

$$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O \quad (2.12)$$

$$\bullet OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad (2.13)$$

The mechanism proposed for the H_2O_2-Fe^{3+} system known as Fenton-like reaction, involves ●OH and the hydroperoxyl radical ($HO_2\bullet$) by following steps (Lindsey et al., 2000);

$$H_2O_2 + Fe^{3+} \leftrightarrow H^+ + FeOOH^{2+} \quad (2.14)$$

$$FeOOH^{2+} \rightarrow HO_2\bullet + Fe^{2+} \quad (2.15)$$

$$HO_2\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \quad (2.16)$$

The rate of reaction 2.14 (76 M^{-1} s^{-1}) is much higher than that corresponding to reaction 2.9 (0.01-0.02 M^{-1} s^{-1}) , therefore in the presence of excess peroxide the Fenton reaction only occurs in first minutes of the reaction. After this short time, the rate of oxidation is controlled by Fenton-like reaction (Bishop et. al., 1968).

As stated above, the mechanism of the Fenton treatment process consists of chemical oxidation and chemical coagulation of organic compounds. Fenton's oxidation process is normally composed of four stages, which are: pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation. Thus, the organic substances are removed at two stages i.e. oxidation and coagulation. In addition, the completion of the oxidation is dependent on the ratio of hydrogen peroxide to organic, while the rate of oxidation is determined by the initial iron concentration and temperature (Pignatello et al., 2006). Moreover, it should be kept in mind that both H_2O_2 and Fe^{+2} concentrations are also important that can react with $OH^{\bullet}$ and inhibit the oxidation reactions if either of them is not in the optimal dosage (Torrades et al., 2003). Many authors suggested Fe^{+2} to H_2O_2 mass ratio to be optimal at 1 to 10, but it must be optimized for particular wastewater to minimize scavenging effects (Malato et al., 2002).

The pH at which Fenton process operates is vital to its effectiveness, as this effects the species of iron present in solution, and thus the rate at which the reaction progresses. Depending upon the target compounds, an ideal range for the Fenton's reactions is between pH 3-4 (Beltran et al., 1993). Above pH 5.5, the effectiveness of Fenton process declines rapidly due to the speciation of iron and other compounds such as the bicarbonate ion, which is known to be a strong scavenger of the hydroxyl radical (Arnold et al., 1995, Tang et al., 1996).

The advantages of Fenton process include relatively cheap, high efficiency, simplicity of operating and possible complete destruction contaminants (Pignatello et al., 2006). Recent studies in Fenton reagent involve reaction modifications, including the use of high concentrations of hydrogen peroxide, the substitution of different catalysts such as ferric iron and naturally occurring iron oxides, and the use of phosphate-buffered media and metal-chelating agents. These conditions, although not as stoichiometrically efficient as the

standard Fenton's reactions, are often necessary to treat industrial waste streams and contaminants in soils and groundwater (Pignatello et al., 2006).

Photo-Fenton is the Fenton oxidation process which includes the use of UV light during the reaction. The process has several advantages, mainly an increase of the degradation rate and reduction in iron consumption and, hence, less sludge generation (Salvadori et al., 2002, Benitez et al., 2001). In the generally accepted mechanisms of Fenton reaction, hydroxyl radicals (•OH) are produced by interaction of H_2O_2 with ferrous salts which shown in Equation 2.9.

The positive effect of irradiation on the degradation rate is due to the photo reduction of Fe (III) to Fe (II) ions and photo dissociation of H_2O_2. Both steps produce additional $HO^{\bullet}$ radicals and regenerated Fe (II) ions that can further react with the remaining H_2O and less Fe (III)-sludge is produced. The photo reduction of Fe (III) and H_2O_2 photo dissociation follows the Equation 2.17 and 2.18, respectively.

$$Fe^{3+} + h\upsilon + H_2O \rightarrow Fe^{2+} + \bullet OH + H^{+} \quad (2.17)$$

$$H_2O_2 + h\upsilon \rightarrow 2\ \bullet OH \quad (2.18)$$

In addition, it has been proven that irradiation of Fe (III) + H_2O_2 mixtures, enhances the reaction rate of oxidant production, through the involvement of high valence Fe intermediates responsible for the direct attack to the organic matter (Malato et al., 2002).

Fenton and Photo-Fenton oxidation processes have been employed successfully to treat different industrial wastewaters, including black olive and oil contaminated wastewaters (Andreozzi et al., 2000, Giannes et al., 2003).

2.4.2 Heterogeneous Processes

2.4.2.1 Heterogeneous Photocatalysis. Degradation and mineralization of organic pollutants by heterogeneous photocatalysis occur in the presence of semiconductor photocatalysts, the most widely used one being titanium dioxide (TiO_2). When TiO_2

absorbs a photon of energy equal to or greater than its band gap width, an electron is excited from the valence band to the conduction band (e^-_{CB}) leaving behind an electron vacancy or hole in the valence band (h^+_{VB}). The combination of the electron is the conduction band and the hole in the valence is referred to as an electron-hole pair, which subsequently migrates to the semiconductor surface and initiates chemical reactions (U.S EPA, 1998). The primary photocatalytic mechanism is believed to proceed as follows:

$$TiO_2 + h\upsilon \rightarrow e^-_{CB} + h^+_{VB} \quad (2.19)$$

At the TiO_2 surface, the holes react with either H_2O or OH^- from water dissociation to form $OH^\bullet$ (Equations 2.20, 2.21). An additional reaction may occur if the electron in the conduction band reacts with O_2 to form superoxide radical ions ($O_2\bullet$) (Equation 2.22). Superoxide radical ion can then react with H_2O to provide additional $\bullet OH$, OH^- and O_2 (U.S EPA, 1998).

$$h^+_{VB} + H_2O \rightarrow \bullet OH + H+ \quad (2.20)$$

$$h^+_{VB} + OH^- \rightarrow \bullet OH \quad (2.21)$$

$$e^-_{CB} + O_2 \rightarrow O_2\bullet \quad (2.22)$$

2.4.2.2 Gamma-Ray and X-Ray Processes. Gamma rays are high energy photons (electromagnetic radiation) that are emitted by excited atomic nuclei in transition to a state of lower excitation. The most common source of gamma rays is radioactive decay of radioisotope cobalt 60 (60 Co), which emits gamma rays at energies of 1.17 and 1.33 million electron volts as it decays to nickel 60 and has a half life of 5.27 years. X-rays are also high energy photons that are generated by accelerating high energy electrons in the form of an electron beam against a material with high energy number (Cooper et al., 1998; McKeown et al., 1998).

When gamma rays and X-rays collide with irradiated water, high energy electrons are generated along the trajectory of the photons which can initiate several thousand reactions as they dissipate energy in irradiated medium. The reactions result in the formation of three primary reactive species responsible for organic compound destruction, namely hydroxyl

radical, hydrogen radical and aqueous electrons (Cooper et al., 1998; McKeown et al., 1998).

Gamma-rays and X-rays have high penetration depths within irradiated water. The effective water penetration depths of 1.25 million volts gamma rays and 1 million X rays are about 76 cm and 27 cm respectively (Gray and Cleland, 1998; Bailey and Lackner, 1995). Therefore, both gamma rays and X-rays can be used to treat flowing waste streams as well as containerized liquid wastes.

2.4.2.3 Electron-Beam Irradiation. The electron- beam process involves irradiation of water with a beam of high-energy electrons produced by an electron accelerator. Electron accelerators can provide electron energies in the range of 0.1 to 10 million volts. High energy electron beams of about 2 million are used for irradiation of water (U.S. EPA, 2001a). The depth of which electron beam could penetrate to irradiated water is significantly less than the depths associated with gamma rays and X rays. A million electron deposits their energy in water within a depth of 4 millimeters (Bailey and Lackner, 1995). As a result, electron beams are typically used to treat contaminated water of relatively shallow depths. Likewise, gamma rays and X-rays, electron-beam irradiation of water causes formation of same three primary reactive species responsible for the degradation of organic compounds.

2.4.3 Ultrasound

In recent years, considerable interest has shown in the application of ultrasound as an advanced oxidation process for the treatment of many contaminants in water. Ultrasound is defined as any sound of frequency above that which the human ear has no response (above 16 kHz). There are three ranges of frequencies are reported for three distinct uses of ultrasound: i) high frequency or diagnostic ultrasound (2-10 MHz), ii) low frequency or conventional power ultrasound (20-100 kHz) and iii) low-to-medium or sonochemical-effect ultrasound (20-1000 kHz) (Ince et al., 2003). In this latter range, where chemical reaction processes are uniquely catalyzed through very extreme temperatures and pressures generated by the formation, growth and collapse of cavitational bubbles (Gogate et al., 2008).

The use power ultrasound has been well known for many years in fields such as medical, flow detections, emulsification, solvent degassing; however chemical applications of ultrasound or “sonochemistry”, in environment processing is still an emerging field. Through highly successful on laboratory scale operations, it has been reported that ultrasound is capable of converting chemical substrates like chlorinated hydrocarbons, aromatic compounds, phenolic compounds and esters into short chain organic acids, carbon dioxide and inorganic ions as final products (Adewuyi, 2001, Mason et al., 1990). Despite this fact, ultrasound still has not been able to find its environmental application at industrial scale operation mostly due to comparatively higher costs of treatment and inefficient power dissipation problems required for treatment. Therefore, the efficacy of cavitation can be significantly enhanced by combining ultrasound with other oxidation processes or by using catalysts. With this intensification, ultrasound can be a suitable technology for degradation of wastewater streams or lowering the toxicity level of the effluent stream so that conventional biological oxidation can be readily applicable (Adewuyi, 2001).

2.4.3.1 Fundamentals of Sonochemistry. As previously indicated, sonochemistry is an emerging field that uses ultrasound to promote chemical reactions. The chemical effects of ultrasound are due to the phenomenon of a “cold boiling” termed acoustic cavitation, which is the production of micro bubbles in a liquid when a large local negative pressure is applied. When a liquid is exposed to an acoustic field, the pressure waves of the sonic vibrations create a time and frequency dependent acoustic pressure, consisting of alternating compression and rarefaction cycles (Dahlem et al., 1998). If the applied pressure is equal to the negative pressure developed in the rarefaction cycle of the wave such that the distance between molecules of the fluid exceeds the critical molecular distance to hold it together, the liquid breaks apart to form acoustic cavities, made of vapor and gas-filled micro bubbles (Dahlem et al., 1998, Suslick, 1990). Acoustic cavitation consists of at least three different stages: These are formation, cavity growth and implosive collapse of bubbles under proper conditions (Suslick, 1994). Figure 2.6 represents formation and collapse of cavitation bubbles.

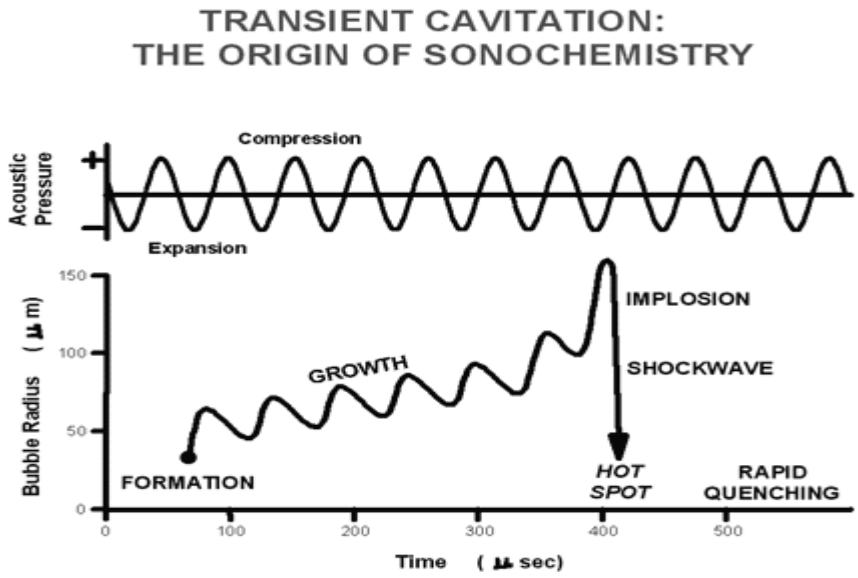


Figure 2.6 Formation and collapse of cavitation bubbles (Reisse et al., 1995)

The first stage, cavity formation, is a nucleated process, by which cavitational nuclei are generated from micro bubbles rapped in micro crevices of suspended particles within the liquid (Suslick, 1994, Hung et al., 1998). In the growth stage, he bubbles grow and expand in a manner restricted by the intensity of the applied sound wave. By high intensity ultrasound, a small cavity grows rapidly through inertial effects, whereas at lower intensities the growth occurs through rectified diffusion, proceeding in a much slower rate and lasting many more acoustic cycles before expansion (Suslick, 1994). The third stage of cavitation occurs only if the intensity of the ultrasound wave exceeds that of the acoustic cavitational threshold (generally a few watts/cm^2 for ordinary liquids exposed to 20 kHz). At this condition, micro bubbles overgrow to the extent where they can no longer efficiently absorb energy from the sound media to sustain themselves and implode violently (Dahlem et al., 1998, Suslick, 1994). It is reported that during collapse stage, such extreme temperatures and pressures are released that the entrapped gases undergo molecular fragmentation (Noltingk et al., 1950).

The violent collapse of a bubble due to acoustic stress can produce large amount of energy and this released energy is the main driving mechanism of sonochemistry. There are several theories as to how this energy is developed. The most highly favoured is that given by the " Hot Spot Theory", which suggests that the collapse is so rapid that the compression of the gas and vapor inside the bubble is adiabatic (Rayleigh et al., 1917,

Weavers et al., 1998). Consequently, temperatures and pressures within collapsing micro bubble can reach values as high as 4000-5000 K and 200-500 atm respectively just before fragmentation (Suslick, 1994). It is also reported that the localized “hot spot” generated by rapid collapse of acoustic cavities is very short-lived (less than 10 µs), implying he existence of extremely high heating and cooling rates. Substituents trapped inside or around a collapsing bubble are also subjected to these extreme conditions (Ince et al., 2001, Suslick, 1994).

Studies in sonochemistry have shown that there are three reaction sites in ultrasonically irradiated liquids (Ince et al., 2001, Mason et al., 1990). These reaction sites are illustrated in Figure 2.7 i) the cavitation bubble itself; ii) the interfacial sheath between the gaseous bubble and the surrounding liquid; iii) the bulk solution

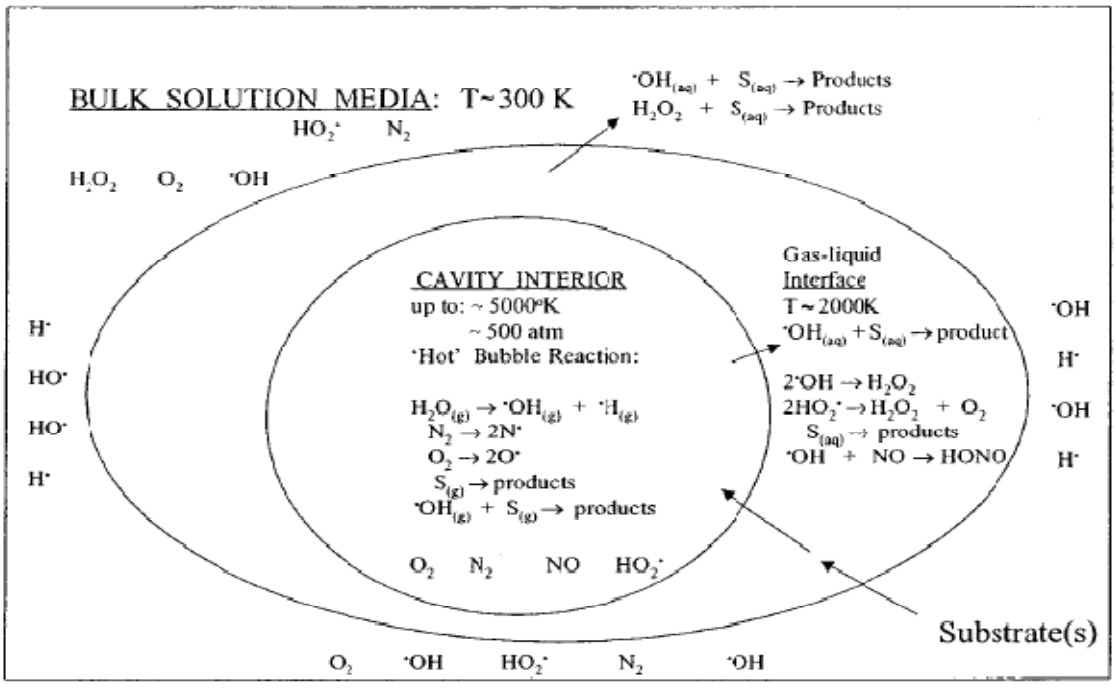


Figure 2.7 Sites of chemical reactions in reaction media (Ince et al., 2001, Suslick, 1994)

The hydroxyl radicals generated by water sonolysis may either react in the gas phase or recombine at the cooler gas-liquid interface or in the bulk solution during cavity collapse to produce hydrogen peroxide and water as follows (Fischer et al., 1986, Petrier et al., 1994, Neyens et al., 2003):

$H_2O \rightarrow))) \bullet OH + H\bullet$ (pyrolysis) (2.23)

$\bullet OH + H\bullet \rightarrow H_2O$ (2.24)

$2 \bullet OH \rightarrow H_2O$ (2.25)

$2 \bullet OH \rightarrow H_2O_2$ (2.26)

$2 H\bullet \rightarrow H_2$ (2.27)

If the solution is saturated with oxygen, peroxyl and additional hydroxyl radicals are formed in the gas phase (due to the decomposition of molecular oxygen), and the recombination of the former at the cooler sites (interface or in the bulk solution) produces more hydrogen peroxide as shown (Riesz et al., 1991, Neyens et al., 2003):

$O_2 + H\bullet \rightarrow H_2O\bullet$ (2.28)

$O_2 \rightarrow))) O + O$ (2.29)

$O + H_2O \rightarrow \bullet OH + \bullet OH$ (2.30)

$H_2O\bullet + H_2O\bullet \rightarrow H_2O_2 + O_2$ (2.31)

In water and wastewater treatment practices, organic pollutants may be destroyed either at the first two sites upon combined effects of pyrolytic decomposition and hydroxylation, or in the bulk solution via oxidative degradation by hydroxyl radicals and hydrogen peroxide. The extent of the oxidation in the latter side is limited by the quantity of uncombined hydroxyl radicals available in solution.

2.4.4 Advanced Oxidation Processes in Olive Mill Wastewaters

In recent years, AOP have been extensively studied regarding their efficiency to treat OME either single processes as pretreatment alternatives or combined in lab-scale. Processes such as electrochemical oxidation, Fenton oxidation, ozonation and photocatalysis can only achieve partial decontamination even after prolonged treatment times. Giannes studied NaCl-assisted electrochemical oxidation which offers a potentially cost-effective treatment process since OME can be destroyed through a combination of

direct and indirect anodic oxidation; the latter occurs via the in-situ generation of powerful oxidants such as chlorine, hydroxyl radicals and oxygen. The initial COD concentration was in the range of 45-60 g/L and after 8 hour electrolysis with the use of NaCl as the electrolyte, 71% of the initial COD degraded and complete odour, colour and suspended solid removal was achieved (Rivas et al., 2001).

Alternatively, Fenton processes are also suitable to treat a wide variety of effluents irrespective of their concentration and origin and are characterized by their simple and versatile operation. As olive oil manufacturing industries are usually small plants with a low, seasonal wastewater flow, a small Fenton unit would suffice to cope efficiently with the effluents produced (Borja et al., 1998). In a recent work of Rivas, OMW treatment with 15 g/L of inlet COD was employed and 85–90% COD reduction achieved in residence times between 1 and 8 h depending on the operating conditions by Fenton Process. The amounts of Fe^{2+} and H_2O_2 are 10 mM and 1M, respectively (Vlyssides et al., 2003). As indicated previously, dosage of H_2O_2 which is used as main oxidant assisted by Fe ions at the treatment of OMW is crucial and its consumption comprises a significant fraction of the operating costs in practice. In this respect, the dosages of the Fenton's components are needed to optimize carefully, thus avoiding waste of costly chemicals. Another Fenton study followed by coagulation was carried out by Vlyssides in which 65% COD, 30% BOD_5 and 100% total phenols removal after 2 h with 2 g/L $FeSO_4 \cdot 7H_2O$ and 5 ml/L H_2O_2 dosage at 20 ^oC (Gernjak et al., 2003). Besides remarkable removal efficiencies, results also revealed that BOD_5/COD ratio, an appropriate definition of biodegradability, increased from 0.32 to 0.56 by following oxidation.

Photocatalysis using solar energy is a promising and cost-effective method of OMW treatment considering that the major olive oil producing countries benefit from high intensity solar irradiation throughout the year. The efficiency of the process has been demonstrated in a recent work by Gernjak, where OMW were treated in various types of pilot-plant photo-reactors using solar light photocatalysis over TiO_2 or solar light coupled with Fenton. After 19 hour operation time with 5 mM Fe^{2+} and 20 g/L H_2O_2 74% COD and 87% total phenols removal was obtained as an important result. With flocculation as pretreatment, COD and phenols removal increased to 89% and 100%, respectively (Benitez et al., 1997).

Ozone, although a powerful oxidant, is not capable of completely treating highly concentrated OMW since it is sparingly soluble in water. Several studies have shown that the extent of COD removal achieved during OMW ozonation even at the most favorable conditions could not exceed 20–30% (Benitez et al., 1999, Chamarro et al., 2001).

3. RESEARCH METHODOLOGY

3.1 Materials

3.1.1 Olive Mill Wastewater (OMW)

Olive Mill Wastewater (OMW) used in all experiments was obtained from Midas Olive Oil Plant located in Akçay, Balıkesir. The chemical and physical properties of the wastewater are given in the Table 3.1.

3.1.2 Chemical Reagents

BOD_5 Reagents

KH_2PO_4, K_2HPO_4, $Na_2HPO_4.7H_2O$, NH_4Cl were used all reagent grade for phosphate buffer solution. $MgSO_4.7H_2O$, $CaCl_2$, $FeCl_3.6H_2O$ and $MnSO_4.4H_2O$ from Merck (Istanbul) were used for the chemical reagent preparation in BOD_5 analysis.

COD Reagents

$K_2Cr_2O_7$, $HgSO_4$, Ag_2SO_4, and H_2SO_4 were used as COD reagents (digestion and sulfuric acid). During the preparation of calibration curve, potassium hydrogen phthalate (KHP) was used as primary standard grade for COD analysis. All chemicals stated above were obtained from Merck (Istanbul).

Fenton Reagents

Hydrogen peroxide (H_2O_2) of industrial grade (35 %, w/v; density: 1.16 kg/ L) and Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) was used as source of Fe^{+2} in the Fenton and photo-Fenton treatment. Reagent grade hydrogen peroxide was obtained from Merck

(Istanbul), whereas $FeSO_4.7H_2O$ used as Fenton reagents obtained from PanReac. Reagent grade H_2SO_4 from Merck (Istanbul) was used for pH adjustment.

Oil and Grease Analysis

Hexane was used for oil extraction in the oil and grease experiments and provided by Merck. Sodium sulfate (Na_2SO_4) in powdered form was also used in this experiment, obtained from Fluka.

3.1.3 Instrumental Equipment

pH Meter: A Metler Toledo pH meter was used to monitor test solution.

Chemical Oxygen Demand (COD) Reactor: A Hach COD reactor was used to heat samples before spectrometric analysis by a DR/2010 model spectrophotometer.

Dissolved Oxygen (DO) Meter: A WTW Oxi 330 Portable Oximeter with WTW Cellox Probe was used to determine dissolved O_2 of the samples.

Mixers: A Velp Scientifica Magnetic Stirrer and Labegg were used to mix the sample solutions.

Gravimetric Balances: A Scaltec SBA 31 was used to weight the biocide in the sample solutions.

Heaters: Nuve FN 500 heater was used to dry the samples for TSS analysis and a muffle furnace was also used to ignite for VSS analysis. An evaporation bath (ECOTEMP TW 12) was used for evaporation hexane during oil and grease analysis.

3.2 Characteristics of the Selected Olive Oil Plant

3.2.1 Process Analysis

Midas Olive Oil Plant, located in Akcay, Balikesir, 5 km away from the town center, occupies 4000 m^2 total area, of which 1200 m^2 for the extraction process. The existing extracting system is a continuous three-phase system. Extraction process in the plant lasts 6 months, from October to March. The average processing capacity of the plant is 30 tons of olive per day. According to data of 2007-2008 seasons, total amount of olives processed in the plant is 2700 t/year. The general steps of the process, material balance, flow diagram and the amount of wastewater produced are shown in the Figure 3.1

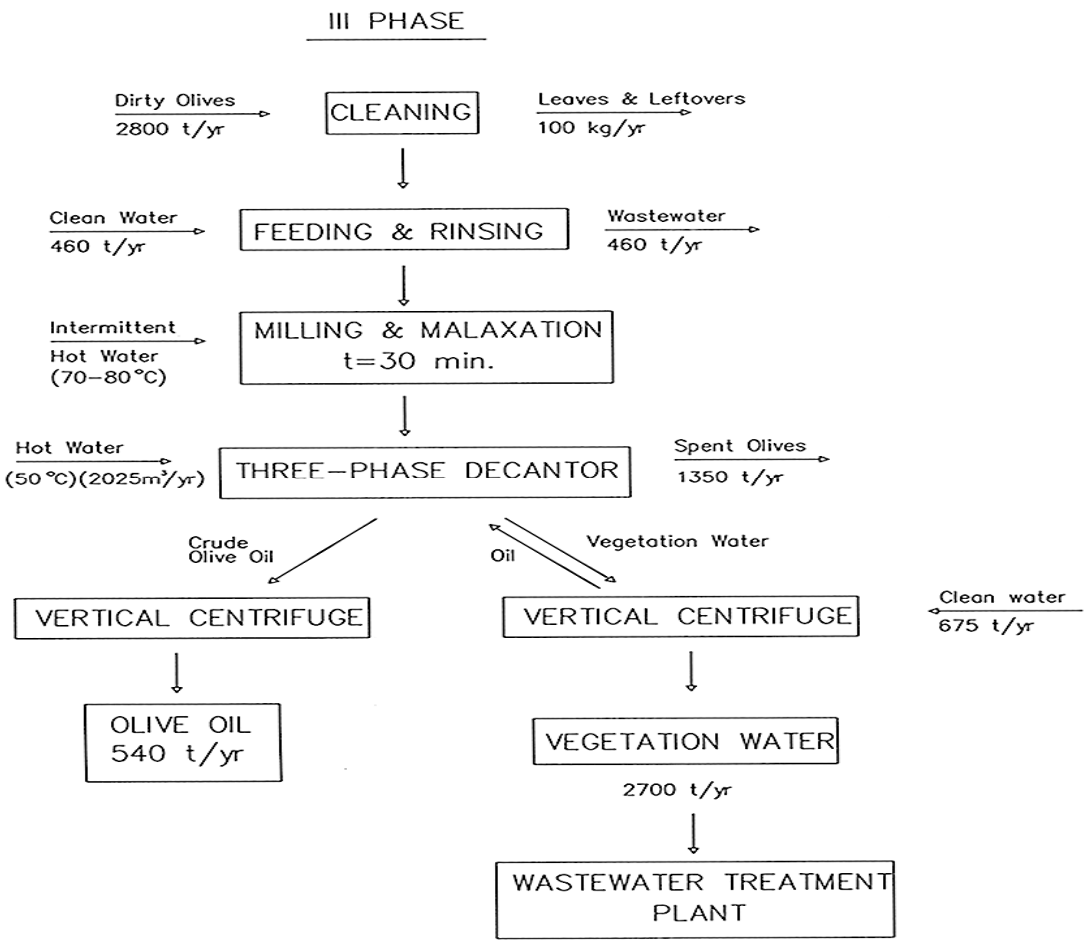


Figure 3.1 Flow diagram of 3-Phase Continuous System

3.2.2 Sampling

The wastewater produced during extraction processes were transmitted into an evaporation pond of 500 m^3 continuously. All samples were collected on February 2008, taken 2 m above from bottom of the evaporation pond in order to prevent excessive accumulation of suspended solids. Samples were transferred immediately to the laboratory within 12 hours. Samples were kept at 4^o C in the cooling room during the experiments.

3.2.3 Composition of the olive mill wastewater

Uniformity of the samples was maintained by shaking refrigerated samples and keeping them at ambient conditions for several hours without any contact with air. The mixed uniform sample was analyzed for pH, TSS, VSS, BOD_5, COD and oil and grease. The results of analysis were given in Table 3.1 below.

Table 3.1 Composition of wastewater used in the entire study

Parameter	Unit	Value
pH	-	4,70
Chemical Oxygen Demand (COD)	mg/L	43,000-50,000
Biochemical Oxygen Demand (BOD_5)	mg/L	14,500-17,500
Total Suspended Solids (TSS)	mg/L	9500
Volatile Suspended Solids (VSS)	mg/L	7073
Oil& Grease	mg/L	1270
Temperature	^oC	19.5
Biodegradability (BOD_5/COD)	-	0.33-0.37

The results indicate that the wastewater is strong in organic content and partially biodegradable (Garcia Montano et al., 2006, Weavers et al., 1998).

3.3 Methods

3.3.1 Experimental Set-up

1) Ultrasonic Bath without UV

Individual and sequential bath experiments were carried out in a stainless steel rectangular tank with dimensions 24x10x10 cm and volume of 2 L. The bath was operated at 35 kHz, 480 W peak output and 85 W input power with one transducer attached underneath the flat base. There is a reaction vessel, placed at the edge of shorter sides of the bath about 1- 1.5 cm in height from the base. Additional heating can be provided by a thermostatic heater and timer also exists in the bath for continuous operations. However, temperature control can not be made easily because there was not considered any cooling equipment for this device. Schematic view of the ultrasonic bath is presented in Figure 3.2.

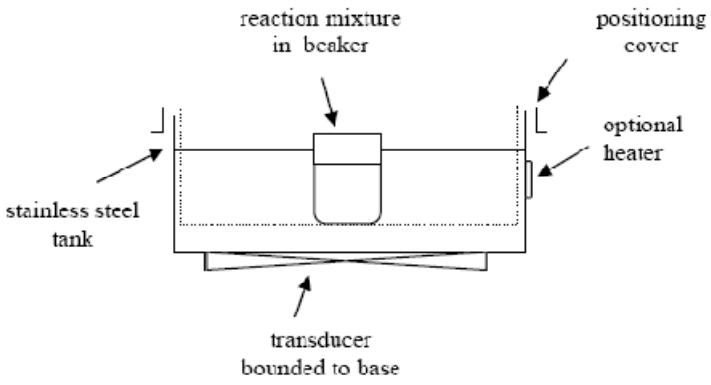


Figure 3.2 Schematic view of the ultrasonic bath (Ziylan, 2009).

2) Ultrasonic Bath with UV System:

The US bath shown in the Figure 3.2 equipped with four low-pressure mercury UV lamps (1.56 Watts m^{-2}), emitting monochromatic light at 253.7 nm which are placed on the top of the bath. The reactor was used to evaluate the combined effect of ultrasound and ultraviolet irradiation. The lamps were located at the top of the reactor with a perpendicular

distance of 9 cm from the surface of solution. This reactor is referred to as “hybrid reactor” in the rest of the study. A schematic view of the hybrid reactor is given in Figure 3.3.

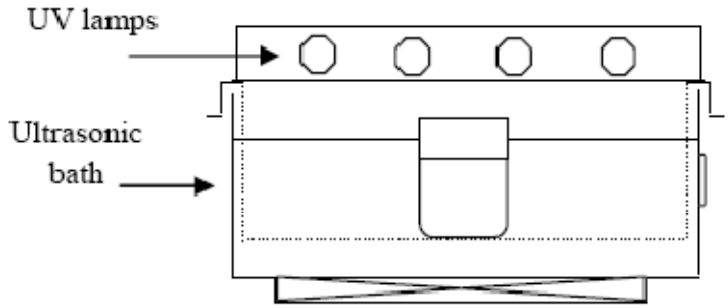


Figure 3.3 A schematic view of Hybrid reactor (UV/US Bath)

3.3.2 Experimental Procedure

1) Preparation of Olive Mill Wastewater Sample:

Fresh samples of the wastewater were kept in a cooling chamber (4^{o}C) and they were prepared daily before each experiment. Each sample was mixed with a magnetic stirrer for 15 minutes to provide homogeneity. All experiments were performed in a round-bottomed beaker (250 ml) and sample volumes always kept constant as 50 ml.

2) Description of the Experimental Processes

The experimental work was mainly divided into five parts which were Sonolysis, Fenton Process, photo-Fenton, Photolysis and Combined Processes.

1) Sonolysis

A 250 ml glass reactor filled with 50 mL of the wastewater sample was immersed in the bath filled with 750 milliliter water in each experiment. Operating conditions such as, temperature, pH and sonication time was selected and the effects of their combinations were also investigated. The temperatures 30±2 ^{o}C and 55±2 ^{o}C was selected to observe the

effect of sonication on organic matter decay. The temperature 55±2 ^{o}C was spontaneously occurred due to the conversion of acoustical energy into heat energy during experiments, whereas 30±2 ^{o}C was provided by adding ice cubes into the water. Drainage valve was useful to maintain water volume at the same level. Water losses in the sample due to evaporation in higher temperatures were completed by adding distilled water. The pH of the solutions in both modes was adjusted to 3.0, 7.0, and 10.0 with 1 N H_2SO_4 and 1 N NaOH. The effect of sonication time investigated in the sonolysis studies were carried out by operating the bath continuously up to 12 hours. The bath only was shut down in every 4 hours for a little time (20 seconds) in order to change the bath water so that some cooling was provided and transducers were protected from excessive heating. The samples were analyzed for pH, T, BOD_5, and COD before and after the experiment.

2) Fenton Process

The single Fenton experiments were conducted in batch mode by using a 250 ml beaker with an OMW volume of 50 ml. There were totally 12 experiments performed in which various amount of Fe^{2+} and H_2O_2 concentrations were used and samples were not diluted. The amount of hydrogen peroxide added was changed between 0.5 and 2.0 M while iron concentrations were ranging from 0.005 to 0.1 M. The reaction solution was stirred with a magnetic stirrer using a constant speed at 100 rpm to maintain a well-mixed solution during the experiments. The pH was set at pH= 3.0 using sulphuric acid (H_2SO_4) and the iron dosage at appropriate dosage was initially added to the solution. The reaction was preceded by adding predetermined dosage of H_2O_2 slowly after 1-2 minutes. The contact time was selected for 1 hour and the precipitate was allowed to settle for another 30 minutes. Samples were then taken from the solution in definite time intervals and analyzed for COD and BOD_5 and results were compared with initial concentrations. A four-hour single Fenton study was also accomplished in order to determine the effect of degradation time.

3) Photolysis

Direct photolysis of the wastewater was tested with UV-light, applied to the sample in a batch mode while slow mixing and heating (80 ^{o}C) was provided at the same time. The

beaker was placed over the apparatus and UV-light was applied from the upper side for five hours. Likewise Fenton Process, pH value of the sample was adjusted to 3.00 with sulfuric acid. Samples taken from the solution were monitored in definite time intervals for organic matter removal.

4) Combined Sonolysis and Photolysis

The test solutions of olive mill wastewater were sonicated for five hours in the presence of UV irradiation in the hybrid reactor described in section 3.3.1. This process was accomplished in continuous mode and no mixing was provided because the ultrasonic waves were sufficient to provide slow mixing in the beaker. However, during the combination of three processes and US/ UV process, temperature rise up to 80^{o} C was remarkable due to synergistic heating effect of US and UV. The samples were analyzed for pH, T, BOD_5, and COD before and after the experiment.

5) Sono-Fenton Process

The test solutions of the samples were sonicated in the presence of Fenton reagents for five hours. The iron concentration of 0.1 M and hydrogen peroxide concentration of 1.5 M were selected regarding to single Fenton process by which best removal efficiencies were achieved. The samples were analyzed for pH, T, BOD_5 and COD before and after the experiment.

6) Sono-Photo Fenton Process

A 50 ml sample was injected into the beaker and immersed in the ultrasonic bath. The bath and UV lamps were turned on after the addition of Fenton's reagent and pH adjustment. The operating conditions were kept constant as same as in Sono-Fenton Process including contact time for five hours. The samples were analyzed for pH, T, BOD_5 and COD before and after the experiment.

7) Sequential Processes

The test solutions of olive mill wastewater tested in US bath and the combination of US/ UV process for four hours and followed by Fenton Process an additional one hour in a batch mode. Effluents from sequential processes were analyzed for pH, T, BOD_5 and COD in order make a comparison with combined interactive processes.

8) Additional Processes

Calorimetry Test:

A calorimetry test was also carried out in order to optimize water volume required in the bath. Although ultrasonic bath work with a fixed power and is not adjustable, the ultrasonic power dissipated to the water differs by using various water volumes. Ultrasonic bath was equipped with a thermometer and the bath was filled with different water volumes. The temperature changes were recorded for a 10 minutes run.

3.3.3 Analytical Methods

Initially the samples were measured for pH, analyzed for chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), total suspended solids (TSS), volatile suspended solids and oil and grease. The removal efficiency of organic matter either individual or combined advanced oxidation processes was characterized later based on two parameters, namely COD (Closed-Reflux Method) and BOD_5 (Dissolved Oxygen Method) using the methods as described in the Standard Method for the Examination of Water and Wastewater (AWWA, 1992).

Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) was determined in accordance with Closed reflux Colorimetric Method (5220D) of Standard Methods. The method contains ignition samples to 150 ^{o}C followed by monitoring absorbance values at 600 nm as COD equivalents in mg O_2/L.

Biochemical Oxygen Demand (BOD_5)

The 5-day BOD was determined by Dissolved Oxygen Method (5210B) described in the Standard Methods of water and wastewater analysis (AWWA, 1992) using an acclimated seed.

Total Suspended Solids (TSS)

Suspended solid was analyzed using gravimetric method described in the Standard Methods (AWWA, 1992).

Volatile Suspended Solids (VSS)

Volatile suspended solids were determined using the same procedure with TSS method stated above. In addition to the process, the samples were ignited to 600^{o} C in order to determine the organic fraction of the TSS.

Oil and Grease

Oil&Grease experiment was carried out using Partition Gravimetric Method (5520B) according to Standard Methods (AWWA, 1992). The method contains the extraction of oil and grease with hexane from wastewater sample following evaporation process.

4. RESULTS AND DISCUSSION

4.1 Determination and Optimization of Power and Reaction Volume in Ultrasonic Bath

Generally, ultrasonic systems transform electrical power into mechanical or vibration energy which is transmitted into sonicated reaction media. During this cycle, some part of the energy is lost due to produced heat and evaporation of liquid. The rest of it plays a crucial role in cavitation. However; it does not mean that all of this cavitation energy is effective for chemical and physical changes in the liquid. Some energy is reflected and some is consumed by sound re-emission. Therefore, there are significant differences in terms of power generated by transducers and delivered into the reactor. Among the methods suitable to measure the amount of ultrasonic power entering a sonochemical system, the most common and easiest is calorimetry, which is based on measurement of heating produced in a definite time interval when ultrasonic irradiation is applied (Mason, 1999). The method involves the measurement of temperature rise T against time using a thermocouple placed in the ultrasonic bath. From T versus t graph, the temperature rise by time (dT/dt) can be obtained either by curve fitting the data to a polynomial in t, followed by constructing a tangent to the curve at time zero. The actual ultrasonic power (P) entering the system can be calculated by changing the value of dT/dt into Equation 4.1 (Gogate et al., 2004):

$$P = (dT/dt) * C_p * M \quad (4.1)$$

Where P = Power dissipated in the system (W)

C_p = Specific heat of the water (4.187 J/g K)

(dT/dt) = temperature change by time at definite time interval (K/s)

M = Mass of the distilled water in the ultrasonic bath (g)

The power which is calculated by calorimetric method is used to determine the ultrasonic intensity in the reactor. Ultrasonic intensity is expressed as W/cm^2 (power per unit emitting area), or W/mL (power per unit volume of water in the reactor).

Determination of Ultrasonic Power. The structure of ultrasonic baths is very simple and laboratory models generally consist of fixed power and frequencies. There are a few variants on this design that some bath operate at different frequencies. However; the ultrasonic bath, which is used in our experiments, is a fixed 35 kHz frequency and an output power of 320 W. As it mentioned above, this output power is not the actual power entering to the system. Therefore, the calorimetric method was conducted to determine the actual power entering to the system or so-called input power. The experiments were conducted by using as liquid distilled water in ultrasonic bath. As reaction volume 500, 750, 1000, 1500 mL volumes were chosen. The results of calorimetric experiments are listed in Table 4.1.

Table 4.1 Temperature change by time at different volumes of water through sonication

Time (s)	**Temperature(K)**			
	500 mL	**750 mL**	**1000 mL**	**1500 mL**
0	296.4	297.3	297.2	297.1
60	298	298.7	298.3	297.8
120	299.9	300.3	299.4	298.7
180	301.8	302	300.6	299.6
240	303.7	303.5	301.9	300.5
300	305	304.5	303.1	301.5
360	306.3	305.6	304	302.4
420	307.6	306.6	304.8	303.5
480	308.9	307.6	305.6	304.1
540	310.3	308.7	306.5	304.7
600	311.7	309.9	307.3	305.3

Plots of T versus time for all applied reaction volumes data fit the best polynomial line are presented in Figure 4.1.a, b, c, d. The values of dT/dt for each reaction volume were estimated from the slope of the curves or the tangent at the point of inflection.

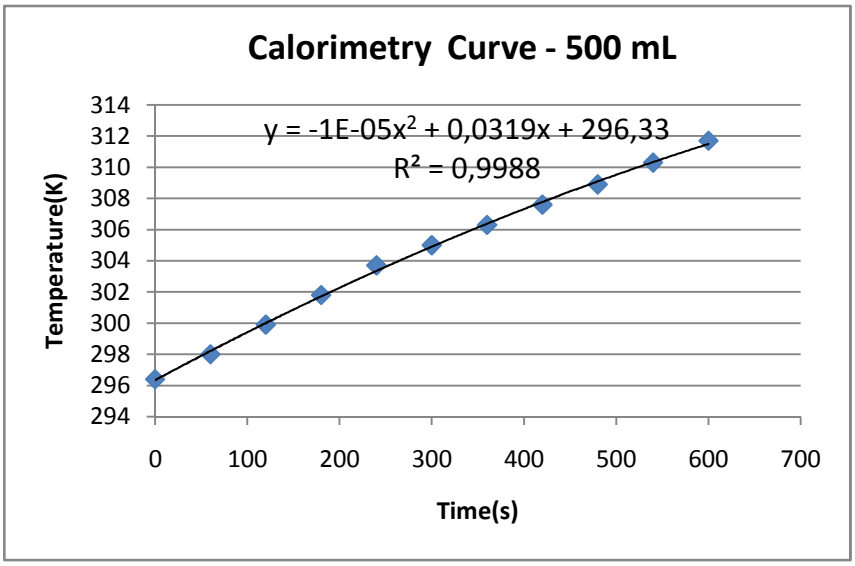


Figure 4.1 a. Plot of T versus time for 500 mL applied liquid volume

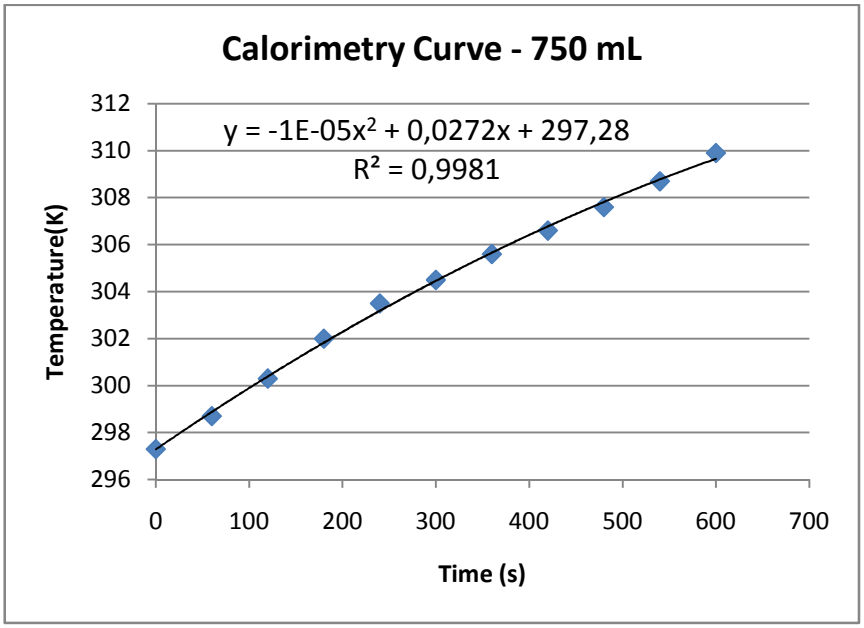


Figure 4.1 b. Plot of T versus time for 750 mL applied liquid volume

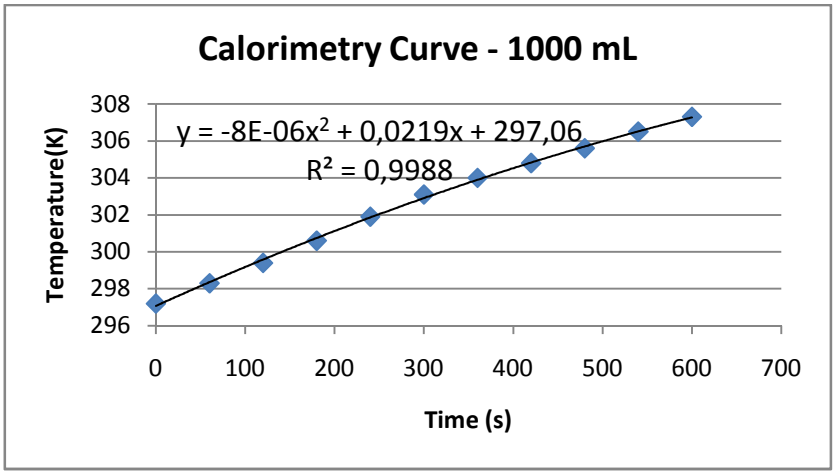


Figure 4.1 c. Plot of T versus time for 1000 mL applied liquid volume

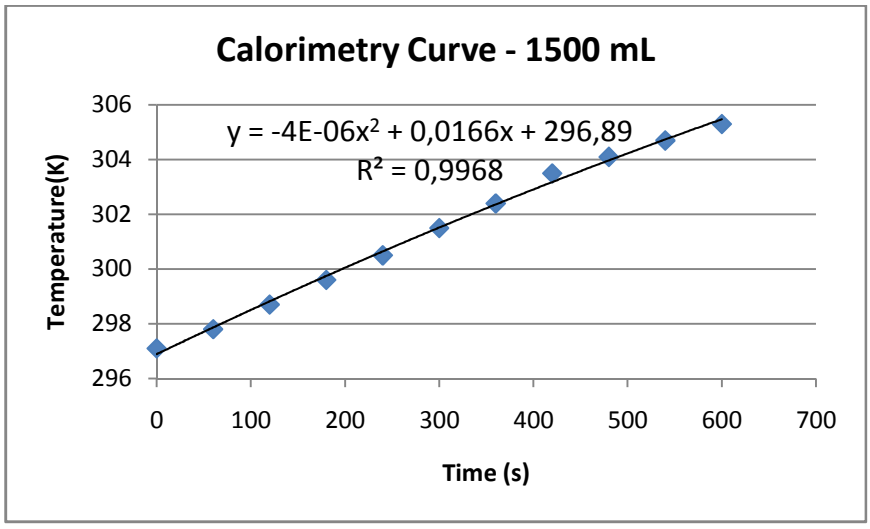


Figure 4.1 d. Plot of T versus time for 1500 mL applied liquid volume

Ultrasonic power entering to the system was calculated regarding to Equation 4.1. Estimations of dT/dt from the curves in Figure 4.1 a, b, c, d and calculated input powers for each liquid volume is given in Table 4.2.

Table 4.2 Calculated input powers for each liquid volume

Liquid Volume (mL)	Estimation of dT/dt	Ultrasonic power (W)
500	0.031	64.90
750	0.027	84.79
1000	0.021	87.93
1500	0.016	100.49

Obviously seen in the table above, the higher the liquid volume the larger is the dissipated power into the solution. However, the magnitude of the input power is not enough to determine optimum range of the liquid volume. Another important definition is the power density which represents the dissipated power per volume of the solution or the liquid. The power density can be found from the Equation 4.2 for any ultrasonic system and expressed in W/mL.

$$\text{Power Density} = \frac{\text{P(W)}}{\text{V(mL)}} \tag{4.2}$$

The calculated power densities at each volume and the deposited powers were summarized in the Table 4.3.

Table 4.3 Estimated power deposition and density of each test volume

Volume (mL)	Deposited Power (W)	Power Density (W/mL)
500	64.82	0.13
750	84.69	0.11
1000	87.82	0.087
1500	100.37	0.066

Despite the fact that the highest power entering to the system at 1,500 mL, the power density at the same volume is nearly half of the others. In addition to this, although the power density of the 500 mL-reaction volume is the strongest, the amount of power entering to the system is rather low compared to others. Therefore, 750 mL was chosen the optimum reactor volume for ultrasonic bath both in terms of power and density.

4.2 Effects of Dilution on Sonochemical Degradation of Organic Matter

In this part of the study, effect of the dilution on sonochemical degradation of organic matter was investigated. Figure 4.2 shows that the comparison of COD removal efficiencies of the samples by sonication at different initial COD concentrations with or without dilution. The dilution rates were chosen 1/20 and 1/40. Contact time was 4h and pHs of the samples were adjusted to 3.00.

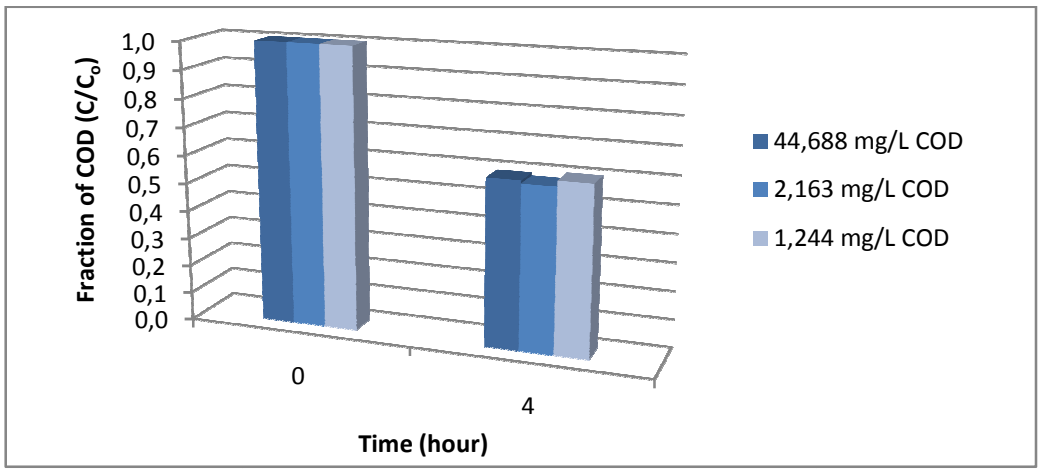


Figure 4.2 COD removal efficiencies by sonication at different initial COD concentrations.

The results indicate that applying sonication to diluted samples has no considerable effect on the degradation of organic matter. The COD removal efficiencies of the 1/20 and 1/40 diluted samples were 42% and 40% respectively, whereas the decrease in COD was 41% without dilution.

4.3 Effects of Operating Conditions on Sonochemical Degradation of Organic Matter

As it was comprehensively explained in section 2.4.3, the chemical effects of ultrasound enhance reaction rates because of the formation of highly reactive radical species formed during cavitation. The influence of ultrasonic energy on chemical activity in the liquid phase or wastewater may involve some direct or indirect relationships of the following: production of heat, promotion of mass transfer, promotion of intimate contact between materials, dispersion of contaminated layers of chemicals and production of free-

chemical radicals (Dahlem et al., 1998, Fogler et al., 1996, Gondrexon et al., 1997). Therefore, operating conditions were considered highly important for sonication experiments in the enhancement of degradation efficiency and biodegradability of organic matter.

In this section, effects of temperature, pH and sonication time on organic matter decay was examined by applying ultrasound to the OMW. In each part of this section, one of the operating conditions was changed and while the others were kept constant. In each experiment, 50 ml OMW sample was sonicated in an ultrasonic bath of 35 kHz frequency. The power input to the system was 85 W and the bath was filled with 750 ml distilled water. The water in the bath was 3.8 cm high from the bottom and it exceeded the sample level in the reaction vessel.

4.3.1 Temperature

The effect of temperature on the degradation and biodegradability enhancement of the sample via heating is illustrated in Table 4.4, Table 4.5 respectively. Heated sample results were obtained through heating 50 ml sample for 4 hours over a heater at two different, constant temperatures. The heated sample results were shown in order to compare the effect of ultrasound uniquely. Temperature values of 30±2 and 55±2 ^{o} C were selected. The first value was preserved constantly during sonication through use of ice cubes. The latter is spontaneously occurred in the bath when samples were sonicated, thus resulting in a gradual temperature increase of the liquid bulk due to heat dissipation. Figure 4.3 represents temperature change in the system by applying ultrasound due to conversion of acoustical energy into heat energy.

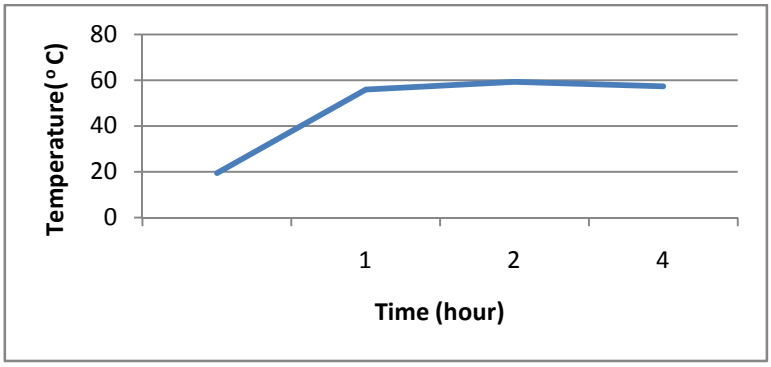


Figure 4.3 Temperature change in the system by applying ultrasound

As it is demonstrated in the graph, the temperature increased sharply in the first hours of the experiments and then it became into an equilibrium around 55-60 ^{o}C. This temperature is the highest point and it was never exceeded in all experiments using ultrasound.

Table 4.4 Effect of heating on improvement of the sample quality at 30±2 ^{o}C

	T= 30±2 ^{o}C				
Time (hour)	COD (mg/L)	R.E. (%)	BOD_5 (mg/L)	R.E. (%)	BOD_5/COD
0	43,251	-	15,534	-	0.35
1	39,989	%7	14,312	%7	0.36
2	36,494	%15	13,760	%10	0.38
4	36,028	%17	13,690	%11	0.38

Table 4.5 Effect of heating on improvement of the sample quality at 55±2 ^{o}C

	T= 55±2 ^{o}C				
Time (hour)	COD (mg/L)	R.E. (%)	BOD_5 (mg/L)	R.E. (%)	BOD_5/COD
0	44,416	-	16,686	-	0.38
1	39,756	%11	15,001	%10	0.38
2	35,096	%21	13,545	%19	0.39
4	33,756	%24	13,349	%20	0.39

The effect of temperature on the degradation and biodegradability enhancement of the sample via sonication is illustrated in Table 4.6, Table 4.7 respectively.

Table 4.6 Effect of sonication on improvement of the sample quality at 30±2 ^{o}C

	Treated Sample by Ultrasound (T=30±2 ^{o}C)				
Time (hour)	COD (mg/L)	R.E. (%)	BOD_5 (mg/L)	R.E. (%)	BOD_5/COD
0	44,932	-	15,876	-	0.35
1	39,057	%13	14,603	%8	0.37
2	36,028	%20	12,702	%20	0.35
4	29,504	%34	10,235	%34	0.35

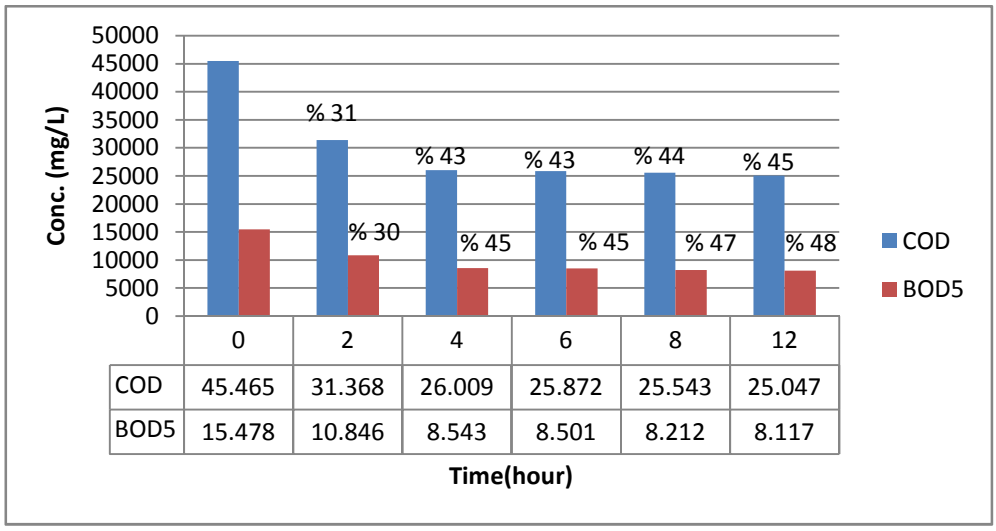
Table 4.7 Effect of sonication on improvement of the sample quality at 55±2 ^{o}C

	Treated Sample by Ultrasound (T=55±2 ^{o}C)				
Time (hour)	COD (mg/L)	R.E. (%)	BOD_5 (mg/L)	R.E. (%)	BOD_5/COD
0	45,348	-	15,972	-	0.35
1	40,688	%10	14,977	%6	0.37
2	31,368	%31	11,164	%30	0.37
4	25,776	%43	9,000	%43	0.37

As the tables demonstrate, initial organic concentration of OMW was quite high. The COD concentrations of fresh samples are in the range of 43,000-45,000 mg/L, while BOD_5 values are around 15,000-16,000 mg/L. In table 4.6 and Table 4.7, it can be seen that the removal efficiency at 55 ^{o} C is much higher than 30 ^{o} C. While 43% improvement in COD and BOD_5 degradation at 55±2 ^{o} C through sonication, these values only reached up to 34% by sonication of the OMW at 30±2 ^{o} C. On the other hand, biodegradability ratios remained unchanged both by heating and sonication compared to initial values.

4.3.2 Contact Time

In the previous section, all experiments were performed up to 4 hours as maximum time limit. Results showed that much of the COD decomposition was accomplished after first hour and the efficiency of decomposition was sharply increased by running contact time. With respect of these findings, the relationship between contact time and removal efficiency was investigated in the case of OMW was sonicated more than 4 hours. Figure 4.4 shows the effect of sonication time on the efficiency of organic removal up to 12 hours. All other operating conditions were kept constantly, as temperature value of 55±2 ^{o}C was selected.



	0	2	4	6	8	12
COD	45.465	31.368	26.009	25.872	25.543	25.047
BOD5	15.478	10.846	8.543	8.501	8.212	8.117

Figure 4.4 The effect of sonication time on the efficiency of organic removal up to 12 hours time-period

The results indicate that no further improvement in COD and BOD_5 occurs after 4-hour sonication. Although the removal efficiency of organic matter by ultrasound until four hour as good as % 43 for COD, it reached in the rest of the 12 hours-period only to 45 %. Similarly, BOD_5 degradation percentage is quite low and in the end of the whole process it still remained less than 50%. Thus, 4-hour was selected as the contact time for the rest of the experiments.

4.3.3 pH

In this part of the study, the effect of pH on the efficiency of organic matter removal was investigated. The previous experiments were conducted as selected pH value of which is the original value of the OMW (4.50- 4.70), some experiments were also carried out by sonication the samples at pH values of 3.00, 7.00 and 10.00 through two different temperatures (30±2 ^{o}C, 55±2 ^{o}C). pH changes were illustrated in Figure 4.5, 4.6 while Table 4.8, Table 4.9 represents the effect of pH on biodegradability change related to removal efficiency of COD, BOD_5.

Table 4.8 Effect of pH on the efficiency of COD, BOD_5 and biodegradability change 4-hour sonication at 30±2 ^{o} C.

	pH= 3.00		**pH= 7.00**		**pH= 10.00**	
Time (hour)	0	4	0	4	0	4
COD (mg/L)	44,882	25,134	45,115	32,300	43,251	26,708
R.E. (%)	-	44%	-	29%	-	38%
BOD5 (mg/L)	15,355	8445	14,885	10,248	16,106	10,032
R.E. (%)	-	45%	-	31%	-	37%
BOD_5/COD	0.34	0.34	0.33	0.32	0.37	0.38

Table 4.9 Effect of pH on the efficiency of COD, BOD_5 and biodegradability change 4-hour sonication at 55±2 ^{o}C.

	pH= 3.00		**pH= 7.00**		**pH= 10.00**	
Time (hour)	0	4	0	4	0	4
COD (mg/L)	44,242	25,218	44,697	32,300	44,797	27,774
R.E. (%)	-	43%	-	31%	-	38%
BOD5 (mg/L)	15,557	8868	15,211	11,104	15,774	10,411
R.E. (%)	-	45%	-	27%	-	34%
BOD_5/COD	0.35	0.34	0.34	0.34	0.35	0.37

According to the results presented by Table 4.8 and Table 4.9, the efficiencies on COD and BOD_5 via sonication differ remarkably by adjusting pH values. While both removal efficiencies of COD and BOD_5 was 34% at pH= 4.70 (Table 4.3.3), these values increased up to 44% in COD and 45% in BOD_5 by decreasing pH value into 3.00 at 30±2 ^{o} C. In addition to this, the same results were obtained at 55±2 ^{o} C. On the other hand, at the pH value of 7.00, the removal efficiencies were rather low. Furthermore, working in alkaline conditions (pH=10.00) resulted in small decline between 5-10% in both parameters. As it clearly seen in the Figure 4.5 and 4.6, pH values are decreased when the experiments were carried out in alkaline condition. However, pH values in acidic and neutral conditions were either remained stable or increased slightly more which could be neglected.

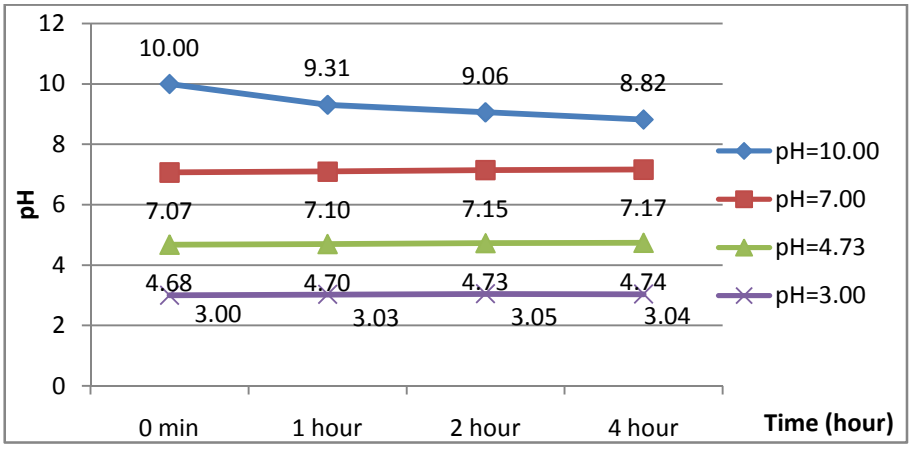


Figure 4.5 pH changes by applying ultrasound at 30±2 ^{o}C.

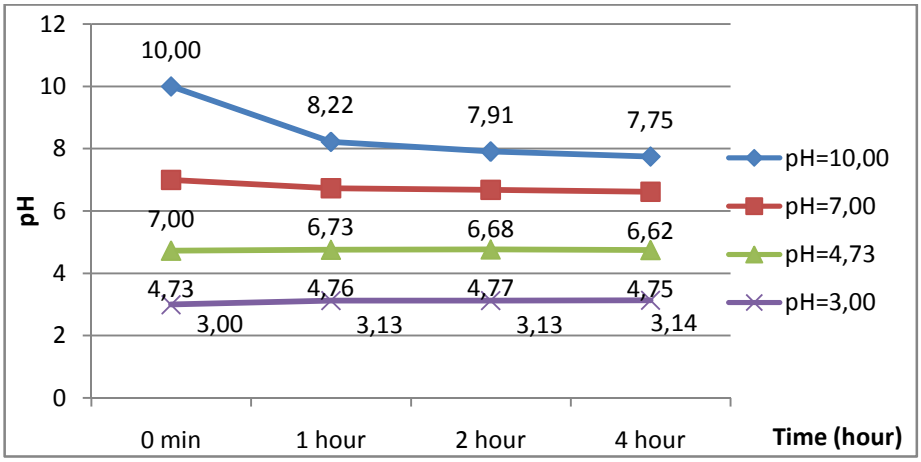


Figure 4.6 pH changes by applying ultrasound at 55±2 ^{o}C.

Putting all together, working with different pH values in sonication experiments has some considerable effects on the efficiency of organic matter removal. First of all, acidic conditions under 4.00 or lower are favourable for treating OMW by ultrasound. Secondly, neutral pH values (pH= 7.00) are ineffective for organic matter degradation both in 30±2 ^{o} C and 55±2 ^{o} C. Thirdly, biodegradability ratios in whole pH ranges remain under 0.5 as BOD_5/COD which is accepted for any kind of wastewater not biodegradable.

4.3.4 Determination and Optimization of Operating Conditions in Ultrasonic Bath System for OMW

Depending upon the results of the previous investigations (Section 4.3.1, 4.3.2, 4.3.3), the best combination of operating conditions by means of the efficiency of organic matter removal, the process which was carried out by applying ultrasound onto the OMW for 4-hour sonication time at pH value of 3.00 at 30±2 ^{o}C. From this point of view, further examinations through combined processes will be conducted under these operating conditions in which ultrasound takes place.

4.4 Application of Fenton Process to OMW Assisted by Ultrasound

Generally, advanced oxidation researches carried out for the treatment of OMW revealed that Fenton Process has proven to be one of the best effective alternative agent dealing with refractory/ low biodegradable wastewaters (Chamarro et al., 2001, Garcia Montano et al., 2006). It is actually a chemical coagulation, precipitation process in which the use of a mixture of hydrogen peroxide and iron salts (Fe^{+2}) produces hydroxyl radicals ($OH^{\bullet}$) at acidic pH (2.00-4.00) in ambient conditions that organic molecules were totally mineralized to carbon dioxide and water as final products (Lunar et al., 2000, Bishop et al., 1968, Walling, 1975). The process was selected as a treatment agent and its effects on the efficiency of the pollutant removal and biodegradability were examined either in single, sequential or simultaneous processes.

Likewise in sonication experiment, effect of the dilution was also investigated on degradation of organic matter by Fenton Process. Figure 4.7 shows that the comparison of COD removal efficiencies of the samples by applying 1 hour Fenton process at different

initial COD concentrations with or without dilution. The dilution rates were 1/20 and 1/40 and pH of the samples were adjusted to 3.00.

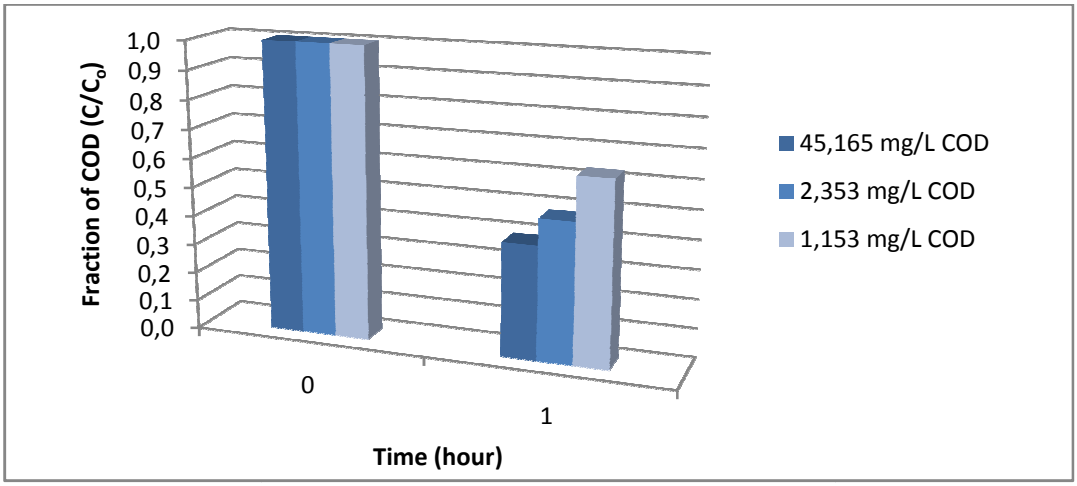


Figure 4.7 COD removal efficiencies by 1 hour Fenton process at different initial COD concentrations.

The results indicate that Fenton Process was more effective in concentrated samples than the diluted ones in terms of the degradation rate of organic matter. The COD removal efficiencies of the 1/20 and 1/40 diluted samples were 48% and 37% respectively, whereas the decrease in COD was 61% without dilution.

4.4.1 The effect of Fe^{2+} Concentration

In Fenton process, hydrogen peroxide is converted to hydroxyl radical in a catalytic cycle with cationic iron acting as catalyst. The efficiency of hydroxyl radical production from peroxide is affected by pH, iron oxidation state and iron chelating (Kang et al., 2000). Especially, it has been reported that ●OH can be efficiently formed under acidic conditions (Mason, 1999).

In this part of the study, the Fenton experiments, which were carried out within 60 min treatment time, and results were illustrated in the Figure 4.8 to observe the influence of various Fe^{2+} concentrations on COD degradation efficiencies. Each experiment was conducted by using 1 M of H_2O_2 with different Fe^{2+} concentrations at the pH value of 3.00

within 60 minutes. The concentrations added as Fe^{2+} are 0.005, 0.025, 0.05, 0.066, 0.085 and 0.1 M respectively.

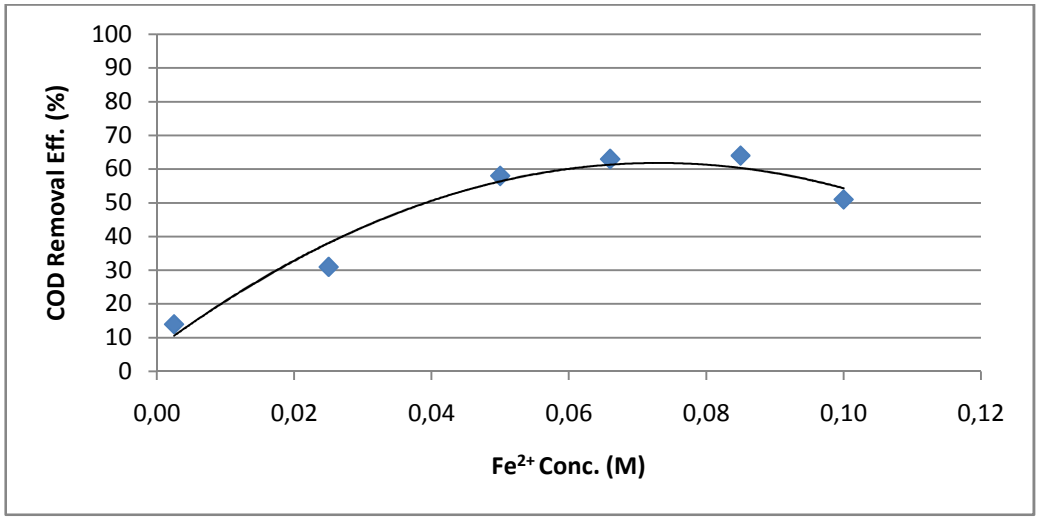


Figure 4.8 The effect of various Fe^{2+} concentrations on COD degradation efficiencies at constant amount of 1 M H_2O_2

The experimental data revealed that the maximum efficiencies 63% and 64% of COD degradation occurred by using 0.066 and 0.085 M Fe^{2+} at a constant amount of 1 M H_2O_2 respectively. The lowest efficiencies were obtained by the addition of 0.005 and 0.025 M concentrations in Fenton process. In addition to this, as the concentration of iron is increased, pollutant removal accelerates until a point is reached (0.085 M) where further addition of iron becomes inefficient. This should be the limiting concentration for Fe^{2+} catalyst at this constant amount of H_2O_2 and further concentrations led to inhibition of the process due to scavenging effects of Fe^{2+} on ●OH radicals (Lindsey et al., 2000).

4.4.2 The Effect of H_2O_2 dose

The effect of H_2O_2 concentration on COD removal was examined by changing the H_2O_2 concentration between 0.1 and 1.5 M while keeping the concentration of Fe^{+2} constant at 0.1 M and COD values ranged at 45,000-46,000 mg/L. The results were shown in the Figure 4.9.

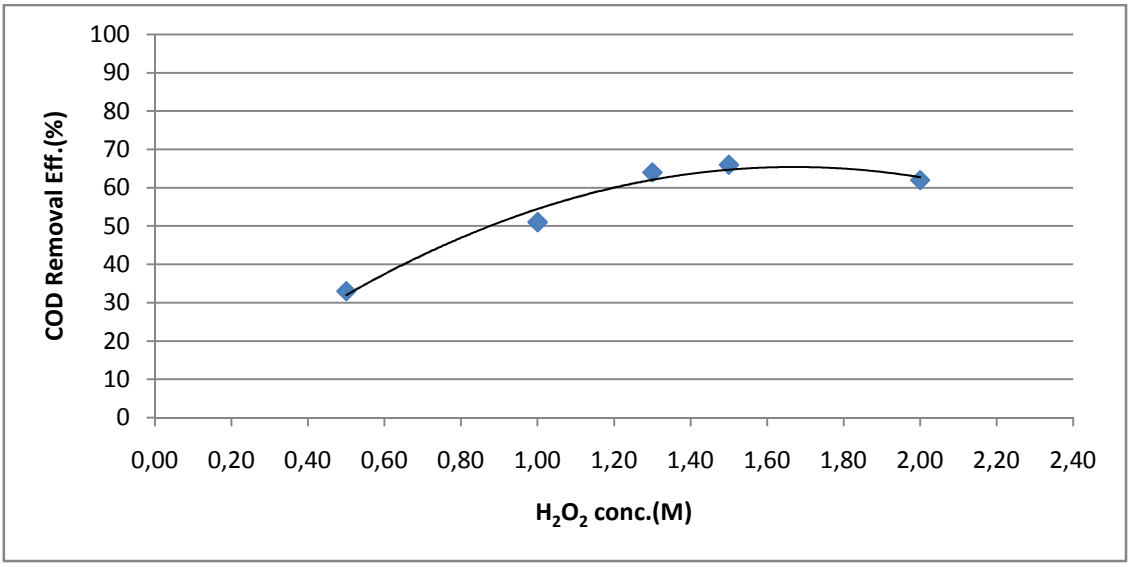


Figure 4.9 The effect of various H_2O_2 concentration on COD degradation efficiencies at constant amount of 0.1 M Fe^{2+}

The best removal efficiency (66%) were accomplished by using 1.5 M of H_2O_2 coupled to the concentration of 0.1 M Fe^{2+}. Likewise the effect of Fe^{2+} concentration, the more H_2O_2 was given to the solution, the more removal efficiency was obtained. After the concentration of H_2O_2 exceeds 1.5 M, COD removal efficiency started to decrease due to the scavenging effects of H_2O_2 on $OH^{\bullet}$ radicals which are the main driving forces in the oxidation of pollutants.

4.4.3 The Effect of H_2O_2 /Fe^{2+} Dosage

Many authors suggested H_2O_2 to Fe^{+2} ratio in Fenton process to be in optimal range but it must be optimized for each particular wastewater to minimize scavenging effects of both reagents (Malato et al., 2002).. In this part of the study, various H_2O_2 and Fe^{+2} concentrations by different molar ratios changing from 5.0 to 40.0 were introduced to the olive mill wastewater. Initial COD concentrations of the samples were around 45,000 mg/L. The effect of H_2O_2 /Fe^{2+} dosage on removal efficiencies and effluent pollutant concentrations are illustrated in Figure 4.10.

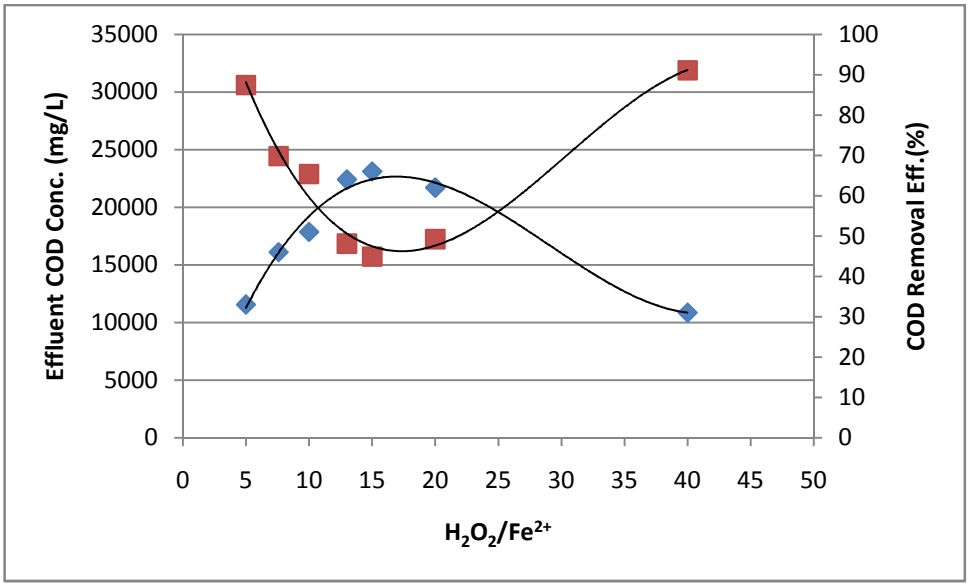


Figure 4.10 The effect of H_2O_2 /Fe^{2+} dosage on removal efficiencies and effluent COD concenrations

The experimental results suggest that for all applied H_2O_2 /Fe^{2+} dosage fit to the best polynomial line in the range of 13-16 in terms of molar ratio expressed. The ratio until 10 and after 30, the degradation efficiencies decreased fewer than 50%. For the reasons stated above, subsequent experiments assisted by Fenton Process will be preceded as the value of molar ratio of 15 taking into consideration.

The results of Fenton oxidation experiments performed with various amounts of H_2O_2 and Fe^{2+} in jar test apparatus for 60 min were shown in Table 4.10 comprehensively.

Table 4.10 Fenton oxidation experiments performed with various amounts of H_2O_2 and Fe^{2+} for 60 min

No	Dosage		0 min		60 min		Removal Efficiency (%)		pH Changes	Biodegradability
	Fe^{2+} (M)	H_2O_2 (M)	COD (mg/L)	BOD_5 (mg/L)	COD (mg/L)	BOD_5 (mg/L)	COD (mg/L)	BOD_5 (mg/L)		BOD_5/COD
1	0.05	0.5	46,336	16,820	26,518	9419	43	44	3.00→1.94	0.35→0.36
2	0.1	0.5	45,455	16,378	30,598	9000	33	45	3.00→1.90	0.36→0.29
3	0.066	0.5	45,230	16,652	24,424	8826	46	47	3.00→1.92	0.37→0.36
4	0.005	1	45,391	16,635	39,094	13,308	14	20	3.00→2.30	0.37→0.34
5	0.025	1	46,209	16,214	31,884	10,053	31	38	3.00→2.02	0.35→0.32
6	0.05	1	45,616	16,950	19,078	8000	58	53	3.00→1.89	0.37→0.42
7	0.066	1	44,015	16,752	15,817	7525	64	55	3.00→1.71	0.38→0.48
8	0.085	1	45,841	16,595	16,832	7355	63	56	3.00→1.67	0.36→0.44
9	0.1	1	46,289	17,310	22,867	8442	51	49	3.00→1.66	0.37→0.37
10	0.1	1.3	46,516	16,800	16,829	6300	64	62	3.00→1.62	0.36→0.37
11	0.1	1.5	45,841	16,300	15,705	6400	66	61	3.01→1.62	0.36→0.41
12	0.1	2.0	45,300	16,024	17,214	6410	62	60	3.00→1.64	0.35→0.37

The effect of Fenton Process to the OMW on organic matter removal was examined by changing the H_2O_2 concentration of 0.5 -1.5 M in 50 ml sample while keeping the concentration of Fe^{2+} between 0.005 to 0.1 M COD constant at 45,000-46,000 and BOD_5 at 16,000-17,000. The Fe^{+2} and H_2O_2 concentrations were varied in the molar ratio H_2O_2/Fe^{+2} from 5 to 200. The ranges of percentage removal in experiments were 14-66% in COD and 20-62% in BOD_5. The maximum effluent concentration for COD and BOD_5 remained at the concentrations of 15,705 mg/L and 6400 mg/L respectively. The best result was achieved at using Fe^{2+} dosage of 0.1 M and H_2O_2 of 1.5 M. However, the least removal efficiency on the removal of organic matter was obtained with a molar ratio of 1/200 (Fe^{2+}/ H_2O_2). Another important thing is that the more decline in pH occurs during batch experiments, the more removal efficiency of organic matter accomplished. It means, pH change is directly related with how much pollutant was oxidized in Fenton Process. It is

evident that at those conditions, a fraction of the initial COD and/or end products generated after the oxidation were converted into low molecular carboxylic acids which are difficult to be further removed by the Fe(II)/H_2O_2 system (Vlyssides et al., 2003).

An additional experiment was also conducted in order to determine the effect of time on the efficiency of organic matter removal in Fenton process. Fenton process with highest efficiency obtained by 0.1 M of Fe^{2+} and 1.5 M of H_2O_2 was applied to OMW for an extended time period of 4 hours and samples were taken at certain time intervals. COD and BOD_5 values of samples were measured and removal percentage of organic matter both in COD and BOD_5 were shown in the Figure 4.11.

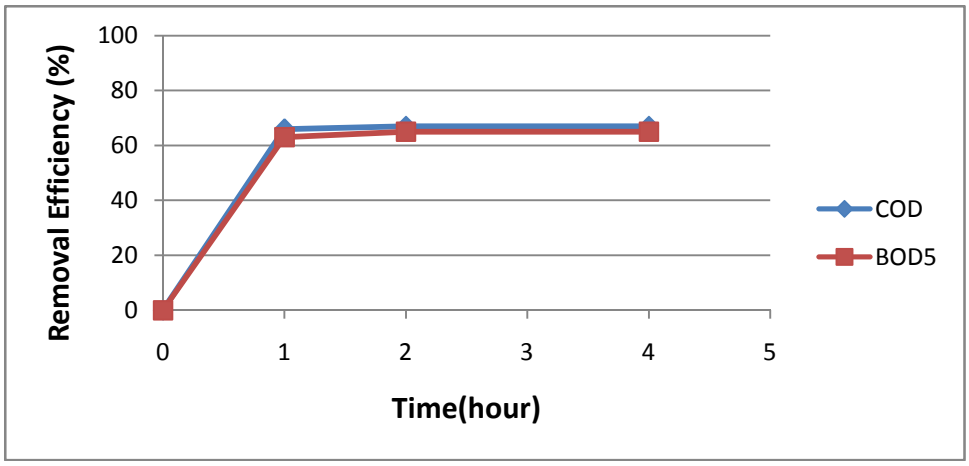


Figure 4.11 The effect of time on the efficiency of organic matter removal in Fenton process for an extended time of 4 hour.

The results from the Figure depicts that an extended time of four hour has no considerable effect of removal efficiency of organic matter. While removal efficiencies were 66% at COD and 61% at BOD_5 performed within 60 min by Fenton Process, after 4 hour they reached only to 67% and 65% respectively.

4.5 Combined US /Fenton System

Application of Fenton Process to the OMW and the effect of various operating conditions were investigated in the previous section comprehensively. In this section, the study will be taken a step forward by applying the process combination of ultrasound and Fenton Process to OMW. The aim of this section is to determine the effect of both processes on the removal efficiency of organic matter and biodegradability ratio change by introducing processes either sequentially or interactively.

4.5.1 Application of Fenton Process Assisted by Ultrasound

Two different ways followed in the application of Fenton's Reagent assisted by ultrasound to the OMW during experiments. One of them is the process which both processes were taken place together at a definite time interval. The second one was considered as a sequential process in which OMW effluent treated by ultrasound was processed with Fenton Process subsequentially. pH was adjusted to 3.00 because both processes are effective in acidic range while temperature control at 30±2 ^{o} C was carried out. Treatment times of four hour for ultrasound and 1 hour for Fenton Process were not changed and molar ratio of 15 (1.5 M H_2O_2/ 0.1 M Fe^{2+}) was selected in Fenton Process. Figure 4.12 shows the effect on the removal efficiency and effluent concentration of organic matter by various combination of Fenton Process assisted by ultrasound. The fifth hour in the sequential process represents the application of Fenton Process to treated effluent.

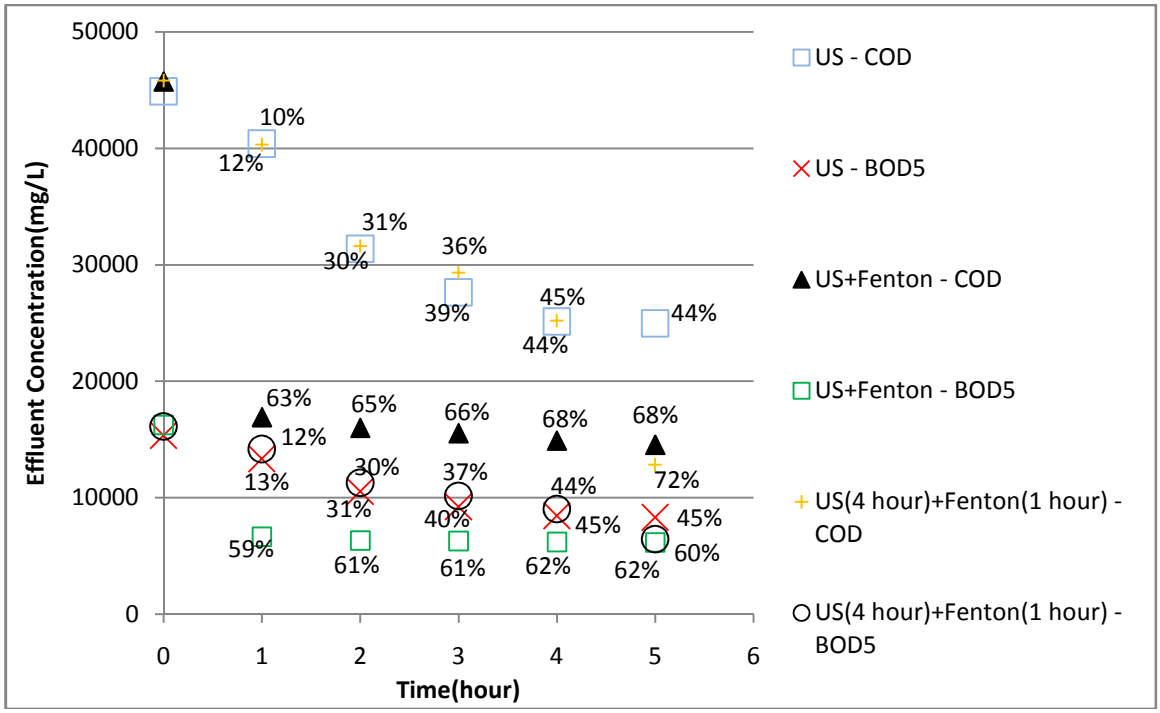


Figure 4.12 The effect on the removal efficiency and effluent concentration of organic matter by various combination of Fenton Process assisted by Ultrasound

As the figure demonstrates, two different combination of both process with their removal efficiencies and effluent concentrations were investigated. Single US process was also shown in the Figure in order to compare the effects of combined processes accurately. Whilst COD removal efficiencies of individual 1 hour-Fenton and 4-hour US process 66% and 44% (Table 4.10) respectively, the effect of combined process for five hours treatment time only reached to 68% and effluent concentrations remained at 14,550 mg/L. When both processes sequentially (US followed by Fenton) applied to OMW, the rate of degradation increased to 72%. The BOD_5 results are parallel to COD.

4.5.2 Comparison of Single and Combined US+Fenton Processes

In summary, combined processes of US and Fenton Process are more effective on the degradation of organic matter compared to single ones. However, when both processes were applied to OMW for five hours period simultaneously, the degradation efficiency rate is so close to the result of individual Fenton Process. In other words, combined US+Fenton system carried out together is predominantly under the influence of Fenton Process in

which ultrasound effect is negligible. Thus, it might be suggested that unique Fenton Process is also able to decompose organic matter as least as US does. On the other hand, second combination of both process (US followed by Fenton) have an increase in degradation efficiency between 5-10% and overall efficiency was reached to 72%. The biodegradability ratio also increased from 0.35 to 0.51 in terms of BOD_5/COD.

4.6. Combined US/UV System

The degradation of organic matter in the OMW has been studied with US, Fenton Process and the combination of those so far. In this part of the study, advanced oxidation experiments will be continued using UV irradiation instead of Fenton process. A treatment system of US accompanied by UV will be questioned in the degradation of organic matter and the enhancement of biodegradability. The pH value of 3.00 was preserved in the general system and treatment time of five hours was also not changed. US treatment was operated at the same conditions (85 W, 35 kHz). However, the overall temperature of the system during the experiments could not be maintained at room temperature of 30±2^o C due to heat transfer caused by UV lamps up to 80^o C in the ultrasonic bath. Therefore, the experiments were conducted without temperature control. The results were shown as the plot of the per cent COD reduction versus time in the Figure 4.13.

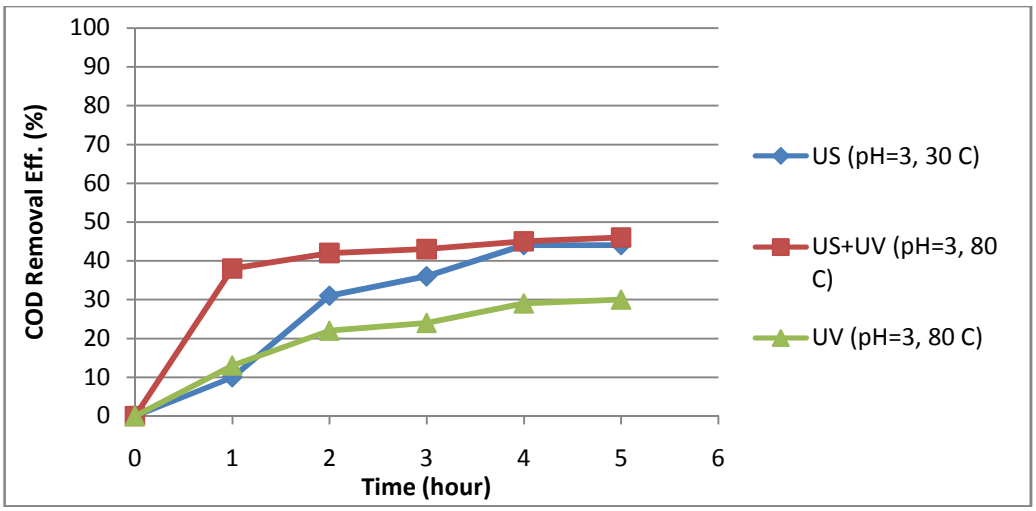


Figure 4.13 Plot of the per cent COD reduction versus time of individual and combined US/ UV process.

From the figure it is observed that the combined effect of ultrasound and UV resulted in higher degradation with 46% removal efficiency compared to individual effects of both ultrasound and UV irradiation. In the individual ultrasound experiment, 44% COD degradation was achieved at a final value of 25,134 mg/ L while 30% accomplished in the presence of UV irradiation with a final value of 31,302 mg/ L COD alone.

BOD_5 results were also parallel to COD and the removal efficiency in terms of BOD_5 was 44% in combined US/ UV process in the end of five hours with a final value of 9074 mg/L remaining from the initial of 16,204 mg/ L. The removal efficiencies for individual US and UV treatment are 43% and 27%, respectively.

The change on biodegradability of the combined and individual processes is quite similar and differs as little as from each other. As it earlier mentioned that single US application has no considerable effect on biodegradability. In addition to this, the biodegradability ratio (BOD_5/COD) also remained unchanged according to the results of individual and combined US/ UV processes. The initial and final ratios of the three processes fluctuate between 0.35-0.40. Figure 4.14 represents the plot of change on biodegradability ratios versus time of single and combined US/ UV processes.

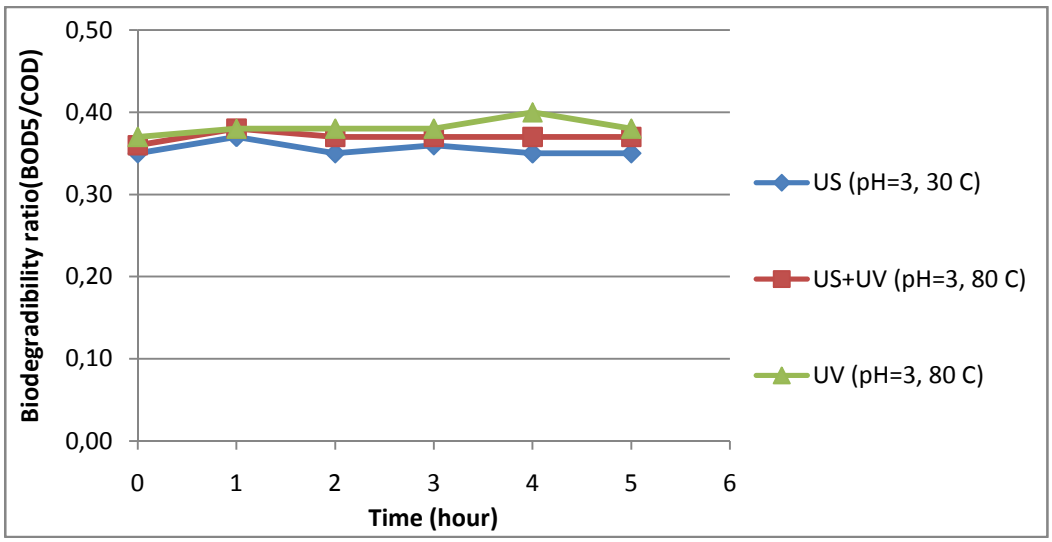


Figure 4.14 Plot of the change on biodegradibility ratios versus time of single and combined US/ UV processes

4.7 Combined US/ UV/ Fenton Process

The experiments performed in this part constitute individual or simultaneous application of UV/US and Fenton Processes.

Comparisons were conducted under similar experimental conditions: treatment time of five hours selected and pH adjusted to 3.00 and no temperature control were made (80^{o} C). Ultrasonic treatment was operated with the same conditions (85 W and 35 kHz). For the combined techniques, UV irradiation was provided with hybrid reactor while 1.5 M H_2O_2 and 0.1 M of Fe^{2+} with a molar ratio 15 were used in Fenton Process. The results of different combinations of US/UV/Fenton processes were shown in the figures 4.15, 4.16, 4.17 in terms of COD, BOD_5 effluent concentrations and changes in biodegradability ratio (BOD_5/COD), respectively.

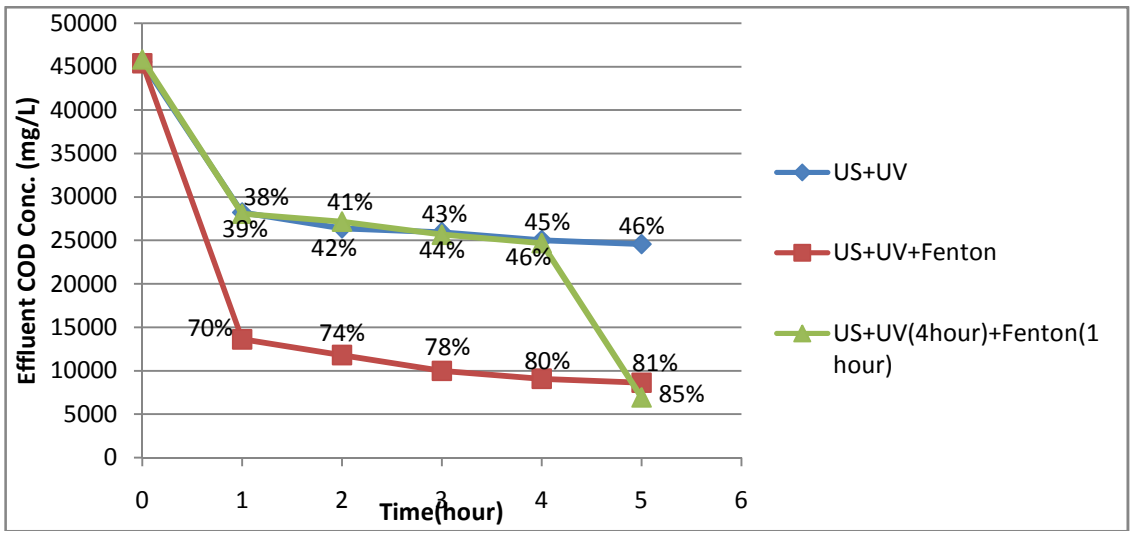


Figure 4.15. COD effluent concentrations and related removal efficiencies of different combinations of US/UV/Fenton processes

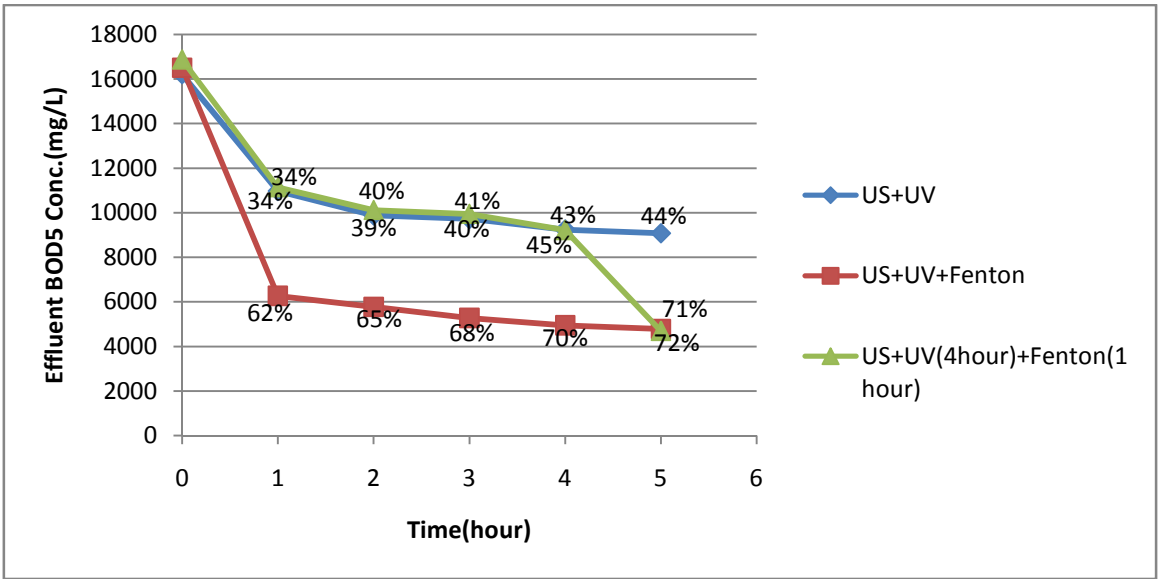


Figure 4.16. BOD_5 effluent concentrations and related removal efficiencies of different combinations of US/UV/Fenton processes

Combinations of US/UV/Fenton processes and the effluent concentrations of COD and BOD_5 were demonstrated as a function of time in the figures 4.15 and 4.16. The UV/US treatment system and its results were also illustrated in order to make a comparison between this process and additional Fenton process operated both simultaneously and sequentially. The fifth hour in the sequential process represents the Fenton Process applied to OMW as a single process. Generally, both COD and BOD_5 results obtained from the figures are parallel to each other. The removal efficiencies of both parameters are 81% and 71% in COD and BOD_5 with a final concentrations of 8624 and 4785 mg/L, respectively, when all three processes applied together for five hours period. These findings are better than the results obtained from the combination of US+Fenton Process (Figure 4.12). The difference between the results obtained by Fenton and photo-Fenton processes can be explained by contribution of UV irradiation to the Fenton Process. As demonstrated in Equation 2.9, Fe^{2+} ions react with H_2O_2 to generate Fe^{3+} and ●OH radical. The presence of UV light reduces ferric ion to Fe^{2+} (Equation 2.17) and reproduced ferrous ion (Fe^{2+}) reacts with H_2O_2 to produce Fe^{3+}. This causes an increase in the length of the chain reaction that result in a more complete destruction of organic compounds (Zepp et al., 1992). The sequential process of 4-hours US/UV followed by 1-hour Fenton's Reagent boomed the degradation efficiencies of organic matter. Through this process, COD removal efficiency

of 85% and BOD_5 efficiency of 72% were achieved in the end of the process, as the initial concentrations of 45,841 mg/L COD and 16,865 mg/L BOD_5 were decreased into 6934 and 4704 mg/L respectively. The overall COD degradation in the whole process is nearly 40,000 mg/L.

US/UV process has no considerable effect on the biodegradability ratio change. However, the assistance of Fenton Process affects this fact in a positive manner. The increase at biodegradability ratio of an initial value of 0.36 into 0.56 was accomplished in the combination of three processes applied together. The more exciting result according to the Figure 4.3.17 is that this initial value around 0.35-0.36 were increased into 0.68 by the application of US/UV followed by Fenton Process in the sequential process.

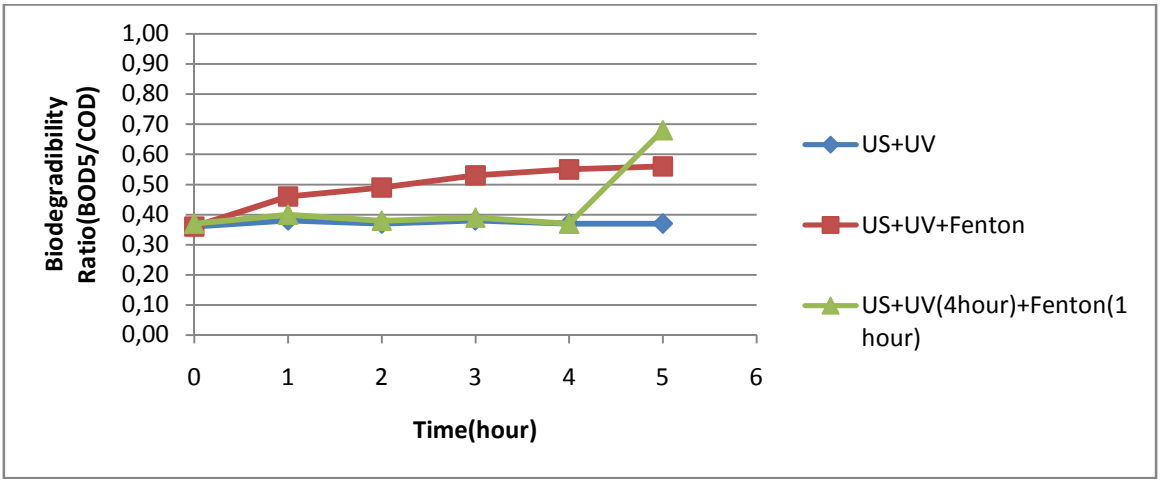


Figure 4.17. Changes on biodegradibility ratio of different combinations of US/UV/Fenton processes

4.8 Comparative Assessment of the Processes

The summary of the all treatment processes carried out in this study, their effect on removal efficiencies of organic matter, biodegradability and the operating conditions for each process are presented in Table 4.11.

Table 4.11 The summary of the all treatment process applied to OMW, their effects on organic matter removal, biodegradability and operating conditions for each process.

Process Type	**Operating conditions**	**% COD Removed**	**% BOD_5 Removed**	**Biodegradability Ratio change**
US	pH= 3.00 5 hour	44	45	0.34 → 0.34
Fenton	pH= 3.00 1.5 M H_2O_2, 0.1M Fe 1 hour	66	61	0.36 → 0.40
Fenton	pH= 3.00 1.5 M H_2O_2, 0.1M Fe 5 hour	67	65	0.36 → 0.39
UV	pH= 3.00 5 hour	30	27	0.37 → 0.38
US/Fenton	pH= 3.00 1.5 M H_2O_2, 0.1M Fe 5 hour	68	62	0.35 → 0.42
US+Fenton	pH= 3.00 1.5 M H_2O_2, 0.1M Fe 4+1 hour	72	60	0.35 → 0.51
US/UV	pH= 3.00 5 hour	46	44	0.35 → 0.39
US/UV/Fenton	pH= 3.00 1.5 M H_2O_2, 0.1M Fe 5 hour	81	71	0.36 → 0.56
US/UV+Fenton	pH= 3.00 1.5 M H_2O_2, 0.1M Fe 4+1 hour	85	72	0.37 → 0.68

According to the Table, total COD removal was found following the order: UV < Ultrasound < US/UV < Fenton < US/Fenton < US+Fenton < US/UV/Fenton < US/UV+Fenton. Figure 4.18 represents the effectiveness of the processes applied to OMW in terms of total COD removal.

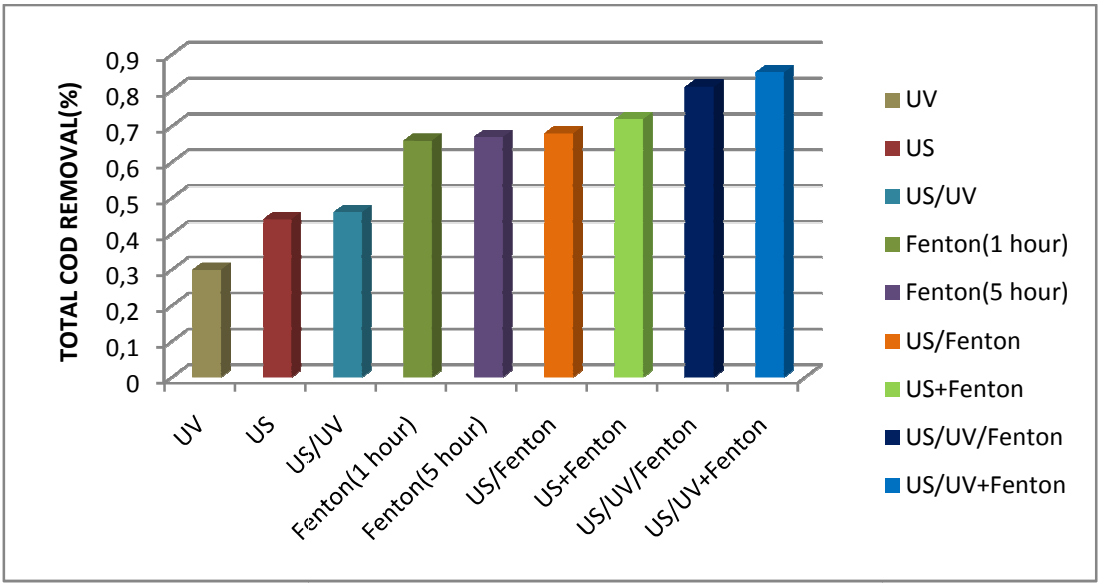


Figure 4.18 The effectiveness of the processes applied to OMW in terms of total COD removal.

The findings reveal that the best results in terms of biodegradability enhancement were achieved where Fenton and US processes take place together either simultaneously or sequentially. In addition to this, the biodegradability enhancement is more remarkable in sequential process, Fenton following US, than simultaneous process of both. However, other test processes have no considerable effect on biodegradability enhancement to OMW.

5. CONCLUSIONS AND RECOMMENDATIONS

In this research, the removal efficiencies of organic matter and the biodegradability enhancement in the treatment of olive mill wastewaters via applying Ultrasound, UV irradiation, Fenton, photo-Fenton and combinations of them were investigated. The aim of the study was to determine the most appropriate process and its operating conditions for the treatment of olive mill wastewaters using advanced oxidation methods. A comparative assessment of Advanced Oxidation Processes (AOP) was also done in the scope of this research.

Generally in all experiments, the results indicate that pH was an important operating parameter and favoured acidic range (pH=3.00). In single and combined Fenton Processes, reagent dose (H_2O_2/Fe) was found to be crucial parameter affecting the efficiency of removal rates.

The results of the single US experiments show that ultrasonic bath system (85W, 35 kHz, 0.11W/ml power density) used in this study is ineffective to produce sufficient hydroxyl radicals for complete mineralization of organic matter via oxidative degradation. The maximum removal efficiencies of single US experiment is inadequate with 44% COD and 45% BOD_5 removal efficiencies in the end of the 5 hour while Fenton process accomplished more than 60% removal alone just in one hour. In addition to this, there is no considerable effect on biodegradability enhancement when ultrasonic bath used in the treatment of olive mill wastewaters alone.

The effect of UV irradiation on the removal efficiencies and biodegradability as a single process or combined with ultrasound was found to be rather low. The major drawback for this fact was considered as increase in turbidity of OMW resulting from the fragmentation of the solid fraction (high suspended solid concentration) by ultrasound which reduces the overall transmitivity of UV radiation and inhibits the photocatalytic degradation. However, the effectiveness of both processes increased when the system was operated by the assistance of Fenton Process either sequentially or simultaneously. The

synergy was the result of increased mass transfer rates and higher ●OH radical formation. In such coloured waters containing high suspended solids, UV assisted US treatment could not be as the best treatment choice.

More specific conclusions of this study were as follows:

1) It was found that pH is the most important controlling parameter and acidic conditions are favourable for treating OMW by ultrasound. The removal efficiencies were 44% in COD and 45% in BOD_5 by decreasing pH value into 3.00 while in neutral (pH= 7.00) and alkaline (pH= 10.00) conditions these values were decreased to %31 in COD, 29% in BOD_5 and %38 in COD and 37% in $BOD_{5,}$ respectively.

2) Initial concentration in ultrasound experiments did not affect the overall COD removal efficiencies. While removal efficiency of undiluted sample by applying ultrasound with initial concentration of 44,688 mg/L COD was 41%, the removal rates of samples with initial concentrations of 2163 mg/L and 1244 mg/L COD were 40% and 42%, respectively. However, dilution of samples has negative impact in Fenton Process due to decrease in removal efficiencies.

3) Overall removal efficiencies of 66% in COD and 61% in BOD_5 were achieved in Fenton Process by using 1.5 M H_2O_2 and 0.1 M Fe^{2+} with a molar ratio of 15.0 (H_2O_2/ Fe^{2+}) at pH=3.00 in one hour. Optimal dosage for Fenton process was found between 13.0 and 16.0 in molar ratio. Moreover, decrease in pH is a good control parameter in Fenton Process and directly related with the amount of pollutant oxidized by Fenton reagents.

4) Operation of the ultrasonic bath up to 12 h and increase the contact time of 5 hours in Fenton Process provided a little increase in removal effiencies which were negligible. Therefore, optimum contact time was selected as 4 hour for US and 1 hour for Fenton due to operating costs in the treatment of olive mill wastewaters.

5) The best results in the study were achieved by the combinations of US/UV and Fenton Process combinations in terms of COD, BOD_5 and biodegradability enhancement. COD

removal efficiency of 81% and BOD_5 efficiency of 71% were achieved in simultaneous process. In the sequential process, 85% in COD and 72% in BOD_5 reduction were achieved in the end of five hour as the initial concentrations of 45,841 mg/L COD and 16,865 mg/L BOD_5 were decreased into 6934 and 4704 mg/L respectively. Biodegradability ratios were also increased to 0,56 from the initial value of 0,36 in interactive process and to 0,68 in the sequential process. The results indicate that sequential process of US/UV followed by Fenton application is quite effective process in the pre or post-treatment of olive mill wastewaters.

Recommendations for future work:

Based on the findings of the study, combinations of US/UV/Fenton Process could not be considered as main treatment process for olive mill wastewaters due to strict requirements of discharge limits. However, it is an effective pre-or post process which contributes to the enhancement of biodegradability and organic matter removal. At this point, the integration of the process with conventional biological methods is considered to be primary option in the treatment of such a hardly biodegradable effluent.

Further studies should be particularly focused on the ultrasound modifications by the use of effective equipment with ultrasonic power output and densities. In addition to those, it is believed that these results should be supported with pilot and full-scale studies for the reliability and applicability of the process in industrial grade.

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