DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

PRETREATMENT OF OLIVE OIL MILL WASTEWATER

by
Hüseyin EVCİL

September, 2005
İZMİR

PRETREATMENT OF OLIVE OIL MILL WASTEWATER

A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the
Degree of Master of Science
in Environmental Engineering, Environmental Science Program

by
Hüseyin EVCİL

September, 2005
İZMİR

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"PRETREATMENT OF OLIVE OIL MILL WASTEWATER"** completed by **Hüseyin EVCİL** under supervision of **Prof. Dr. Adem ÖZER** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Prof. Dr. Adem ÖZER

Supervisor

Prof. Dr. Ayşe FİLİBELİ

(Jury Member)

Assoc. Prof. Nuri AZBAR

(Jury Member)

Prof. Dr. Cahit HELVACI

Director

Graduate School of Natural and Applied Sciences

ACKNOWLEDGMENTS

Firstly, I would like to thank my supervisor Prof. Dr. Adem ÖZER for his guidance, invaluable advises and support. It has been a great honor and privilege for me to work with Prof. Dr. Adem ÖZER.

Secondly, I am grateful to Prof. Dr. Füsun ŞENGÜL and Prof. Dr. Ayşe Filibeli for their patients and endless support.

In addition, I would like to thank Dr. Zihni YILMAZ for his guidance, support and valuable advises.

I am also grateful to Research Assistant Ebru ÇOKAY ÇATALKAYA, Research Assistant Ezgi OKTAV, Dr. Nurdan BÜYÜKKAMACI and Research Assistant Hasan SARPTAŞ for their helps and motivation, in every stage of my thesis.

I wish to thank Technicians Yılmaz SAĞER and Orhan ÇOLAK for their helps in my experimental studies.

I am also grateful to Anıl KOMUTAN, Özgür CANLI, Lütfü KIPKIP, Yılmaz OLUCUK, Oya Gül EDİŞ for their morale support and encouragement.

Finally, I am very grateful to my family for their morale support, endless patient.

Hüseyin EVCİL

PRETREATMENT OF OLIVE OIL MILL WASTEWATER

ABSTRACT

Since thousands of years, olive has been a worthwhile plant for human. Olive fruit and olive oil, which is produced from this fruit, are important components of Mediterranean cuisine, because of its energy, its satisfying special taste and vitamins that are included. In Mediterranean countries such as Greece, Italy, Lebanon, Portugal, Spain, Syria, Tunisia and Turkey 11 million tons of olives are produced per year from which about 1.7 million tons of olive oil is extracted. At the end of the olive oil production, these countries came face to face with olive oil mill wastewater which is known as Alphechine and has high pollution parameters. Olive oil mill wastewater (Alphechine) included high organic matter, suspended solids, phenols and oil grease. Therefore, it is thought that the olive mill effluent causes an important environmental problem.

The aim of this study was to investigate the characterization and treatability of the olive mill wastewater. In this study seven olive oil samples which were taken different times of harvesting season from olive oil industry were investigated. Selected methods were applied single or one after the other. In the name of treatability studies, physical and chemical treatment methods were applied.

In the first part of experimental studies, different physical treatment methods such as sedimentation, filtration and centrifugation were applied on raw wastewater. Sedimentation experiments were applied in two parts such as pilot plant scale and laboratory scale. To pilot plant scale experiments, sedimentation column were designed and installed in olive oil factory which was manufactured with 3 phase extraction method. Maximum COD removal efficiency in sedimentation experiment was 42 % and it was obtained at the end of two weeks retention times at sedimentation column. In filtration experiments cartridge filter, filter clothes and filter paper were used. Maximum COD removal efficiency of filtration was obtained 35.3 % with combination of cartridge filter and filter clothes. At the same time with this combination % 81 SS reduction were obtained. In centrifugation experiments 58.8 % COD removal efficiency was obtained.

In the second part of experimental studies, chemical treatment studies were done. HCl, $Ca(OH)_2$ and zeolite were used to coagulation-flocculation-precipitation. After acid cracking with HCl 48 % removal efficiency was obtained. When sedimentation with ten months and acid cracking applied respectively, 68 % COD removal efficiency was obtained. After applying acid cracking and centrifugation combination, 60.3 % COD removal efficiency were obtained. Study with $Ca(OH)_2$ didn't give the sufficient result (23.5 %), but combination of acid cracking, $Ca(OH)_2$ and centrifugation were give best removal efficiency such as 73.5 %. In experiment with zeolite, 38.3 % COD removal efficiency were obtained. After acid cracking, zeolite was added and 68.8 % COD removal efficiency was obtained.

As a result of all experimental studies observed that, applying physical and chemical treatment methods were not enough to achieve the discharge standards. Therefore, further treatment is needed to reduce the COD reduction. Generally, better treatment efficiencies obtained with methods using more steps. Physical treatment, chemical treatment and biological treatment alternatives should be applied sequentially for achieving wastewater discharge standards for olive mill wastewater.

Keywords: Acid cracking, Alphechin, Alpeorujo, Chemical Treatment, Jamila, ,Lime treatment, Olive oil mill wastewater, OWM, Margine, Olive oil cake, Physical Treatment, Zeolite.

ZEYTİNYAĞI ATIKSULARININ ÖN ARITIMI

ÖZ

Zeytin, yüzyıllar boyunca insanlar için oldukça faydalı bir bitki olmuştur. Zeytin meyvesi ve bu meyveden elde edilen zeytinyağı, sağladığı enerji, kendine özgü lezzeti ve içerdiği vitaminler sayesinde, Akdeniz mutfağının vazgeçilmez bir öğesi konumuna gelmiştir. Akdeniz ülkeleri olan Yunanistan, İtalya, Lübnan, Portekiz, İspanya, Suriye, Tunus ve Türkiye' de yıllık 11 milyon ton zeytinden ortalama 1,7 milyon ton zeytinyağı elde edilmektedir. Bu ülkeler, üretim sonucunda kirlilik parametreleri çok yüksek değere sahip ve "Karasu" olarak bilinen zeytinyağı atık suları ile karşı karşıya kalmışlardır. Zeytinyağı atık suları (Karasu) yüksek organik madde, askıda katı madde, fenol ve yağ – gres içermektedir.

Bu çalışmanın amacı, zeytinyağı atık sularının karakterizasyonunun ve arıtılabilirliğinin incelenmesidir. Bu çalışmada, hasat sezonunu değişik zamanlarında alınmış örnekler incelenmiştir. Arıtılabilirlik çalışmaları adına, fiziksel ve kimyasal arıtılabilirlik çalışmaları uygulanmıştır. Uygulanan yöntemler tek ve birbiri ardınca kombine olarak uygulanmıştır. Arıtılabilirlik çalışmaları adına fiziksel ve kimyasal arıtım metotları uygulanmıştır. Aynı zamanda bu kombinasyon ile % 81 askıda katı madde giderimi sağlanmıştır.

Deneysel çalışmaların ilk kısmında fiziksel arıtma yöntemlerinden çökeltim, filtrasyon ve santrifüj metodları ham su üzerine uygulanmıştır. Çökeltim deneyi pilot ölçekli ve laboratuar ölçekli olmak üzere iki kısımda uygulanmıştır. Pilot ölçekli deneyler için çökeltim kolonu tasarlanmış ve 3 fazlı üretim yapan bir zeytinyağı fabrikasına yerleştirilmiştir. Çökeltim deneylerinde maksimum COD giderimi % 42 olarak iki hafta bekleme süresiyle çökeltim kolonundan elde edilmiştir. Filtrasyon deneylerinde, kartuş filtre, filtre bezleri ve filtre kâğıdı kullanılmıştır. Filtrasyon deneylerinde maksimum COD giderimi % 35,3 olarak kartuş filtre ve filtre bezlerinin kombinasyonundan elde edilmiştir. Santrifüj yöntemiyle % 58,8 COD giderimi elde edilmiştir.

Deneysel çalışmaların ikinci kısmında kimyasal çöktürme ve arıtılabilirlik çalışmaları yapılmıştır. HCl, Ca $(OH)_2$ ve zeolit kimyasal çöktürme için kullanılmıştır. HCl ile yapılan asit kraking deneylerinden sonra % 48 COD giderim verimi elde edilmiştir. 10 hafta bekleme süresinden sonra uygulanan asit kraking işleminden sonra % 68 COD giderim verimi elde edilmiştir. Asit kraking ve santrifüj kombinasyonu ile % 60.3 COD giderimi elde edilmiştir. Ca $(OH)_2$ ile yapılan çalışmalar etkili sonuç (%23,5) vermemiştir, fakat asit kraking, $Ca(OH)_2$ ilavesi ve santrifüjden oluşan kombinasyon ile birlikte en iyi giderme verimi % 73,5 olarak elde edilmiştir. Zeolit ile yapılan deneylerde %38,3 COD giderme verimi elde edilmiştir. Asit krakingden sonra uygulanan zeolit ilavesi ile % 68,8 COD giderim verimi elde edilmiştir.

Tez kapsamında yapılan deneysel çalışmalar sonucunda uygulanan fiziksel ve kimyasal yöntemlerin deşarj standartlarını sağlamak için yeterli olmadığı gözlemlenmiştir. Bu yüzden ileri arıtma yöntemleri, COD değerini düşürmek için kullanılmalıdır. Genel olarak en iyi giderim verimleri birden fazla basamak sayısına sahip arıtılabilirlik çalışmalarından elde edilmektedir. Fiziksel arıtma, kimyasal arıtma ve biyolojik arıtma yöntemlerinin ardışık olarak uygulanmasıyla alıcı ortam deşarj standartları sağlanabilir.

Anahtar Kelimeler: Asit kraking, Fiziksel arıtım, Karasu, Kimyasal arıtım, Kireçle arıtım, Prina, Zeytinyağı atıksuları, Zeolit.

CONTENTS

Page

CHAPTER ONE
INTRODUCTION

1.1. Literature Survey

1.1.1. General

Recent archeological findings off the northern coast of Israel gave details on the olive oil production knowledge of the ancient inhabitants of the Mediterranean areas. According to this research the Neolithic dwellers of this region invented the usage of olives between 8000 and 7000 years ago (Galili, E., & Sharvit, 1998).

Olive oil is nearly totally produced in the Mediterranean region. Three quarters of the annual production in the world comes from European Union countries around the Mediterranean Sea. Today the olive grooving area extends between the 30^{th} and the 45^{th} Northern Parallels. Olives are also grown in Northern India, in Argentina, Mexico, Peru and in the united States; but the best olives solely grow in the Italian Peninsula, where the ground varieties and efficient production techniques allow to obtain a product which is definitely superior to the European Community average (Vossen, 2001). As the demand of olive oil is rapidly increasing worldwide, environmental pollution posed by olive mill wastes (OMW) is a growing problem especially in the Mediterranean region. The olive oil producer countries have been facing a serious challenge to find an environmentally sound and economically viable solution in handling and disposal of OMW.

Solid and liquid OMW are dark-colored wastes and contain high amounts of organic materials. They are composed of many complex substances that are not easily degradable. Production facilities are usually associated with emissions of strongly odorous volatile compounds. When their wastes are disposed into the environment, they create odor nuisance, too. Deterioration of natural water bodies due to olive oil mill wastes is a serious problem as indicated by coloring, appearance of an oily shine, and increased oxygen demand. They also affect the soil quality, are toxic to plant life, and create odor nuisance when disposed into the soil. Therefore, direct discharge of olive mill wastewaters into receiving media is not permissible and certain measures must be taken before disposal of the OMW into the environment (Azbar et al, 2004).

Although the duration of campaign for processing olives is continued from November to February, the amount and pollution potential of wastewater are very high (Beltran et al., 1999). Pollution abatement for olive mill wastewater is difficult. Olive mill wastewaters are high strength and the processing units are small, and cannot withstand the cost of treatment (Lolos et al., 1994).

The difficulties of treatment of olive mill wastewaters are mainly related to;

- High organic loading,
- Seasonal operation,
- High territorial scattering,
- Presence of organic compounds, which are hard to biodegrade such as phenolic compounds and long-chain fatty acids (Ergüder et al., 2000).

Various treatment methods for the treatment of olive mill wastewater and olive residues can be used. The great variety of compounds of the wastes needs several technologies to remove the harmful compounds for the environment. Most of the following methods have been tested in laboratory scale and only some of them used in industrial scale. The mostly used treatments are drying/evaporation, thermal treatment, and biological treatment (aerobic and anaerobic), lagooning, filtration, ultra filtration, membrane filtration, precipitation/flocculation, wet oxidation, adsorption, evaporation, distillation, electrolysis, and composting.

Physical treatment, chemical treatment, oxidation and vacuum evaporation processes were being applied to OMW taken from olive oil processing mill using one by one or all together of different treatment techniques. In this seminar we told about, these pre treatment methods and biological treatment processes effectives about removing about the pollution.

Main problem regarding the disposal of OMW is to find an environmentally friendly and economically viable solution. In biochemical treatment of these olive oil mill wastewaters, high capital and operating cost units with limited efficiency have to be installed due to high organic loads and high chemical oxygen demand (COD) to biological oxygen demand (BOD) ratios. Due to the presence of toxic organics mostly coming from the broken seeds, these wastes are toxic to bacteria and direct biological treatment is not possible. (Gonzalez, et al., 1990) In addition, these wastes are mostly generated from small enterprises having limited financial resources and usually far from each other. The latter creates difficulty in establishing central treatment and disposal facilities.

The yearly world olive oil production is estimated at around 1.5 to 1.7 millions ton/year. Over 95% of the olive trees (714 millions) and over 97% of the agricultural area dedicated to growing olive is in the Mediterranean area. Olive oil production in the EU countries represents 75% of the world production. The main producers are Italy, Spain, Greece, Tunisia and Turkey. In Greece the mean annual olive oil production is around 300,000 annual tons, in Spain it varies between 400,000 and 500,000 tons per year and in Italy production of olive oil vary seasonally from 400,000 to 500,000 tons, at an average olives yield of 2.2 to 3.1 tons/hectare. In 1997 olive oil production in Turkey was estimated at around 200.000 is tons/year (Improlive, 2000).

Various treatment methods for the treatment of olive mill wastewater and olive residues can be used. The great variety of compounds of the wastes needs several technologies to remove the harmful compounds for the environment. Most of the following methods have been tested in laboratory scale and only some of them used in industrial scale. In the case of vegetation water the mostly used treatments are drying/evaporation, thermal treatment, and biological treatment by fungi. Compost and livestock feeding manufacture could follow this treatment. For the liquid waste, the other possible methods are, either in single or in combined ways, aerobic treatment (bioremedation), lagooning, anaerobic treatment, filtration, ultrafiltration, membrane filtration, wet oxidation, precipitation/flocculation, adsorption, evaporation, distillation, electrolysis, co-composting of diverse mixture of different wastes. A lot of factors must be considered to choose the treatment methods among different methods, e.g. waste state (liquid or solid), waste amount, costs and investment, required area, specific training of the workers, noise and odor emissions, seasonal trouble (Aragon, 2000).

In the last few years, several attempts to utilize by products (vegetation water and olive residue) from olive mills have been described in technical literature. The main subjects are, animal feed, direct application of olive mill wastewaters to soils, agro-chemicals, activated carbon, materials, proteins and food ingredients, enzymes, carbohydrates, organic fertilizers, fatty-acids, cosmetics, antioxidants, Pharmaceuticals, including vitamins, olive oil as raw materials for biochemical synthesis (Demichelli & Bontoux, 1996).

On the other hand, there are studies indicating that OMW may also be regarded as an economic resource. Among these practices, use of OMW as soil conditioner, biomass fuel, compost, or as starting material to obtain valuable products such as antioxidants, enzymes and biogas fuel may be counted. Recycle and reuse of process water for irrigation purposes may also be considered, but acceptable water quality must be guaranteed.

In order to avoid the economic and social chaos leading to potential crisis in olive production due to the requirements of very expensive OMW treatment investments, several provisory legislation and ministerial decrees were promulgated and strategic plans were applied in some countries. One of them has foreseen spreading of wastewaters on land, such as in Italy. Spain almost totally changed the production techniques from press and three-phase (oil-water-paste) continuous systems to two-phase systems to produce less waste. Extensive field studies and research indicating the high fertilizing and soil conditioning value of OMW were carried out in Spain and Italy (Rozzi, A., & Malpei, 1997).

1.1.2. The Olive Tree and Olive Oil Manufacturing

The olive-tree and the oil obtained from its fruits are very ancient elements that have been accompanying the Mediterranean Civilization since its birth, gaining important, deep and religious meanings. The olive branch symbolizes peace, the trunk stands for fertility and prosperity, and the oil represents the divine essence. The most ancient growing of the "Olea Europea" has been discovered in the Southern Caucasus, west of the Iranian Plateau, in Syria and Palestine. The cultivation then spread to the Greek Islands, above all to Rhodes, Cyprus and Crete. Then through the Greeks it reached all the Mediterranean Countries, where it found the greatest expansion (Oktav, 2001).

The Phoenicians helped spread the olive tree and they thought the peoples they visited during their periodic commercial journeys how to gain the oil from its fruits. After it reached the Greek settlements, the Romans extended the olive tree cultivation first to the rest of Italy and subsequently to the conquered territories: the Province and the Iberian Peninsula.

Today the olive growing area extends between the 30^{th} and the 45^{th} Northern Parallels. Olives are also grown in Northern India, in Argentina, Mexico, Peru and in the United States; but the best olives solely grow in the Italian Peninsula, where the ground varieties and the efficient production techniques allow to obtain a product which is definitely superior to the European Community average (Vossen, 2001).

OMW highly polluting wastewater generated during the extraction of oil from the fruit. Olives have been cultivated in the countries surrounding the Mediterranean Sea for thousands of years and the wastewater produced oil extraction generate a significant amount of organic pollution. Olive oil can be extracted either simply by pressure (in figure. 1.1) or by centrifugation, using either a 2-phase (in figure 1.2) or 3-phase system (in figure 1.3). In all cases, the olives are firstly washed, and then crushed and ground. The 3-phase extraction method was developed '70's in order to reduce labor costs and increase processing capacity and yield whilst classical methods can process around 8-10 tones of olives per day, 3-phase continuous system can process 30-32 tones per day with a fraction of labor requirement. Unfortunately, this technology also uses around 50% more water than the simple pressing method (around 80-100 liters of water per 100 kg. of fruit processed) and generates around 50% more wastewater per unite mass of fruit processed (1.7 kg wastewater per kg olive processed compared to 0.9 in the classical method). As consequence, more recently, the 2-phase process (with uses much less water than the 3-phase) was developed. This also has inherent environmental problems associated with it, in that although it produces no wastewater (margine) as such, it combines that wastewater that is generated with the solid waste (grignon) to produce a single effluent stream of semi-solid (30% solid by mass). This doubles the amount of 'solid' waste requiring disposal, and it cannot be composted or burned without some form of (expensive) pretreatment. It is also unsuitable for solvent extraction to produce more oil for soap manufacture (Sekerratt G., et al., 1999).

Olive oil production is divided into three fields:

1. Oil mills, which process the olives into oil and oil cake,
2. Refineries, where the non-consumable oil is refined,
3. Plants where the oil cake is processed and residual oil is extracted from the waste resulting from olive oil extraction.

To get the highest possible yield of valuable virgin oil, the olives have to be processed at low temperature (<40ºC). For oil extraction 3-processes are applied:

a. Pressing, traditional system,
b. Continuous process with three-phase decanters,
c. Continuous process with two-phase decanters,

Oil extraction can be divided into seven steps:

I) Delivery:

The olives are delivered and stored in the yard in collection boxes. This offers the possibility to determine the quality and rate of yield, and serves as basis for the settlement of accounts between the oil mill and olive farmer. The production plant is fed in charges. The olives are filled in baskets, transported by donkey carts to the soil funnel, and from thereby a belt conveyor to the first processing stage.

II) Washing of the olives:

The olives are filled in charges into a soil funnel and transported by a belt conveyor into a sucking device, where leaves, wood particles and other disturbing solids are removed. Subsequently they are cleaned in a washing plant. In some plants the washing water is recycled into the process after sedimentation of the solids or filtration. In other plants the olives are directly processed without being washed. For washing of the olives 100 - 120 l of water per 1000 kg of olives are required. With the help of a perforated vibrating screen they are transported into a funnel. By the funnel tip they get into the loading opening of an eccentric worm pump, which conveys them into a grinding device.

III) Grinding:

The olives are ground up, together with their stones, and mixed into a homogeneous pulp. This is carried out in a stone-mill consisting of a horizontally lying granite block with a granite millstone resting perpendicular to it. Metal mills and hammer mills are also used for this purpose. If frozen or very dry olives are processed, a small quantity of water is added (100 - 150 liter per 1000 kg of olives).

IV) Mixing/beating of the olive pulp:

In downstream-arranged malaxeurs the pulp is mixed after adding of warm water. For further breakdown of the olive cells and to create large oil droplets, the pulp is beaten. For this purpose salt is often added which aids the osmotic breakdown of cells in the olives and so the separation of the oil and water from each other is eased.

Beating of the olives is repeated several times. For oil extraction by centrifuges the pulp is heated to improve the separation process. After beating the pulp is further ground up. In a malaxeur up to 100 % water are added before conveying the pulp by an eccentric worm pump into the two-phase- or three-phase decanter.

V) Oil extraction:

In small oil mills the olive oil is extracted in batch operation using the traditional press method. The oil extracted is collected in containers and clarified by sedimentation. About 200 kg of oil result on an average from one ton of processed olives. To improve the separation of oil and pulp, biological or chemical aids can be added that attack the cell walls. With traditional presses the energy demand for olive oil extraction processes is 40-63 kWh per ton of processed olives, and 90 - 117 kWh with three-phase decanters.

VI) Purification of the oil:

By means of a vibrating screen fine solids that might still be contained are removed from the oil. To enable the separation of small wastewater quantities and suspended solids that accompany the oil, 100 - 150 liter of water per 1000 kg of centrifuged oil are normally added to the purification process, which is achieved with the help of centrifugation.

VII) Extraction of residual oil:

The high-loaded wastewater from the three-phase decanter is treated by means of a vibrating screen and a centrifuge, the residual oil is extracted. The oil centrifuged twice flows into a collecting tank and is pumped by eccentric worm pumps in surface or underground storage tanks. The solid waste from oil extraction by pressing still contains about 6 % oil, using the continuous three-phase decanter, still 4 % olive oil. The oil content in the solid-liquid mixture from the dual-phase decanting process is 2.5% to 3.5 %. In specialized plants the solvent extraction process is used for this purpose. First the waste is completely dried and then extracted using hexane as solvent. The dry residues can be used as concentrated fodder. In some extraction plants the stones are separated from the pulp after extraction and used as fuel for heating of the driers. The pulp is sold as fertilizer or fodder. In some oil mills the solid waste from the press is directly used as fuel for the heating of water.

There are there basic olive oil production methods are available at the over all the world; the pressure 'classical' extraction, 3 - phase centrifugal extraction, 2 - phase centrifugal extraction. These production methods details are given below in Figure 1, 2 and 3.

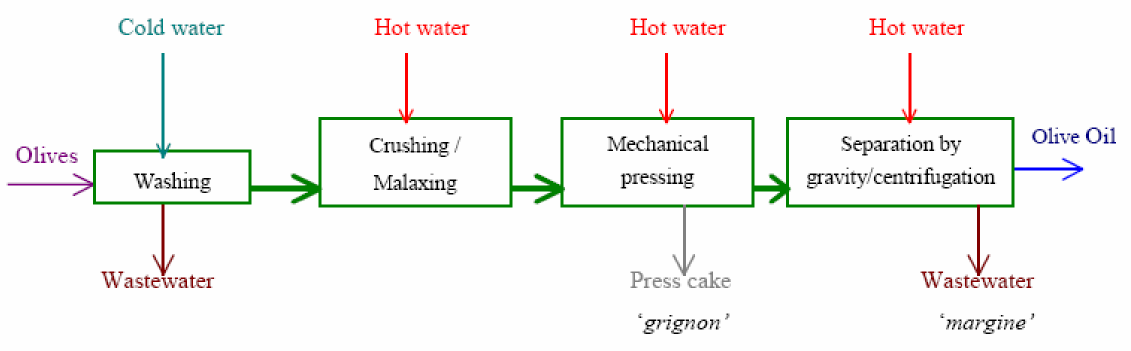

Figure 1.1 The Pressure 'Classical' Extraction of Olive Oil

Press-extraction (Figure 1) is a mechanical process, involving the application of pressure to a stack of mats smeared with olive paste which are alternated with metal discs and placed on a frame that is fitted with a central spike. In oil mills which use the single pressing method or the super-presses, the oil yield depends upon the pressure that is applied to extract the oil. In the continuous (centrifugation) processes (Figures. 2 and 3 below), the olive paste has to be diluted with warm water before separation. In Tunisia, the classical method of oil extraction accounts for around 40 % of oil production, super pressing systems around 22%, mixed mills 8% and continuous presses 30% (Improlive – Final Report 2000).

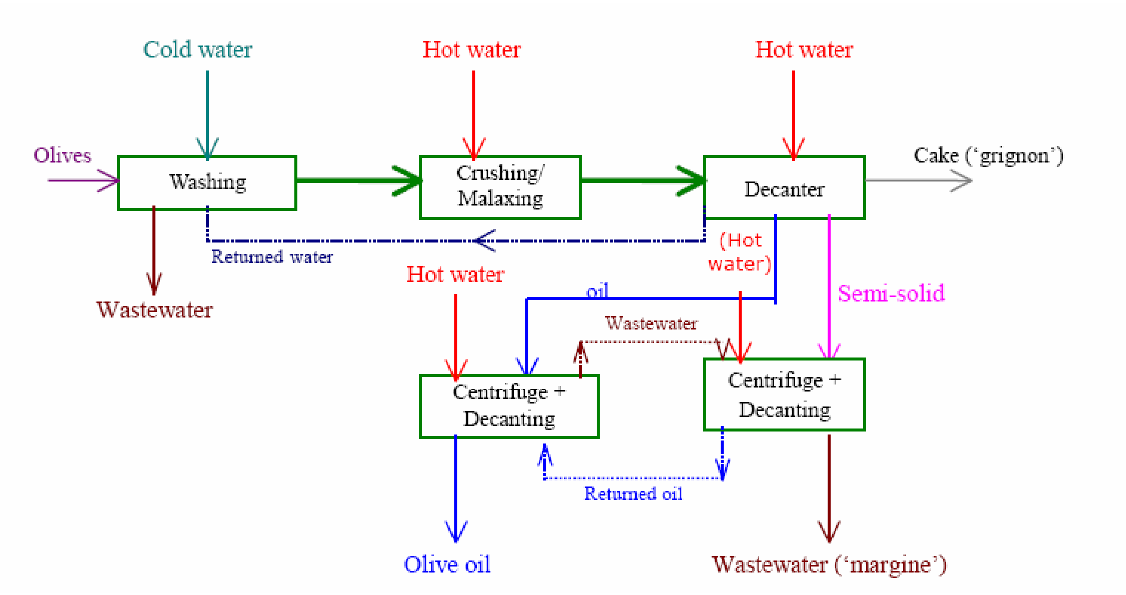

Figure 1.2 The 3-Phase Centrifugal Extraction of Olive Oil

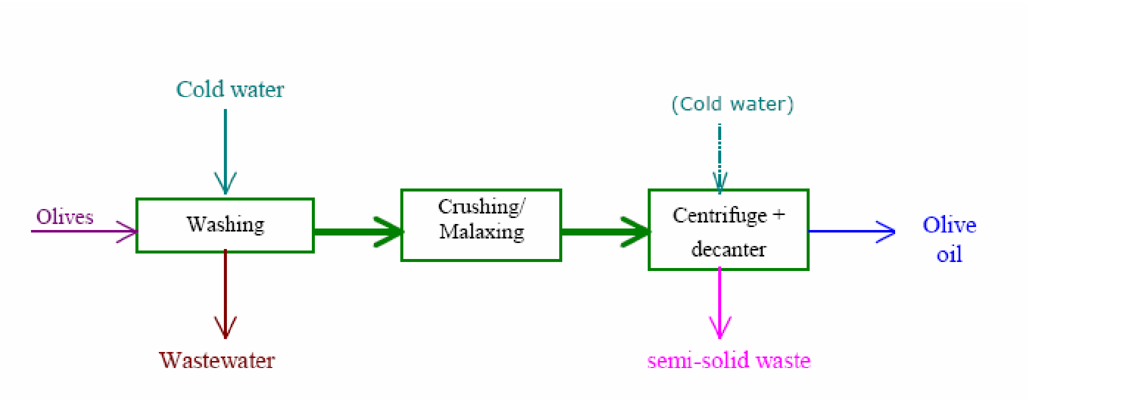

Figure 1.3 The 2-Phase Centrifugal Extraction of Olive Oil

Press process is traditional method. In this process, the olives are washed, crushed and kneaded with addition of water called as process water. The resulting paste is then pressed to separate the oil and the vegetation water which is the liquid phase of the process from the solid phase that is called olive cake. Finally, the oil is separated from the wastewater by vertical centrifugation or decanting (Demichelli&Bontoux, 1996). In centrifugation system, horizontal centrifuge (decanter) is used. It substitutes the press, allowing continuous operations. Depending on the decanter used during the production, two processes can be distinguished:

3-Phase System: It requires process water. After the process, three phases produce: oil, wastewater, and olive cake. This process needs addition of significant quantities of water, therefore, it generates a considerable volume of olive mill wastewater (three times more than the traditional system) (Masghouni&Hassairi, 2000).

2-Phase System: No process water is added during the process and only two phases produce: oil and olive cake. This system is ecologically attractive because the aqueous phase (olive mill wastewater) is almost reduced to zero. The major part of vegetation water is retained by the solid phase. For the two variants, the obtained solid phase is rich in water (50-60% of water) and contains 2-3% of residual olive oil (Masghouni&Hassairi, 2000).

The total amount of wastewater generated by the production of olive oil in the olive growing countries of the Mediterranean is in excess of 30 x 106 m3 per year. This olive oil mill effluent (OME) is extremely polluting with a very high chemical oxygen demand (COD) concentration (up to 200g l-1), and constitutes a major source of organic pollution in the Mediterranean region, posing a threat to both surface and groundwater quality, and creating a smell nuisance. OME is produced during those months of the year when the olives are pressed (usually November to March). In Tunisia, OME is referred to as 'margine', and the solid waste resulting from the oil extraction process is called 'grignon'. OME has a complex composition and contains a large number of organic compounds - many of which are toxic and difficult to fully degrade in microbiological systems. This is particularly true for the long-chain fatty acids (such as octa- and hexadecanoic acid) and the polyphenolic compounds that are present. The exact composition of the mill wastewater emulsion depends upon the type of oil extraction process used. Oil extraction by the classical method generally produces a more polluting effluent than that generated by the continuous method.

Table 1.1 Water characteristics of OMW (Olive Oil Mill Wastewater) obtained from conventional and continuous processes (Şengül, 1991)

Parameter	**OMW (Conventional P.)**	**OMW (Continuous P.)**
pH	4.5-5.0	4.7-5.2
Total Solids	% 12	%3
Total VSS	% 10.5	%2.6
Total Mineral SS	% 1.5	%0.4
Suspended Solids	%0.1	%0.9
COD (mg/l)	120.000-130.000	40.000
BOD (mg/l)	90.000-100.000	33.000
Sugar	%2-8	% 1.0
Total Nitrogen	%5-2	% 0.28
Organic Acids	% 0.5-1.0	-
Polyalcohols	% 1.0-1.5	% 1.0
Pektin, tannin etc.	% 1	% 0.37
Polyphenols	% 1.0-2.4	%0.5
Oil	% 0.03-10	% 0.5-2.3

Table 1.2. Comparative for the olive oil extraction processes (Improlive, 2000)

PRODUCTION PROCES	INPUT	AMOUNT OF INPUT	OUTPUT	AMOUNT OF OUTPUT
Traditional Pressing process	Olives Washing Water Energy	1000 kg 0.1 -0.12 m^3 40 - 63 kWh	Oil Solid Waste (c.25% water +6 % oil)OMW(c. 88% water)	c.200 kg c.400 kg c.600 kg
There - phase Decanter	Olives Washing Water For decanter Water to Polish the impure oil energy	1000 kg 0.1-0.12 m^3 0.5 - 1 m^3 c. 10 kg 90-117 kWh	Oil Solid Waste (c.50% Water + 4% oil) wastewater (c.94% water +1% oil)	c.200 kg c.500-600kg c. 1000-1200kg
Two - phase Decanter	Olives washing water Energy	1000 kg 0.1-0.12 m^3 <90-117kWh	Oil Solid Waste (c. 60 % water + 3 % oil)	200 kg 800 - 950 kg

Table 1.3. Composition of olives (Improlive, 2000)

CONSTITUENTS	PULP(%)	STONE(%)	SEED (%)
Water	50-60	9.3	30
Oil	15-30	0.7	27.3
Constituents containing nitrogen	2-5	3.4	10.2
Sugar	3-7.5	41	26.6
Cellulose	3-6	38	1.9
Minerals	1 - 2	4.1	1.5
Polyphenols (aromatic Substances)	2 -2.25	0.1	0.5-1
Others	-	3.4	24

Terminology of olive oil sector was given in Table 1.4.

Table 1.4. Terminology of olive oil sector related with wastes (Improlive, 2000)

Name	Description
Flesh, pulp (En)	Soft, fleshy part of the olive fruit
Stone/pit/husk (En)	Nut, hard part of oil
Kernel, seed (En)	Softer, inner part of nut
Alpeorujo, orujo de dos fases, alperujo (Sp)	Very wet solid waste from the two phase decanters
Orujo, orujo de tres fases (Sp) Prina (Gr/Tr) Pomace (It) Grignons (Fr) Husk (It/Tu)	Wet solid wastes from the three phase decanters and processes
Orujillo (Sp)	De-oiled orujo, de-oiled alpeorujo
Alpechin (Sp) Margine (Gr) Jamila (It)	Liquid waste from the three-phase decanters and processes
Alpechin-2 (Sp) Margine-2 (Gr) Jamila-2 (It)	Liquid fraction from secondary alpeorujo treatments (second decanting, repaso, etc.)

Key: En, English; Sp, Spanish; Gr, Greek; It, Italian; Tu, Tunisian; Tr, Turkish; Fr, French

1.1.3. Treatment and Utilization Methods of Olive Mill Wastewater

1.1.3.1 Physical Treatment of Olive Mill Wastewater

Olive mill wastewater (OMW) is characterized by high values of COD, BOD, and phenolic content. A series of treatment steps composed of settling, centrifugation, and filtration was consecutively used to condition OMW wastewater. The filtrate was then subjected to a post-treatment process, such as adsorption on activated clay. Al-Malah et al. (2000) used different concentrations of activated clay. Maximum adsorption capacity was achieved in less than 4 h. The maximum removal of phenols and organic matter was found about 81%, and 71%, respectively.

1.1.3.2 Chemical Treatment Methods of Olive Mill Wastewater

1.1.3.2.1 Chemical Precipitation. In a chemical precipitation study in Grease, lime precipitation was investigated. The sludge produced of the addition of 0.5-3% CaO reduced the concentration of suspended solids in the vegetation waters by 28% whereas 77 % of the oil and grease are distributed in the precipitate fraction. The COD as well as the toxic load in terms of phenolic compounds are not strongly affected by the addition of CaO (Lolos et al., 1994).

In another chemical treatment experiment, calcium hydroxide, magnesium sulfate and aluminum sulfate have been used. The values of COD have been determined after the treatment of OMW with the chemicals. The COD value dropped to 20-30 % with calcium hydroxide, when it was added until the pH of the waste reached 11 (Tsonis et al., 1989).

In chemical treatment studies of olive mill wastewater, different coagulants such as ferric chloride, aluminum chloride, ferrous sulfate, calcium hydroxide, and their combinations sometimes added by different anionic polyelectrolytes and sulfuric acid were tested by several researchers. For example, COD and suspended solid removal efficiencies of 50–90% were obtained in a chemical treatment study (Samsunlu, A. Et al., 1998).

Aktas et al. (2001) reported that after lime precipitation process, COD values of the wastewater samples could be reduced by 42-46 %. The average removal percentage of the other parameters are 29-47 % for total solids, 41-53 % for volatile solids, 74-37 % for reduced sugar, 95-96 % for oil-grease, 74-63 % for polyphenols, 38-32 % for volatile phenols and 61-80 % for nitrogenous compounds, respectively.

Centrifugation proved capable to fully separate suspended solids. Changes in the chemical environment had a considerable influence on the centrifugation yield At pH = 2 (acidification by H_2SO_4) the highest oil recovery (47 %) and a simultaneous high COD decrease (68 %) were achieved Furthermore, the sediment obtained from centrifugation at pH ^{m} 2 were more cohesive, with the lowest volume (15 %) and water content (80%) (Mitrakas et al., 1996, p 10).

1.1.3.2.1 *Chemical Oxidation.* Chemical oxidation using ozone or advanced oxidation technologies based on the generation of hydroxyl radical is a possible way to reduce COD and polyphenol content. In a study, chemical oxidation of olive mill wastewater using ozone alone and combined with hydrogen peroxide or UV radiation was studied. COD reduction of 80 or 90% was obtained with ozone doses between 3 and 4 g in the presence of 10 M initial hydrogen peroxide concentration or 254 nm UV radiation while total carbon concentration was between 40 and 60%. Both the aromatic content and colour was nearly disappearing with less than 0.5 g of ozone applied (Beltran et al., 1999).

1.1.3.3. Biological Treatment of Olive Mill Wastewater

1.1.3.3.1 Aerobic Biological Treatment of Olive Mill Wastewater. Olive mill wastewater is rich in phenols, inhibiting biodegradation and showing some degree of ecotoxicity. Therefore, in order to achieve aerobic biological treatment of olive mill wastewaters, the key is the elimination of the phenols. The major point is the decolorization, biodegradation and biotransformation of the phenolic compounds, abundant in the olive mill wastewaters, by different kinds of microorganisms. The process needs to be effective for degradation of both simple phenols and high molecular weight polyphenols. Either free or immobilized microorganisms can be used in continuous or batch processes (Demichelli&Bontoux, 1996).

The pretreatment of olive mill wastewater (OMW) with the white rot fungus Phanerochaete chrysosporium decreased the COD concentration. Experiments showed that the COD of OMW decreased from 105 g/L to 85 g/L after a natural sedimentation and removal of the insoluble compounds. OMW was allowed to settle and the supernatant would be used for the feeding of the aerobic fermentation (Gharsallah et al., 1999).

The presence of phenolic inhibitors requires the use of microorganisms able to utilize aromatic compounds. Garcia et al. (2000) studied the capability and kinetic behavior of several fungi to deal with such a waste reducing the phenol content of OMW. The removal of total phenols relative to the total organic load consumed, which might indicate a measure of the selectivity with microorganisms which remove phenols among other organic compounds present, indicates the sequence: Phanerochaete chrysosporium \ AspergilIus nigeT \ Aspergillus terreus.

1.1.3.3.1 Anaerobic Biological Treatment of Olive Mill Wastewater. Olive oil process is a seasonal production. After this production, huge amount of wastewater generates. Olive mill wastewaters also have high organic loading. All of these conditions make anaerobic treatment a very attractive option for the treatment of these wastewaters. The most important reason for preferring of anaerobic digestion as a treatment method are the feasibility to treat wastewaters which has high organic load and the techno-economical structure of the olive mill wastewater (Dalis et al., 1996).

Anaerobic treatment of olive mill wastewater was investigated in batch reactors. Olive mill residue was mixed with olive mill wastewater in certain ratios, olive mill residue was treated efficiently under anaerobic conditions. Anaerobic cultures needed an adaptation period of 15-25 days for olive mill residue with and without olive mill wastewater. Finally, 85-93 % COD removal efficiencies were achieved. Furthermore, treatment of 1 L olive mill wastewater by anaerobic methods resulted in production of 57.1 ± 1.5 L of methane gas which can be used for heating and electricity production (Ergüder et al., 2000, p 243).

An upflow anaerobic sludge blanket reactor (UASBR) was operated for about six months in laboratory scale in another study. The effects of pH, feed strength and hydraulic retention time on the performance of the anaerobic treatment process were determined. In the first part of the study, the reactor was operated with feed COD concentration from 5 000 to 19 000 mg/L and retention time of 1 day, giving organic loading rates from 5 to 18 kg COD/m^{3}d Soluble COD removal was around 75%

under these conditions. In the second part of the study, feed CODs were varied from 15 000 to 22 600 mg/L while retention time ranged from 0.83 to 2 days; soluble COD removal was around 70%. A methane conversation rate of 0.35 m^3 per kg COD removed was achieved during the study (Ubay&Oztiirk, 1997, p 287).

The anaerobic digestion of olive mill wastewater (OMW) can be carried out only on a diluted substrate because aromatic compounds and lipids are toxic for methanogenic bacteria. Agitation decreases methane formation in anaerobic digestion of unmodified OMW. Acidified OMW is less toxic than is raw waste. Pretreatment of OMW by fermentation with Aspergillus niger decreases the toxicity for methanogenic bacteria and facilitates anaerobic digestion. Moreover, agitation did not affect gas production (Hamdi, 1991, p 173).

Optimization of the sequence of microbial treatments (aerobic and anaerobic) is important so that a maximum level of degradation is achieved. Anaerobic digestion usually involves bacteria, while aerobic processes use fungi. In general, the aerobic process is undertaken firstly. In particular, high level of lignolitic enzymes can be obtained by the use of lignin-degrading fungi. In a study in Italy, phenol degradation levels between 66 and 94 % have been reported after a sequence combining two fungi and one bacterium (Demichelli&Bontoux, 1996, p 15).

The results of some anaerobic treatment studies of olive mill wastewater are given in Table 1.5.

Table 1.5 Studies on anaerobic treatment of olive mill wastewater

Retention Time	**Influent Concentration (g/L as COD)**	**Loading Rate (kg COD /m^3.day)**	**COD Removal Efficiency (%)**	**Reference**
1 day		5-18	75	Ubay&Oztürk, 1997
	10	5.25-18.65	70-80	Beccari et al.,

				1996
	8-27		85	Erguder et al.,2000
		3	65	Rozzi et al, 1988
18 hours	6	8	89	Boda et al., 1996
9 days	10-30	4.40	75	Hamdi, 1991
3.2 days	25	7.80	92	Martin et al., 1993

1.1.3.4. Irrigation Method

In some countries, irrigation method was applied such as Spain and Italy. In this method, controlled discharge onto ground is very important due to its high amount of phenolic substances. Some Italian scientists claimed that there is no side effect to use olive oil wastewater for irrigation of field which sunflowers and corns are grown, controlly. A study headed by Spanish scientists indicates increasing in the content of organic matter, total and dissolved nitrogen, phosphorus, salt and heavy metal in the field where olive oil mill wastewater is discharged with the flow rate of 1000 m3/he.yr. In the field that was fed less amount of olive oil mill wastewater such as 100 m^3/he.yr, biological degradation is occurred in this area. There is some legislation to prevent toxicity effect of olive oil processing wastewater for agricultural purposes. One of them is issued in Italy in 11th of November 1996 with the legislation number 547. This legislation limits discharging of olive oil mill wastewater to the agricultural area. According to this legislation 50-m^3 wastewater from conventional production system can be spread onto a hectare field per year, whereas this amount is 80 m^3 for continuous production processes (Official Newspaper of Republic of Italy, 1996).

1.1.3.5. Bardenpho Proceses

A scientist was undertaken to evaluate the efficiency of applying olive oil mill wastewater as a non-nitrogenous external carbon source in the second anoxic stage of a five stage modified Bardenpho system for nutrients removal in order to assure consistently very low concentrations of total nitrogen (well below 3 mg/L) in the treated effluent. Addition of olive oil mill wastewater was found acceptable only up to 50 mg sCOD of mill waste/L of wastewater fed to the system because at higher additions color problems in the treated effluent were encountered. The required dosage of olive oil mill wastewater was found to be in the range 4.6-5.4 mg sCOD/mg NO_3-N removed. At the same time higher removal of phosphorus was done. Addition of physico-chemically pretreated olive oil wastewater with lime to the second anoxic tank at a rate of 22-45 mg sCOD/L of municipal type wastewater fed (ratio of volume of the mill waste added to the volume of the municipal type wastewater fed 1:1000- 1:1200) resulted in a treated effluent with total nitrogen below 3 mg/l and soluble phosphorus well below 1 mg/L (Tsonis S.P, 1997).

1.1.3.5. Lagoons Method

One of the treatment methods is to collect wastewater in the lagoons and let them evaporate. Seasonally production of wastewater and this easy way, led to be preferred this method for long time. Disadvantages of the method are necessity of large fields and the distance between manufacturing plant and the field and also wastewater leakage into the ground water. As an alternative method, evaporation panels were used to treat wastewater with high impurities in Portugal. This technology is based on mass transfer between water film flow on the panels and airflow. An effective solid-liquid phase was observed on the panels that are located with the slope 30. Liquid was evaporated by natural factors such as high temperature and wind whereas solids were remained on the panels. It is noted that solid parts can be used as fertilizer (Duarte E.A., 1996).

1.1.3.6. Two Chemical Oxidation Processes (Fenton Reagent and Ozonation)

Beltran-Heredia J., et al., have investigated degradation of olive oil mill wastewater by means of two chemical oxidation processes (Fenton's reagent and ozonation) and their consecutive treatments with aerobic microorganisms have been studied. Fenton's reagent treatment moderately reduces COD and to a greater extent the polyphenolic compounds. Ozonation contributed to low conversion of COD and moderate reduction of polyphenols. The aerobic biological treatments degrade to values higher than 70 % and 90 % for COD and polyphenolic compounds, respectively. A kinetic study has been carried out in each process, determining the representative kinetic parameters of each model (Beltran-Heredia J., et al., 2001).

1.1.3.7. Vacuum Evaporator Distilation

LED Italia S.R.L has treated OMW by vacuum evaporation method. Before vacuum evaporation OMW stored in a tank and it is neutralized by sodium hydroxide in order to satisfy the weak acids which otherwise would distill together with the water part. Evaporation is carried out through a heat pump vacuum evaporator at the 5-kPa pressure and 380°C temperature operative conditions. The evaporator produces two streams: a distillate (continuously produced) and a concentrate (automatically, uncontinuously discharged). The distillation yield is about 90%. The distillate is sent to a storage tank. It is a colorless liquid, with 3000-4000 ppm COD content (LED Italia S.R.L,1998).

Another scientist studied on evaporation and distillation of olive oil mill wastewater. Evaporation and distillation processes have been often used to treat wastewater from olive oil mill effluent: the effluent COD reduction varies widely with the characteristics of the waste. In this work, they reported some distillation tests on centrifuged olive oil mill effluent to analyze the effect of storage time on the evaporation behavior of the waste. Experimental data showed that the ageing processes caused increasing of the concentrations of volatile compounds. According to a preliminary model such a behavior described in terms of a chemical and a biochemical reaction between a few pseudo compounds. In particular obtained results indicate that a long storage time must be avoided if olive oil mill wastewaters have to be treated by evaporation or distillation because the increase in the volatile pollutant concentration significantly reduces the equipment separation efficiency (Annesini MC., et al., 1991).

1.1.3.8. Yeast Growth Method

A few researchers have studied wastewater produced from the processing of olive oil, which had high chemical oxygen demand (COD) level (100-200 g/L), and the high level of other organic and inorganic compounds. They examined the growth of the yeast Yarrowia Lipolytica ATCC 20255 on olive mill wastewater. The results presented show that the yeast is capable of reducing the COD level by 80 % in 24 h, when grown in a 3.5-liter fermenter. This produces a useful biomass of 22.45 g/L and the enzyme lipase. During the process, most of the organic and inorganic substances are consumed (Scioli C., et al., 1997)

1.1.3.9. Electrochemical Method

Latest scientific research shows that olive oil wastewater, a toxic liquid associated with the production of olive oil, was treated by electrochemical method using Ti/Pt as anode and Stainless Steel 304 as cathode. In this technique, sodium chloride 4 % as an electrolyte was added to the wastewater and the mixture was passed through an electrolytic cell. Due to the strong oxidizing potential of the chemicals produced (chlorine oxygen, hydroxyl radicals and other oxidants) the organic pollutants were wet oxidized to carbon dioxide and water. A number of experiments were run in a batch, laboratory scale, and pilot plant. According to the results of this study, after 1 and 10 hours of electrolysis at 0.26 A/cm^2, 20 and 80.4 % reduced total COD, VSS were reduced by 1 and 98.7 %, and total phenolic compounds were reduced by 50 and 99.4 %. Respectively, the mean energy consumption was 1.273 kWh per kg of COD removed and 12.3 kWh per kg of COD removed for 1 and 10 h. These results strongly indicate that this electrolytic method of total oxidation of olive oil wastewater is not feasible. However it could be used as an oxidation pretreatment stage for detoxification of the wastewater (Israilides CJ., et al., 1997).

1.1.3.10. Enzymes

"One research project is geared at the production of lignolytic enzymes from the aerobic bioconversion of olive mill wastewater by white-rot fungi and the implementation of this process at industrial scale. The identification of some bio transformation products from olive mill wastewater has already been achieved." (Demichelli&Bontoux, 1996, p 18).

Olives are rich in simple and complex phenolic compounds with potential antioxidant properties, which may have a protective action on human health. During olive oil processing however, a large fraction of these phenols are lost in mill wastewater and poured into the Mediterranean environment. The aim of the proposed research was to improve the knowledge on the biological activities of antioxidant phenols, which was obtained from olive oil processing wastewater, and to define procedures for their extraction and valorization as health food supplements and/or natural food antioxidant. The other activity of this study was consisted in the setting up methods for the recovery of olive oil mill wastewater phenols, based on the use of resins for the adsorption of phenols directly from the wastewater. Investigator suggested the use of enzymes (pectinolytic, proteolytic etc.) to pretreat the wastewaters in order to remove macromolecules and minimize co-adsorption. Investigator also suggested the use of calcium acetate, which they found to be very effective in effective in precipitating macromolecules. From 1 liter of wastewaters, investigator stated, they have been able to recover 30 mg of ortho-diphenols (Universities Of Milan, Project EU n. CT973039, 1997-98-99-2000).

1.1.3.11. Land Treatment

Direct irrigation of soil with olive mill wastewater to save water and fertilizer has long been proposed normally less than 800 m^3/ha doses are used. Limitations of its use are due to the phytotoxic effect of olive mill wastewater that is caused by its polyphenol and salt contents. However, average doses of olive mill wastewater have beneficial effects such as increasing soil fertility, microbial population (especially N_2 fixing bacteria), improving the stability of the soil aggregates and in some instance crop yield. Land treatment of olive mill wastewater needs a stretch of flat land close to the mill, where the soil has an adequate porosity, permeability, and hydraulic conductivity, thus allowing infiltration of the olive mill wastewater, and avoiding stagnancy and runoff. Evaporation ponds caused serious negative effects such as odors, insect proliferation, leakages, infiltration and silting with sludge. However, the main problem with evaporation ponds is their insufficient capacity (Cabrera et al. 1996, p 217-218).

Some researchers have shown that the controlled spreading of raw wastewaters on agricultural land may have a positive effect on the olive plantations, as well as on other crops such as grape wine, corn, or sunflower. However, this practice is to be considered only after a thorough evaluation of all of the environmental impacts. For example, experiments with 1000 m^3 ha^{-1} per year or more of raw wastewaters laid on limestone containing Spanish soils have resulted in an increase in organic matter, total and soluble nitrogen, available phosphorus, and salts. But it also increased the mobility of heavy metals, and caused lixiviation of sodium and nitrate into deep soil, which are unwanted effects. On the other hand, when low wastewater volumes, such as of the order of 100 m^3 ha^{-1} per year are used, it is suggested that the soil could act as a biofilter for the treatment of olive oil wastewaters (Demicheli & Bontoux, 1996).

1.1.3.12. Evaporation—Hydrolysis --Oxidation (EHO)

A group of researchers collaborated to develop the evaporation-hydrolysis oxidation (EHO) method for the treatment of olive mill wastewaters. In this method, following preconcentrating step by evaporation, hydrolysis under controlled heat input and subsequent oxidation by air take place. EHO process is carried out in several steps:

- Removal of the sludge for utilization in pulp oil manufacturing and fuel production.
- Removal of residual fatty acids as much as possible by means of a ceramic ultrafiltration membrane.
- Removal of substances with phytotoxic effects from the wastewater.
- Recovery of materials that could be used for the production of industrial oils or as fuel.
- Collection and transportation of olive oil wastewaters and further treatment of the water obtained if necessary.

The EHO process is at the prototype development stage. The capital investment of a pilot plant treating olive oil wastewaters from a Greek district with an average olive oil production of 1400 tons per year was given as about 14million Euros with an annual operating cost of nearly 1 million Euros (Improlive, 2000).

1.1.3.13. Membrane Process

Membrane filtration such as reverse osmosis or ultrafiltration is applied on olive mill wastewaters after some pretreatment steps. In this case, wastewater is separated into two phases: treated wastewater (permeate), and concentrate (retentate). The concentrate can be sent to incineration or landfilled for final disposal (Improlive, 2000).

1.1.3.14. Composting

Composting is considered as one of the most suitable ways of disposing of unpleasant wastes and increasing the amount of organic matter that can be used to restore and preserve the environment. The composting method is controlled by bio-oxidative process. This process involves a heterogeneous organic substrate in the solid state, evolves by passing through a thermophilic phase and a temporary release of phytotoxin. After this process, CO_2, water vapour, mineral products and stabilized organic matter are produced. For this reason, composting is a practical and ecological way of recycling olive mill wastewater. It is possible to transform olive mill wastewater and olive residue added to a bulking agent into organic fertilizers or soil amenders with no phytotoxic effects (Monteoliva-Sanchez et al., 1996).

In a composting study, solid residue from olive oil extraction as bulking material and olive mill wastewater as continuously fed wastewater was used in demonstration plant. Composting temperature was controlled between 45 and 65° C by air supply and the wastewater addition was fed mainly in order to keep the moisture in the range of 45 to 60% and secondly to replace the carbon substrate. During 23 days of operation in the thermophilic region, the system was fed with 263 m^3 wastewater in total, which means an average rate of 11.4 m^s/day wastewater or 2.9 kg wastewater per kg solid residue. The total bioenergy production was estimated to be about 90 000 000 kcal (Vlyssides et al., 1996, p. 187).

1.1.3.15. Acid Derivates

Two linear compounds were isolated from the ethyl acetate extract of residues resulting from olive oil processing. These compounds were characterized by NMR and identified as 3-[l-(hydroxymethyl)-(E) 1-propenyl] glutaric acid and 3-[l-(formyl)-(E) 1-propenyl] glutaric acid Spectra of the products resulting from reduction and saponification confirmed the proposed structures. These products are structural components of a more complex molecule, oleuropein, which confers a bitter taste to olives (Gil et al., 1998, p 1311).

1.1.3.16. Animal Feed

In a research, the use of olive cake in livestock rations was investigated. The incorporation of up to 20% olive cake in fattening rations was reached. The effects of feeding olive cake on the visceral organ mass of lambs, and the estimation of olive cake digestibility by broilers were also studied (Demichelli&Bontoux, 1996, p 17).

1.1.3.17. Materials

The preparation of composite materials consisting of olive stones as filler and a thermoplastic or thermosetting polymer is an interesting approach. The focus of the investigation is being put on the relationship between the structure and properties of the materials as well as their prospective applications. Composite manufacturing is already operational at laboratory scale and is being studied at pilot plant scale (Demichelli&Bontoux, 1996, p 18).

1.2. Objective and Scope

This thesis is designed to investigate treatment alternatives for olive oil industry. Investigation of wastewater characteristics, examining the possible wastewater treatment methods that would result the best reduction in pollution content were the main aims of the thesis.

In the light of aforementioned studies on treatment of olive mill wastewaters, major objectives of this thesis can be summarized as fallows:

1) In physical treatment experiments; to select the optimal retention time and select the best physical treatment method.
2) In chemical treatment experiments; to select the best effective chemical coagulant, optimal dosages and optimal retention time.
3) In dewatering unit for olive cake's, to select the best effective methods.
4) To select the optimal area requirement and dimensions for drying for olive cakes.

Characterization study of olive mill wastewater and olive cakes were done and materials and methods, which were applied during experimental studies, are given in

Chapter II. Experimental studies, obtained results and conclusion part are given in Chapter III.

Different physical and chemical treatment studies were applied. In physical treatment part different physical treatment methods were done. Applied physical treatment studies were sedimentation experiment, filtration experiment and centrifugation experiments. Sedimentation experiments were done in two way which were small scale (laboratory scale) and large scale (pilot plant). Different retention times were applied for the sedimentation experiment. In filtration experiment cartridge filter and filter clothes which had a different pore diameter and made with polyester were used. In centrifugation experiments were done by using SED –Merlin TBX 506.

In chemical treatment part, different chemical type and dosages were done. To find the optimal dosages, jar tested were applied. Used chemicals were Ca $(OH)_2$, HCl and powdered zeolite. Ca $(OH)_2$ dosages were applied in two way; powdered $Ca(OH)_2$ and $Ca(OH)_2$ solution.

At the same time different olive cake samples which were taken in different olive oil factories. Investigated olive cakes were taken from classical pressing, 2-Phase and 3-Phase extraction manufactured olive factories. In this stage, olive cakes water contents were investigated. To dewatering the olive cakes and physical and chemical treatment sludge were dried in different conditions. These sludge were waited in normal air temperature at 25 ^{o}C in laboratory and at 103 ^{o}C in incubator. Under the light of these drying experiments, total dried area for the amount of unit sludge was calculated.

CHAPTER II
MATERIALS AND METHODS

2.1. Materials

Characterization and treat ability studies of olive mill waste water from olive oil processing industries were the main concept of this thesis. The samples were taken between February 2004 and March 2005 time period.

Different treatment methods, which are physical and chemical treatment methods were applied to the effluent samples to find the most suitable treatment methods. At the beginning and end of the treatment process COD, PH, Suspended Solid Matter, Total solid matter and Oil and Grease measurement were done.

All the experimental studies were carried out according to Standard Methods (APHA, AWWA, 1992).

All of experimental studies were based on the discharge limits according to the Water Pollution Control Regulation in Turkey. Waste water discharge Standards of Olive Oil Manufacturing Industry in Turkey are given Table 2.1.

Table 2.1 Wastewater discharge standards and sewerage of olive oil manufacturing Industry in Turkey

Parameter	Unit	Composite Sample (2h)	Composite Sample (24h)
COD	mg/L	250	230
Oil and Grease	mg/L	60	40
pH	_	6 - 9	6 - 9

2.1.1. Properties of the Using Chemical Materials

2.1.1.1. Lime

The lime is produced by Işık Chemical Industry**.** Molars of lime is M=36.5 g/mole. Purity of lime was 93.8 % and grain's largeness was +3.8 μ. Water content was 7 %.

2.1.1.2. Hydrochloric Acid (HCl)

Used Hydrochloric acid was known as technical hydrochloric acid. Molar of HCl was 36.5 g/mole and purity of HCL was 50 %.

2.1.1.3. Zeolite

Properties of used zeolite were given in Table 2.2.

Table 2.2 Chemical and Physical Properties of Zeolite

Name of material	Natural zeolite
Chemical name	Hydrated aluminosilicate of alkali metals and metals of alkali earths
Mineral form	Clinoptilolite
Chemical type	Molecular sieve
Empiric formula	$(Ca, K_2, Na_2, Mg)_4Al_8Si_{40}O_{96} .24H_2O$

Table 2.2 (Continue)

Chemical Compositions				
SiO_2	65.0-71.3%		Co	< 3 ppm
Al_2O_3	11.5-13.1%		Cu	3 ppm
CaO	2.7- 5.2%		Sn	< 1 ppm
K_2O	2.2- 3.4%		Pb	10 ppm
Fe_2O_3	0.7- 1.9%		As	0.8 ppm
MgO	0.6-1.2%		Cd	< 0.1 ppm
Na_2O	0.2-1.3%		Hg	0.02 ppm

SELECTIVITY				
$Cs^+ > NH_4^+ > Pb_2^+ > K^+ > Na^+ > Ca_2^+ > Mg_2^+ > Ba_2^+ > Cu_2^+ > Zn^{2+}$				
TiO_2	0.1-0.3%		Si/Al	4.8-5.4

ION EXCHANGE PROPERTIES		
Partial exchange capacity		min. 0.70 mól/kg
Total exchange capacity		1.2 – 1.5 mól/kg
Sorption of steam by dehydrated rock	at relative humidity of 52%	7.5 – 8.5g H_2O/100g
	at relative humidity of 98%	13.5 – 14.5g H_2O/100g

Table 2.2 (Continue)

PHYSICAL-MECHANICAL DATA				
Softening temperature	1 260 ^oC		Porosity	24-32%
Melting temperature	1 340 ^oC		Effective diameter of pores	0,4 nm (4 angstrom)
Pour point	1 420 ^oC		Relative density	70%
Compression strength	33 MPa		Whiteness	70%
Specific weight	2 200 - 2 440 kg/m^3		Mohs hardness	1.5 – 2.5
Volume weight	1 600 - 1 800 kg/m^3		Grindability according to VTI	kVTI = 1.628
Appearance and odour	grey-green – without odour			
DATA ON REACTIVITY				
Stability against acids	79.50%		Hazardous decomposition	none
Thermal stability	do 400 ^oC		Hazardous polymerisation	does not occur
Solubility in water	0			

2.2 Methods

Physical and chemical treatment experiments were applied to the raw olive oil industry wastewater. At the same time different physical and chemical treatment methods were applied consequently. In second part of this thesis olive oil cakes which are taken in 2 different olive oil factory (2 phase and 3 phase extraction processing) physical properties were investigated. Olive oil cakes water content and water give capacity were investigated.

2.2.1. Physical Treatability Experiments

The applied physical treatments methods were sedimentation, filtration and centrifugation. At sedimentation method, the experiments were done in laboratory scale and large scale (settling column). Large scale settling experiment equipment was located Olive Oil Factory in Bornova. At large scale experiment part different retention times were tried. In laboratory scale parts of settling experiments less retention times were tried. Other physical treatment method was filtration experiment. In filtration parts, samples were filtrated by different filter equipment which has different pore diameters. Another physical treatment method was centrifugation. In centrifugation parts different centrifugation velocities were applied on the samples.

2.2.1.1. Sedimentation Experiments

2.2.1.1.1 Sedimentation experiment (Large Scale). In sedimentation part of this thesis sedimentation column was designed and installed. This column was located in Bornova. Figure of this sedimentation column are given in 2.1.

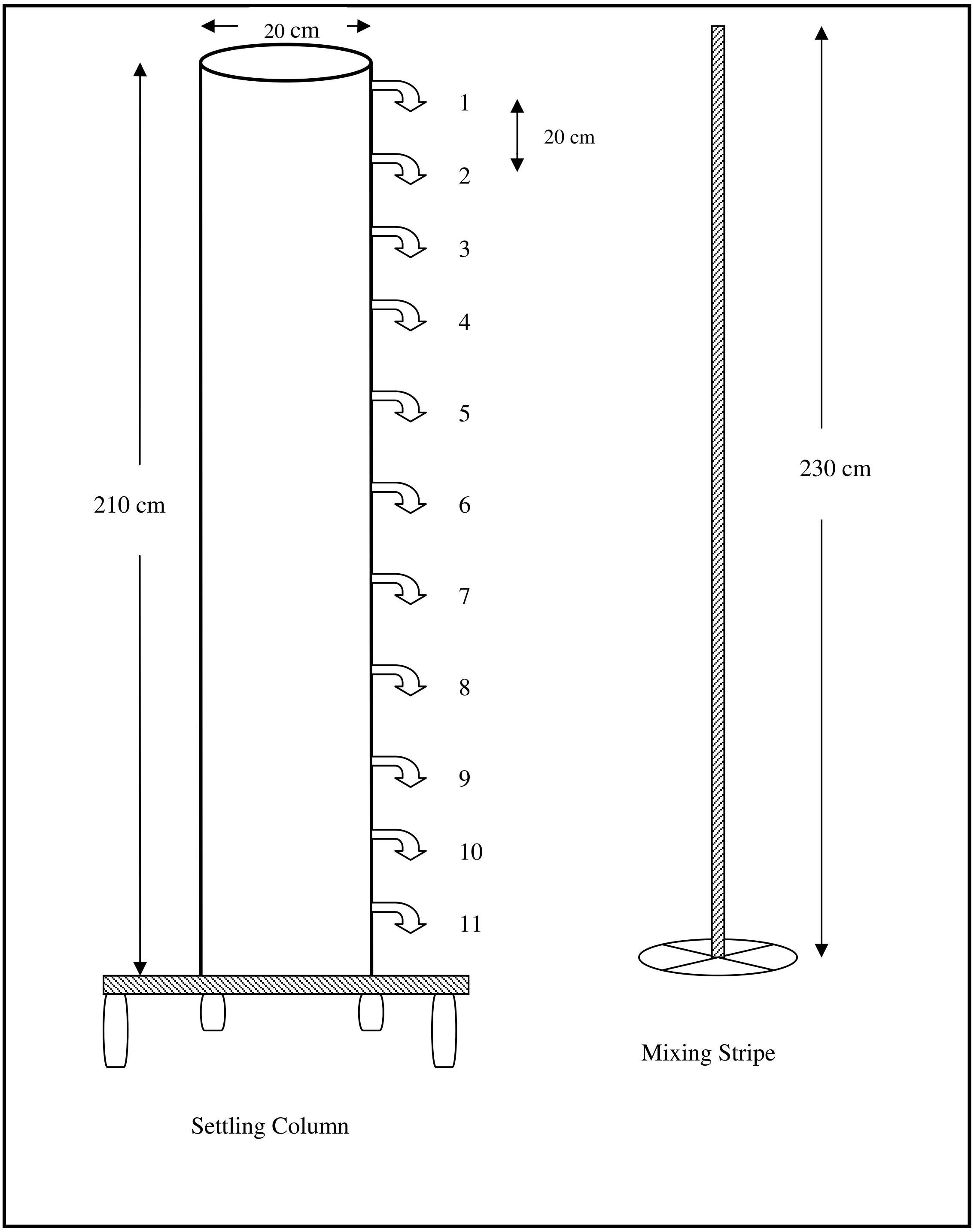

Figure 2.1 Sedimentation column (Located in Bornova)

The sedimentation column was made of stainless crom-nickel steel. It has a cylindrical shape. The diameter of column is 20 cm and the height of the column is 210 cm. Volume of the column is 66 liters. There is a 11 valves located on the settling column with 20 cm distance. This column was located in Bornova since February 2004.

The working principle of this sedimentation column is so; firstly sample filled drum which has an 80 liter of volume with diver pump. In this drum samples were mixed and homogenized. 500 ml sample was taken from this drum to investigate the beginning pollution characteristic of sample. After this procedure sedimentation column was filled with this homogeny samples. After filling part sample was mixed with a mixing stripe which is made of stainless steel. Sample was mixed 10 – 15 times up and down after filling procedure. After this sample was waited sedimentation procedure. In these experiments 1 day, 1 week and 2 weeks Retention times were applied.

Sample which has taken from different valves of this column was analyzed. Total Solid Matter and Suspended solid matter concentrations of samples were measured.

2.2.1.1.2. Sedimentation Experiment (Laboratory Scale). These sedimentation experiments were done at laboratory conditions with small scales (liters degree). Beakers which has a 1 liter volume were used this experiments. At the same time imhoff cone was used to see how much sludge was settled and how much supernatant was constituted. Firstly glasses were filled 1 liter of sample and mixture with a stirring unit with slow mixing at 45 rpm and rapid mixing with 225 rpm. After mixing procedure, imhoff cone was filled with 1 liter of homogenized sample and settling was observed. Using imhoff cone was given better and sensitive results than 1 liter of beakers. Retention times were taken with 1 hour, 3 hour and 1 day. In this part, SS, COD and pH analysis were measured.

2.2.1.2 Filtration Experiment with Cartridge Filter and Filter Clothes

In filtration experiment filter clothes which have a different pore diameter were used. Before the treatment with cartage filter mechanism, pH of sample was decreased to 2 and after this procedure, pH increased to 4 for the filtration treatment. When the pH was decreased to 2, there're an acid cracking was done which is a chemical treatment method. After acid cracking, in order to not damage to the filter clothes and cartage filter, pH was increased to 4. Before the filter clothes mechanism, Cartridge filter mechanism was used. Cartridge Filter has a 25 µm. pore diameter. After cartridge filter, sample was gone through filter cloths and filtered from four different filter cloths with different permeability. They are numbered as Number I, Number II, Number III and Number IV, respectively. Air and water permeability of filter clothes were given in Table 2.3. In Figure 2.2 stage of filtration is given.

Table 2.3 Air and water permeability of four different filter clothes

Filter Cloth Number	**Air Permeability (l/dm2.h)**	**Water Permeability (l/m2.h)**
Filter Cloth I	15.0	1 190
Filter Cloth II	12.0	952
Filter Cloth III	7.2	571
Filter Cloth IV	3.2	254

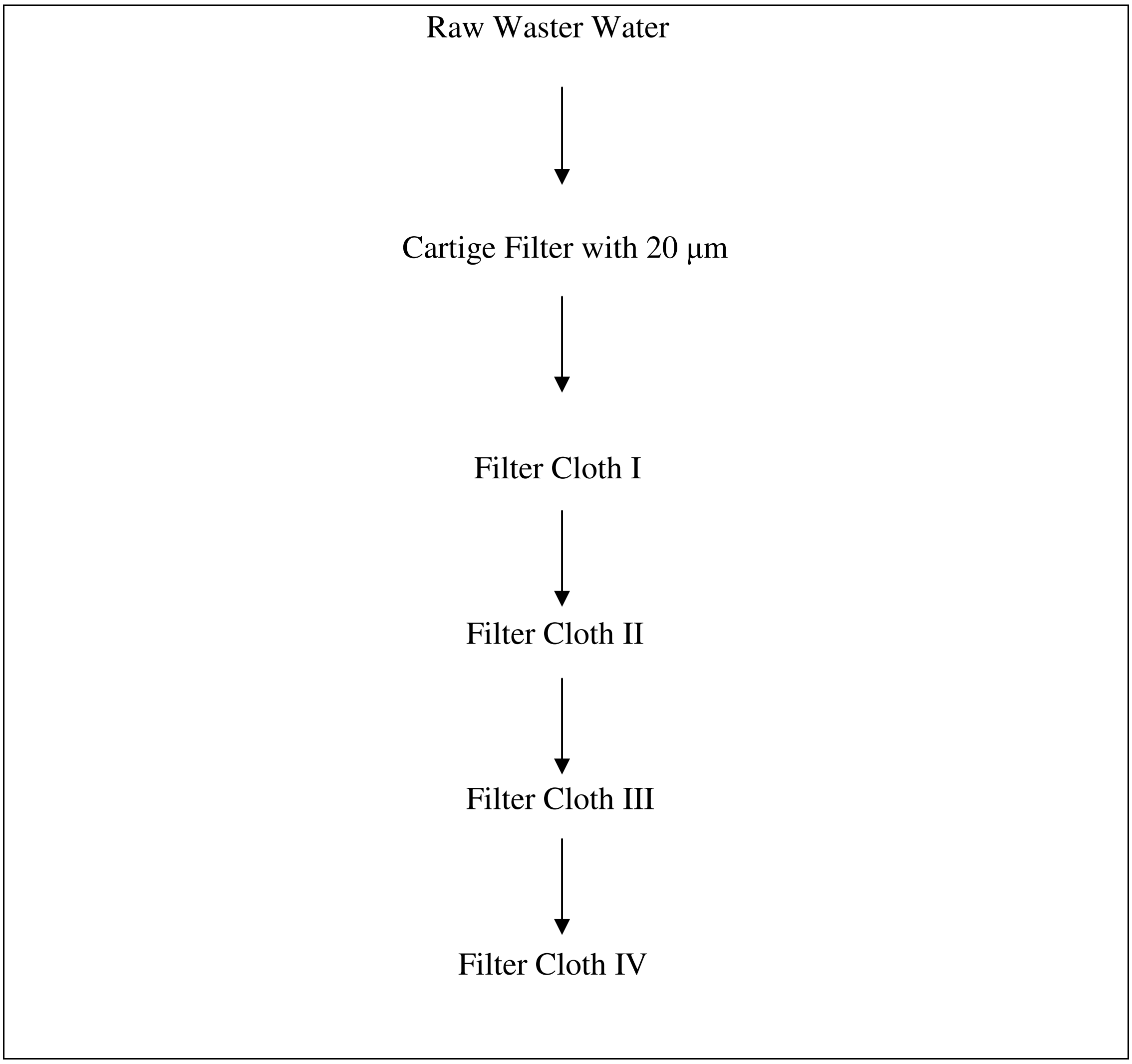

Figure 2.2 Stages of filtration with cartridge filter and filter cloths

2.2.1.3. Centrifugation experiment

These experiments were done in a laboratory scale in Dokuz Eylül University Wastewater Laboratory. Centrifugation is used for the dewatering of olive oil mill wastewater. Centrifugation experiments were done by using SED –Merlin TBX 506.

Different chemical treatment methods were applied after centrifugation process. Different combinations were constituted. These combinations were given in Figure 2.3.

Raw olive oil mill wastewater	→	Chemical treatment Process with $Ca(OH)_2$	→	Centrifugation
Raw olive oil mill wastewater	→	Chemical treatment Process with HCl	→	Centrifugation
Raw olive oil mill wastewater	→	Chemical treatment Process with powdered zeolite	→	Centrifugation

Figure 2.3 Applied centrifugation combinations

Centrifugation proved capable to fully separate suspended solids. Changes in the chemical environment had a considerable influence on the centrifugation yield. At pH = 2 (acidification by H_2SO_4) the highest oil recovery (47 %) and a simultaneous high COD decrease (68 %) were achieved. Furthermore, the sediment obtained from centrifugation at pH = 2 were more cohesive, with the lowest volume (15 %) and water content (80 %) (Mitrakas et al, 1996, p 10).

For separating liquids of different density, thickening slurries, or removing solids, the centrifugation process is widely used in industry. The process is applicable to the dewatering to the dewatering of waste water sludge and has been widely used in both United States and Europe (Metcalf & Eddy, 2003 P: 1559).

2.2.2. Chemical Treatability Experiments

Chemical treatability experiments were carried out on raw wastewater. Coagulation and flocculation treatment methods with different coagulants were applied. HCl, $Ca(OH)_2$, powdered zeolite were used for coagulation and flocculation to treat the raw waste water. Jar tests were done to determine the optimal dose of chemicals.

Applied, chemical treatment combinations were given below;

a) Treatment with HCl
b) Treatment with $Ca(OH)_2$
c) Treatment with powdered zeolite
d) Treatment with $Ca(OH)_2$ + powdered zeolite
e) Treatment with HCl + powdered zeolite
f) Treatment with HCl + $Ca(OH)_2$ + powdered zeolite

Application of chemical coagulation process that; the chemical destabilization of particles in wastewater to bring out their aggregation during perikinetic and Orthokinetic flocculation (Metcalf & Eddy, 2003 P: 477).

2.2.2.1. Chemical treatment with $Ca(OH)_2$

In this study, beakers filled with raw olive oil mill wastewater while sample was rapid mixed at 200 rpm for 5 minutes and slow mixed at 45 rpm for 15 minutes, and different Ca $(OH)_2$ dosages were applied. Ca $(OH)_2$ was applied with two way; these are powdered Ca $(OH)_2$ and Ca $(OH)_2$ solution.

Pretreatment (before dewatering) of liquid sludge with lime has been used for either the direct application of liquid sludge to land, or combining benefits of sludge conditioning and stabilization prior to dewatering. In the former case, large quantities of liquid sludge have to be transported to land disposal sites, which limits utilization of lime pretreatment of sludge to small treatment plants . When pretreatment is used prior to dewatering, dewatering has been accomplished by a pressure-type filter press. Lime pretreatment is seldom used with centrifuges or belt-filter presses because of abrasive wear and scaling problems (Metcalf & Eddy, 2003 P: 1502).

2.2.2.2. Chemical Treatment with HCl (Acid cracking)

In this study, beakers filled with raw olive oil mill wastewater while sample was rapid mixed at 200 rpm for 5 minutes and slow mixed at 45 rpm for 15 minutes and different HCl dosages were applied. The aim of this experiment was to get more sludge layer forming and max COD efficiency. In other words, the aim of this experiment was to set more particles in this manner more sludge volume was formed. Supernatant was used for the COD and SS analysis.

2.2.2.3. Zeolite Adding

Zeolite is an adsorbant and coagulant material and using vide variety of treatment stages for odour removal, oil separation, absorption etc. In this experimental study, the aim of zeolite was applied to make use of solid-liquid separation ability. Powdered zeolite was used for this experiment.

In this study beakers filled with raw OMW and different zeolite dosages were applied, sample while sample was rapid mixed at 200 rpm for 5 minutes and slow mixed at 45 rpm for 15 minutes. Mixed sample was settled for different periods. Liquid phase was being located at the upper part of the sample and solid part was settled to the bottom of the sample. Supernatant was taken from the upper part of the mixture and analyzed.

2.3. Sampling

There are a lot of factors were effected to the olive oil production. These are using technology (classical pressing methods, 2 and 3 phase extraction methods), age of olive tree, season and the weather conditions. Olive oil industry has not a continuously production period. Harvesting of the olive oil is doing one time in two year.

Therefore olive oil mill wastewater characteristic is very different from year to year. In this study, different samplings which have taken for a two years along were investigated.

The olive oil factory was located at the corner of Ege University crossroads in Bornova /İZMİR. This factory was processed with 3 phase extraction methods.

The experimental studies were carried out as soon as possible when the samples were taken from the industries. However when it was necessary to keep the wastewater, it was kept in refrigerator at 4 ^{o}C and no pH adjustment was made to keep the samples for a long time, since pH value of samples was between 4 and 5.

2.4. Analytical Methods

COD, pH, Color, oil and grease, suspended solid measurements were done on the influent samples.

All experimental studies were carried out according to Standard Methods (APHA, AWWA, 1992)

2.4.1. COD Analysis

COD values were determined by using Dichromate Reflux Method according to APHA Standard Methods. Olive oil mill wastewater has got a high COD values, therefore samples were 1/50 or 1/100 before COD measurement. Firstly 5 ml H_2SO_4 was added into the diluted samples, 0,5 g mercury sulphate was poured into COD bottles, and then 10 ml potassium dichromate and 25 ml sulphiric acid were added. COD bottles were heated for 2 hours and after the heating procedure cooled to room temperature. Then 80 ml distillated water and ferroin indicator was added into the solution. The last step was titration with ferrous ammonium sulphate (FAS). COD concentration was calculated by using fallowing equation.

$$\text{COD (mg/L)} = \frac{\text{(Used FAS for sample–used FAS for blank) x8000xdilution fac.xN}}{\text{ml sample}}$$

* N is normality's of ferrous ammonium sulphate. This value is known as 0, 1 N.

2.4.2. pH Analysis

pH measurement was done by using 890 MD pH METER.

2.4.3. Suspended Solid Matter Analysis

This method was based on the gravity theory. It was applied by gravimetric method in 0, 45 µm pore diameter filter paper model, according to 2450 D of Standard Methods. In this method, biomass in suspension was determined by filtering the sample through milipore filters (0, 45 µm) and drying until constant weight in an incubator at 105 ^{0}C . Immobilized biomass concentration on support particles were determined by washing cells from certain number of particles (about 200) into top water and determined cell concentration after filtration and drying of filter paper.

Calculations were made by using the following equation:

$$M_{SS} = \frac{(A - B) \times 1000}{V} \quad \text{x Dilution factor}$$

Where, A is weigh of filter residue, (mg); B is weight of filter, (mg) and V is volume of sample

2.4.4. Total Solid Matter Analysis

The definition of Total Solids is so; the residue remaining after a wastewater sample has been evaporated and dried at a specified temperature (103 – 105 ^{0}C)
For this experiment porcelain cup were used. Firstly these cups were weighted and tare of cups were noted. After samples were put in the porcelain cup and heated for a time periods at 105^{0}C. Waited to all water evaporated from the cup. After then, cooled in desiccators and weighted.

Calculations were made by using the following equation:

$$M_{TS} = \frac{(A - B) \times 1000}{V}$$

Where, A is weigh of cup and sample, B is tare of cup and V is volume of sample.

2.4.5. Oil and Grease Analysis

It was applied by partition gravimetric method according to 5520-B of Standard Methods (APHA, AWWA, 1992).

2.4.6. Color Analysis

The measurement of color in emulsion was performed using a HACH 2000 colorimeter.

CHAPTER THREE
RESULTS AND DISCUSSIONS

3.1. Wastewater Characteristic

All of the waste water samples were taken from olive oil factory which was located at the corner of Ege University crossroads in Bornova /İZMİR. This factory was processed with 3 phase extraction methods. All samples were taken to the different times in two years at the seasons of harvesting. Each of the samples has been analyzed and wastewater characteristics of these samples are presented in Table 3.1.

Table.3.1. Characteristics of all raw wastewater samples (3 Phase centrifuge extraction)

Sample Name	Sample Dates	pH	COD (mg/L)	TSM (mg/L)	SS (mg/L)	Oil And Grease (mg/L)	Color (Pt-Co)
Sample I	19 February 2004	4. 80	87 600	59295	2 748	N.M	41.500
Sample II	1 March 2004	4. 60	76 400	48760	N.M	N.M	N.M
Sample III	5 April 2004	4. 40	72 300	52335	N.M.	N.M	N.M
Sample IV	29 November 2004	5. 27	124 000	N.M.	74 000	N.M	88 500
Sample V	3 January 2005	5. 14	136 000	N.M.	14 840	N.M	N.M
Sample VI	7 February 2005	4. 90	120 000	N.M.	18 600	2 870	N.M
Sample VII	4 March 2005	4. 96	96 000	N.M	N.M	N.M	N.M

N.M.: Not Measurered

COD concentration of olive oil mill samples which were used in experimental studies changed from 72 400 mg/L to 136 000 mg/L. In spite of all samples were belonged the same olive oil factory; COD values were showed differences between each samples. Olive oil mill wastewater characteristic were effected from Depending on olive tree varieties and seasons of harvest. Monthly COD changing were showed in Table 3.1, clearly.

Average value of COD concentration was about 102 000 mg/L. pH values of samples were changed from 4,4 to 5,27. In the light of the literature survey and this thesis we could say that; olive oil mill wastewater had a high COD concentration values and low pH values.

Suspended solid and total solid matter concentration of wastewater were also high. All samples had a dark brown color.

3.2. Treatability Experiments

Treatability experiments were done in two parts; Physical and chemical treatability experiments.

3.2.1. Physical Treatability Experiments

Sedimentation, filtration and centrifugation methods were supported to other treatment methods which were chemical and biological treatments. The goal of physical treatment method was to find the optimal retention time, to get more supernatant. In this part, sedimentation, filtration and centrifugation methods were applied by oneself and one after another.

3.2.1.1. Effect of Sedimentation

Sedimentation process was applied with two ways; laboratory scale and large scale. In large scale experiments, sedimentation column which were installed and located in olive oil factory at Bornova were used. In laboratory scale experiments part, were done at Dokuz Eylül University Wastewater Laboratory.

In large scale experiments 1 day, 1 week, 2 weeks retention times were applied and at laboratory scale experiments small retention times (1 hour, 3 hours and 1 day) were tried.

3.2.1.1.1 Laboratory scale sedimentation experiment with different Retention Time. To laboratory scale settling experiments, 1 liter of beakers and imhoff cones were used. No chemical materials were added. Sample I were used for this experiments. Beakers were filled with 1 liter of sample while sample was rapid mixed at 200 rpm for 5 minutes and slow mixed at 45 rpm for 15 minutes. After mixing, to see more clearly settling and solid-liquid separation, homogenized sample were poured in imhoff cone and waiting one, three hours and 1 day. 1 ml sample were taken and diluted with 1/50 diluted rate to COD measurements and 1/20 diluted to SS measurements. Results are given in Table 3.2, 3.3

Table 3.2 Effect of sedimentation on COD removal at laboratory conditions with different retention times

	pH	COD Concentration (mg/L)	COD Removal Efficiency (%)
Raw Wastewater	4.8	87 600	-
Supernatant with 1 hour	-	72 000	18
Supernatant with 3 hour	-	68 000	22
Supernatant with 1 day	4.9	64 000	27

Table 3.3 Effect of sedimentation on SS removal at laboratory conditions with different retention times

	SS Concentration (mg/L)	SS Removal Efficiency (%)
Raw Wastewater	2 728	-
Supernatant with 1 hour	2 100	23
Supernatant with 3 hour	2 073	24
Supernatant with 1 day	1 855	32

COD and SS removal efficiency were as same as both of retention time 1 and 3 hours and 1 day later reduction of SS was 32 %. If we were think that economy is important factor to treatment plant, we selected the less retention time.

3.2.1.1.2 Large scale sedimentation experiments with 1 Day Retention Time. As a first experiment as a large scale experiment, Sample I were used. Firstly, 80 liter of barrel were filled with olive oil mill wastewater and homogenized. After this procedure, homogenized wastewater filled in sedimentation column which were had a 20 cm diameter, 2 meter height and 66 liter of volume. The column was given in Figure 2.1. After the filling procedure, wastewater which was filled in column was mixed with a mixing stripe as a 5 minutes slow and 15 minutes rapid. But in this mixing were done not automatic or mechanical system, mixing were done with hand force as up and down, therefore, mixing velocities were not measured.

After the mixing procedure, sampling was waited for a one day and after this period column was emptied from first valve to last valve which were located on column respectively. Firstly emptying sample were filled in a transparent bottle and looked for a physical seems of the samples and then decided, if sample supernatant or sludge part of total samples. If taken sample at valves were seemed clearly then we put in clear water barrel, if not we put it in sludge barrel. After this separation procedure, we were get 43 liters of supernatant and 23 liters of sludge with 65 %, 35 % respectively.

Upper valves named as a valve I (one) and another valves named with this order from top to bottom. Samples were taken each of the valves and analyzed, the result are given in Table 3.4, 3.5, 3.6.

In Table 3.4 raw wastewater, supernatant and sludge samples were analyzed.

Table 3.4 Effect of sedimentation on COD removal with 1day retention time

	pH	COD Concentration (mg/L)	COD Removal Efficiency (%)
Raw Wastewater	4.8	87 600	-
Supernatant	5.1	69 400	21
Sludge Part	4.2	85 200	3

As seem in Table 3.4, 21 % COD removal efficiency were achieved at supernatant. At sludge part 3 % COD removal efficiency were achieved but, after the treatment, sludge part could be treated with sludge unit therefore, low COD removal efficiency value was undervalued. One day later, pH value were increased 4.8 to 5.1 meanwhile in sludge part pH decreased 4,8 to 4,2. Sludge part were had more acidic condition.

Table.3.5. Effect of sedimentation on SS removal with 1day retention time

	SS Concentration (mg/L)	SS Removal Efficiency (%)
Raw Wastewater	2728	-
Supernatant	2128	28
Sludge Part	2890	-

At SS measurements, SS concentration of supernatant decreased from 2728 mg/L to 2128 mg/L with a 28 % SS removal efficiency. At sludge part SS increased 2728 mg/L to 2890 mg/L.

Table.3.6. Effects of sedimentation on total solid matter (TSM) removal with 1 day retention time

	TSM Concentration (mg/L)	**TSM Removal Efficiency (%)**
Raw Wastewater	59 295	-
Supernatant	45 490	23
Sludge Part	81830	-

In TSM measurement, TSM concentration of supernatant were decreased 59 295 mg/L to 45 490 mg/L with a 23 % removal efficiency. After one day waiting period, density of sludge was increased and it was more viscose than raw wastewater.

At the same time sample which were taken from each of the valves were analyzed and results are given in Table 3.7, and 3.8.

In Table 3.7 SS measurement are given. This table was showed SS concentration chancing in sedimentation column. Taken samples were mixed two by two, valves 1 to valve 11.

Table.3.7. SS concentrations chancing in sedimentation column with 1 day retention time

Mixed Valves Names	**SS concentration (mg/L)**
Valves 1 and 2	2 734
Valves 3 and 4	2 780
Valves 5 and 6	2 798
Valves 7 and 8	2 820
Valves 9,10 and 11	2 890

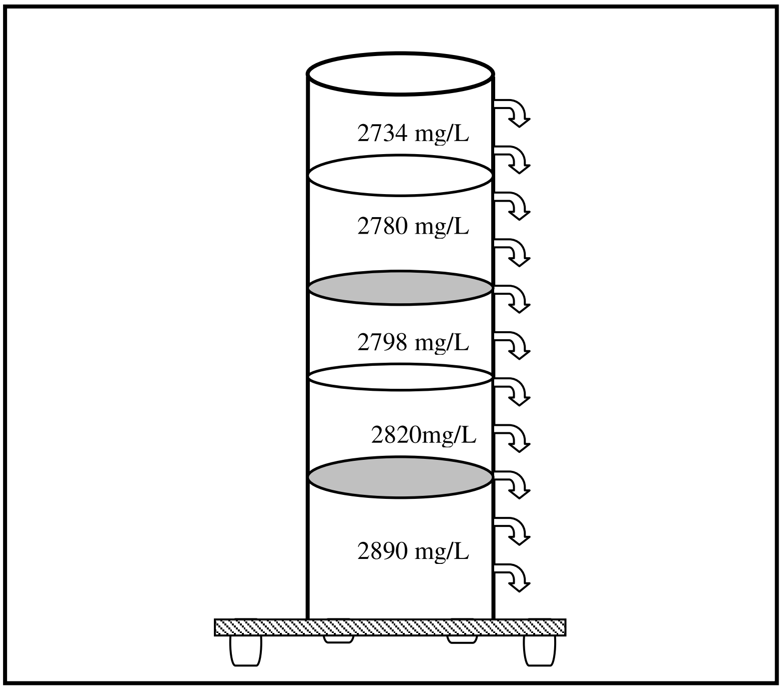

Figure 3.1. SS concentrations chancing in sedimentation column with 1 day retention time

In Table 3.8, TSM measurement are given. This table was showed TSM concentration chancing in sedimentation column. Taken samples were mixed two by two, valves 1 to valve 11.

Table 3.8 TSM concentrations chancing in sedimentation column with 1 day retention time

Mixed Valves Names	SS concentration (mg/L)
Valves 1 and 2	48 400
Valves 3 and 4	52 335
Valves 5 and 6	53 050
Valves 7 and 8	57 600
Valves 9,10 and 11	72 760

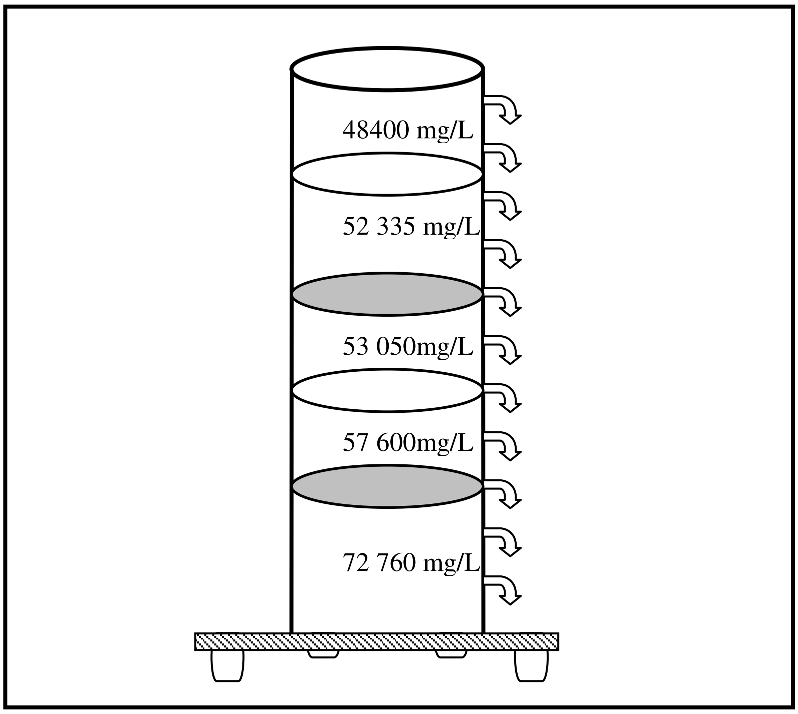

Figure 3.2 TSM Concentrations chancing in sedimentation column with 1 day retention time

3.2.1.1.3 Large scale sedimentation experiment with 1 Week Retention Time. In this experiment, retention times were taken one week. For this experiment Sample II were used. At the end of the one week retention time, 36 liter of supernatant and 30 liter of sludge with 55%, 45% respectively were observed.

At the end of the 1 week, beginning COD concentration were decreased 76 400 mg/L 52 400 mg/L and TSM were decreased with 48 760 mg/L to 36 640 mg/L. Results are given in Table 3.9 and 3.10, 32 % COD removal efficiency and 25 % TSM removal efficiency was achieved.

Table 3.9 Effects of sedimentation on COD removal with one week retention time

	pH	**COD Concentration (mg/L)**	**COD Removal Efficiency (%)**
Raw Wastewater	4.6	76 400	-
Supernatant	5.3	52 400	32
Sludge Part	4.4	71 700	6

Table 3.10 Effects of sedimentation on TSM removal with one week retention time

	TSM Concentration (mg/L)	**TSM Removal Efficiency (%)**
Raw Wastewater	48 760	-
Supernatant	36 640	25
Sludge Part	68 875	-

At the same time, TSM measurements which were taken each of valves were done. Results are given in Table 3.11.

Table 3.11 TSM concentrations chancing in sedimentation column with 1 week retention time

Names of valves	**TSM Concentration (mg/L)**
1 and 2	36 640
3	38 940
4	39 120
5	48 355
6	49 340
7	60 250
8	65 430
9	67 640
10	68 640
11	68 875

At Figure 3.3 TSM concentration chancing in sedimentation column were showed.

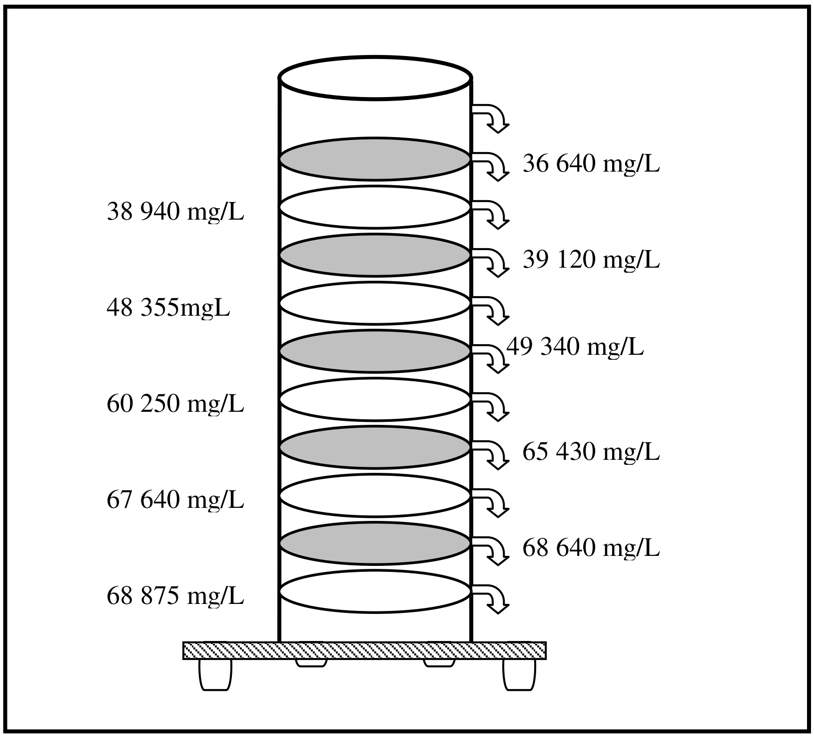

Figure 3.3 TSM concentrations chancing in sedimentation column with 1 week retention time

As results, at the end of the one week retention time, solid and liquid phase separations were observed. Observed separation were showed that, if retention time were increasing, then solid and liquid phase separation were more effected than less retention time, but more retention time needed more storage areas, therefore we must find the optimal retention time for the COD removal efficiency.

3.2.1.1.4 Large scale sedimentation experiment with 2 Weeks Retention Time. In this experiments 2 weeks retention times were applied. Sample III was used for this experiment. Aim of this experiments to find the most suitable retention time. At the end of the two weeks retention time, 33 liter of supernatant and 33 liters of sludge with % 50, % 50 respectively were observed. At the end of the 2 weeks, beginning COD concentration were decreased 72 300 mg/L to 42 300 mg/L and TSM were decreased with 52 335 mg/L to 31 320 mg/L. Results are given in Table 3.12 and 3.13.

Table.3.12 Effects of sedimentation on COD removal with two weeks retention time

	pH	COD Concentration (mg/L)	COD Removal Efficiency (%)
Raw Wastewater	4.4	72 300	-
Supernatant	4.9	42 300	42
Sludge Part	4.2	61 400	15

In sludge part, COD reduction was reached 15 %. Observed solid – liquid separation were more clearly then the other retention times. In Table 3.11 it was showed. TSM removal efficiency was achieved to the 34 %.

COD and TSM removal efficiency were effective increasing to the retention time with positive way. These are acceptable reduction efficiency value for the pre treatment.

Table 3.13. Effects of sedimentation on TSM removal with two week retention time

	TSM Concentration (mg/L)	TSM Removal Efficiency (%)
Raw Wastewater	52 335	-
Supernatant	34 740	34
Sludge Part	72 760	-

At Figure 3.4 valves were grouped and TSM chancing in sedimentation column were showed that in this figure.

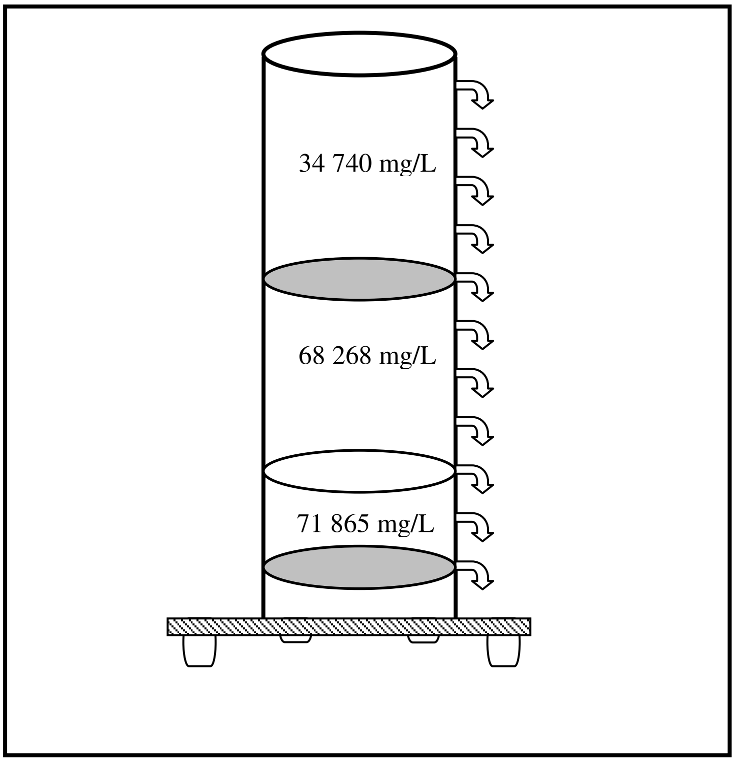

Figure 3.4 TSM concentrations chancing in sedimentation column with 2 week retention time

3.2.1.2 Effect of Filtration

Filtration was applied in two parts. These were filtration of cartridge filter different filter clothes and filtration with filter paper. The aims of filtration were COD, SS and oil-Grease optimal reduction. In filtration experiments, Sample VI was used.

3.2.1.2.1 Effect of Filtration with Cartridge Filter and Filter Clothes. In this part, the sample which was pre treated with cartridge filter was filtered from filter clothes which were installed in membrane cell one after the other. Filter clothes were made of polyester. These filter clothes were sold as air permeability in market. The air and water permeability value of these filter clothes were given in Table 3.14.

Table 3.14 Air and water permeability used filter clothes in filtration experiments

Filter Clothes	Air Permeability(L/dm^2.h)	Water permeability(L/m^2.h)
Filter Clothes I	15	1 190
Filter Clothes II	12	952
Filter Clothes III	7.2	571
Filter Clothes IV	3.2	254

20 liter of raw olive oil waste water sample were filled in feeding tank and filtrated with cartridge filter which has a 25 µm. pore diameter. Cartridge filter filtration was done with 1 hour time period. Flow rate of cartridge filter were 0, 4 L/s. After the filtration 1 - 2 mm solid matter accumulation were observed on cartridge filter. At the end of the filtration, maximum pollution reduction yield were observed in suspended solid matter parameter. Total removal efficiency was 49,9 %. Although total removal efficiency of COD was 22.5 %, oil and grease removal efficiency were few value. After the filtration with cartridge filter, COD, SS and oil – grease removal efficiency were given in Table 3.15.

Table 3.15 COD, SS and Oil-Grease removal efficiency after filtration with cartridge filter

Parameter	Raw waste water	Filtrated water	Removal Efficiency
COD (mg / L)	120 000	93 000	22.5
SS (mg / L)	18 600	9 320	49.9
Oil and Grease(mg / L)	2 870	2 715	5.4

After Cartridge filtration, the sample which was filtrated with cartridge filter was filled in feeding tank. All of the filter clothes were cut to install the membrane cell. Filter clothes were cut and the dimensions of filter clothes were 10.5 cm x 15 cm after cutting procedure. Filtration process were done with 100 L/h flow rate and atmospheric pressure. Firstly, filter clothes I (one) which has the biggest pore diameter was installed in membrane cell. 20 liter of sample were filtrated with this filter clothe at 110 minutes. Filtrated olive oil mill sample were collected different place. Afterwards, filter I was taken to the system and filter II was installed in membrane cell. Filtration of the all sample with filter II was completed in 120 minutes. Same operations were applied on sample III and IV. Total filtration periods of filter clothes III and IV were 200 and 600 minutes respectively. Input samples of the filter clothes and output samples of the filter clothes were taken and pollution parameters were analyzed. Pollution parameters and removal efficiencies were given in Table 3.17, 3.18, 3.19.

Table 3.16 Filtration periods and filtration flow rates of filtrations from cartridge filter and filter clothes

	Cartridge Filter	**Filter Clothes I**	**Filter Clothes II**	**Filter Clothes III**	**Filter Clothes IV**
Filtration Period (min)	60	110	120	200	300
Flow Rate (L/h)	1 440	100	100	100	100

Total period of filtration were 790 minutes (13.2 hours). Approximately daily filtration operation with this system was done two times. The capacity of this system was totally about 40 liters per day. If we planted bigger system for filtration we could filtrated more wastewater with this system and less retention time.

Table 3.17 COD concentrations and removal efficiencies after the filtration with each of filter clothes

Parameter	**Raw Wastewater**	**Cartridge Filter**	**Filter Cloth I**	**Filter Cloth II**	**Filter Cloth III**	**Filter Cloth IV**
COD (mg / L)	120 000	93 000	87 000	83 200	81 600	77 700
Total COD removal efficiency (%)	-	22.5	27.5	30.7	32.0	35.3

Table 3.18 SS concentrations and removal efficiencies after the filtration with each of filter clothes

Parameter	**Raw Wastewater**	**Cartridge Filter**	**Filter Clothe I**	**Filter Clothe II**	**Filter Clothe III**	**Filter Clothe IV**
SS (mg / L)	18 600	9 320	4 440	3 996	3 596	3 530
SS removal efficiency (%)	-	49.9	76.1	78.5	80.7	81.0

Table 3.19 Oil and grease concentrations and removal efficiencies after the filtration with each of filter clothes

Parameter	**Raw Wastewater**	**Cartridge Filter**	**Filter Clothe I**	**Filter Clothe II**	**Filter Clothe III**	**Filter Clothe IV**
Oil and Grease (mg / L)	2 870	2 715	2 258	1 758	1 383	1 110
Oil and Grease removal efficiency (%)	-	5.4	21.3	38.7	51.8	61.3

In spite of 61.3 % oil and grease removal efficiency were not reached wastewater discharge standards of olive oil manufacturing industry in Turkey (40–60 mg/L). SS removal efficiency was 81 % and COD removal efficiency was 35.3 %. These removal efficiencies were used for only pre treatment, because wastewater discharge need to more steps treatment plant or advanced treatment.

3.2.1.2.2 Effect of Filtration with Filter Paper. In this part of experiments, filter paper which was known as blue type filter paper and Sample IV were used. At Figure 3.5 mechanism of system were showed. 200 mL sample were filtrated in filter paper and filtration period and filtrated sample volume were measured, the result are given in Table 3.20. Sludge parts of water content and solid content were analyzed. Sludge solid matter content was measured as 24.5 % and 75.5 % of water content. These values were good for sludge elimination. Filtrated water COD and SS concentration were given in Table 3.21.

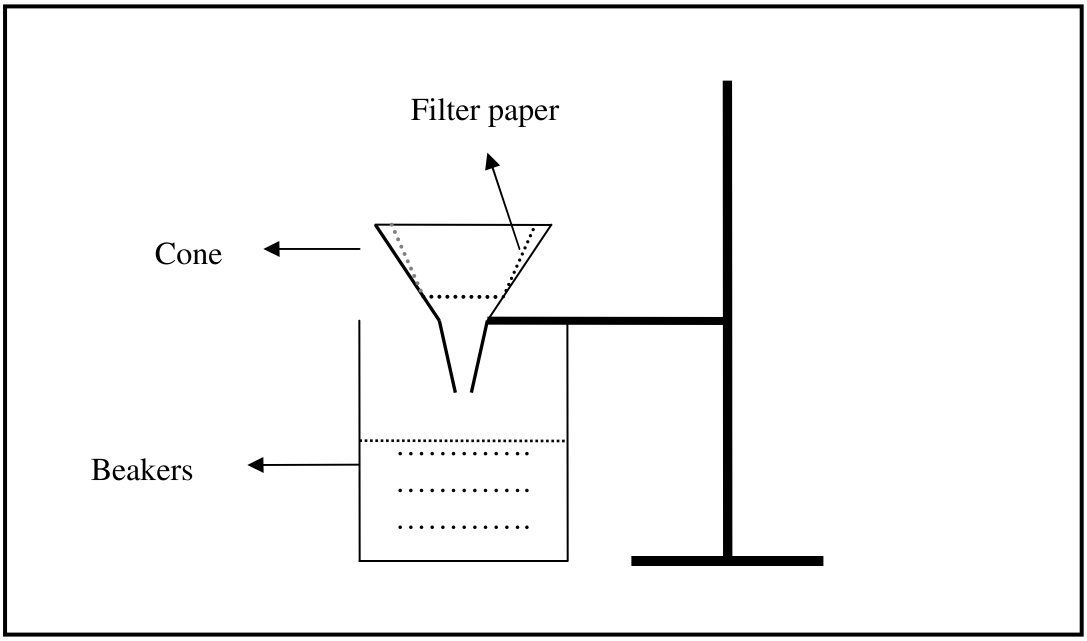

Figure 3.5 Mechanism of filtration with filter paper

Table 3.20 Filtration periods and filtrated samples volumes of filtration with filter paper (Total filtrated was 200 mL)

Time (min)	**1**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**
Filtrated Sample (mL)	2	10	14	18	22	16	29	32	36	40

Table 3.21 COD, SS concentrations and removal efficiencies of filtrated sample with filter paper

	pH	**COD (mg/L)**	**SS (mg/L)**
Raw Wastewater	5.27	124 000	74 000
Filtrated Water	4.95	84 000	56 400
Removal efficiency (%)	-	32.3	23.7

Although, filtration with filter paper was give good result for COD removal, pores plugging were constituted big problem. If use and throw away filter paper used, this was not an economical solution and treatment methods. Improving with back wash system, pores would be cleaned when the system working, then continuously treatment could be done. At the same time the negative way of filter paper treatment was filtration periods. 200 ml sample were filtrated in 2 hours, with 20 cm^2 of filter paper. One liter of sample was filtrated about 10 hours. If 1 liter of sample were filtrated, about 10 hours with 20 cm^2 of filter paper, then 1 m^2 of filter paper could be filtrated 1 liter of sample about 1.2 hours. In one day periods 20 liter of sample will be filtrated. In 3 phase extraction method olive oil factory 30 m^3 of wastewater were collected in wastewater pools per day. In the light of these numbers, we say that small filtration mechanisms with filter paper needed large areas.

3.2.1.3 Effect of Centrifugation

Centrifugation experiments were done in Dokuz Eylül University Wastewater Laboratory, with a using SED –Merlin TBX 506.

Raw wastewater was centrifuged at 7000 rpm. Centrifugation was completed about 25 minutes. To centrifuge, 15 mL centrifugation tubes were used. After the centrifuge process, COD, SS and pH measurement were done. Results were given in Table 3.22.

Table 3.22 Effect of centrifugation on COD and SS removal

	pH	**COD (mg /L)**	**COD removal Efficiency (%)**	**SS (mg / L)**	**SS Removal Efficiency (%)**
Raw Wastewater	5.14	136 000	-	14 840	-
Centrifuged Sample	4.85	56 000	58.8	8 350	43.7

Also, centrifugation process was applied after the chemical treatment methods which were acid cracking, Ca $(OH)_2$, and zeolite adding. These results were given in chemical treatability experiments part.

Centrifugation process was gave the best result in physical treatments units. First investment and operating involved were normal for the big olive oil factories, because coming budget from selling olive oil cakes were pay these investment and operating expenses. Smaller olive oil factories could be collected in a main pool and shared to the maintenance expenses. But in any case, removal efficiency of COD was not enough for discharge standards. We must use to combinations of different treatment methods.

Different physical treatment methods were applied to the wastewater but any of them were enough for discharge standards. The main results table was given in Table 3.23.

3.23 Removal efficiencies of applied physical treatment methods

Methods	COD Removal Efficiency (%)	SS Removal Efficiency (%)	TSM Removal Efficiency (%)
Sedimentation 1 Hour at Laboratory	18.0	23.0	-
Sedimentation 3 Hours at Laboratory	22.0	24.0	-
Sedimentation 1 Day at Laboratory	27.0	32.0	-
Sedimentation 1 Day at Column	21.0	28.0	23.0
Sedimentation 1 Week at Column	32.0	-	25.0
Sedimentation 2 Weeks at Column	42.0	-	34.0
Filtration with Cartridge Filter	22.5	49.9	
Filtration with Cartridge Filter and Filter Clothes	35.3	81.0	-
Filtration with Filter Paper	32.3	23.7	-
Centrifugation	58.8	43.7	-

Table 3.24 Maximum COD removal efficiencies of applied physical treatment methods

Method	Explanation	COD Removal Efficiency (%)
Sedimentation	2 weeks Retention Times	42.0
Filtration	Cartridge Filter and Filter Clothes	35.3
Centrifugation	7000 rpm	58.8

As seen from Table 3.24 max COD removal efficiencies were obtained 58,8 % with centrifugation. Centrifugation process investment and maintenance costs were very high for small olive oil factories, therefore, sedimentation with 2 weeks retention time was applied, but there was another problem opposed. Needed treatment areas of sedimentation process were very big. Olive oil factory's lands were enough only operation and small pools about 100 tons. For example in two weeks periods, needed pool volumes would be about 50 tons and 1 month later, pool would be filled completely. COD removal efficiencies were obtained 35.3 % with filtration with cartridge filter and filter clothes. These materials were cheaper than the other treatments process materials. As a result of physical treatment part, centrifugation and filtration could be used for physical treatment as a pretreatment.

3.2.2. Chemical Treatability Experiments

Chemical treatment is used for olive mill wastewater as a pre treatment method. In general chemical precipitation is applied to wastewater. The average removal percentage of the waste characteristics parameters are 20 – 30 % for COD, 29.3 – 46.9 % for total solids, 41.2 – 53.2 % for volatile solids, 74,4 – 37.0 % for reduced sugar, 77.1 – 95.8 % for oil-grease, 75.3 – 62.5 % for polyphenols, 38.4 – 32 % for volatile phenols and 60.5 – 80.1 % for nitrogenous compounds (Aktas et al., 2001; Lolos et al., 1994).

Chemical treatability experiments were applied on raw wastewater and physical treated wastewater. Applied chemical coagulants were HCl, $Ca(OH)_2$, and zeolite. Properties of these materials were given in Table 2.2.

3.2.2.1 Experimental Studies with HCl (Acid Cracking)

In this experiment, technique HCl which had a 36.5 g/mole molarities and 50 % purity were used. Sample V were used for this experiment. These experiments were done same as sedimentation experiments. Designed sedimentation column which were given at Figure 2.1 were used.

Beginning pH value of Sample V were 5.27. Firstly, 66 liter of mixed olive oil mill wastewaters were filled in sedimentation column and pH was decreased from 5.27 to 2.5 with 9 ml / L HCl dosages which had 50 % purity. After this procedure, five minutes rapid mixing fallowed by half an hour slow mixing, and 3 hours settling. After settling, 65 % upper media (supernatant) and 45 % sludge forming were observed. In acidic condition, oil emulsion was broken and free oil was collected at surface of wastewater. This operation increased the removal efficiencies in all parameter studied. COD concentration decreased from 124 000 mg / L to 64 000 in supernatant part and 108 000 mg / L in sludge part. Results are given in Table 3.25.

Table 3.25 COD removal efficiencies obtained with HCl Addition

	pH	**COD (mg / L)**	**Color (Pt – Co)**	**COD Removal Efficiency (%)**	**Color Removal Efficiency (%)**
Raw Wastewater	5.27	124 000	88 500	-	-
Supernatant	2.5	64 000	12 500	48.0	85.9
Sludge	2.74	108 000	60 000	13.0	32.2

Sample I was used for Acid cracking experiments. Sample I was filled a barrel which was waited for 10 months. Barrel's volume was 80 liters. After 10 months later, to measurement 2 liter of sample were taken. After the measurement observed that; COD value was decreased from 87 600 mg / L to 52 000 mg / L. There was no chemical added; only settled with a big retention time, COD value decreased with 40.6 % removal efficiency. After 10 months later, acid cracking was applied on this sample. pH value was decreased from 4.84 to 2 with 11 ml / L HCl dosage. Results are given in Table 3.26. Five minutes rapid mixing and five teen minutes were applied and settled for 3 hours. At the end of 3 hours, 45 % upper media, 25 % mixed media and 40 % sludge were observed from beaker. After acid cracking, COD value was decreased from 52 000 mg / L to 28 000 mg / L. Totally, 68 % removal efficiency was observed.

Table 3.26 COD removal efficiency of ten months waited olive oil mill obtained with HCl

	pH	**COD (mg / L)**	**COD Removal Efficiency (%)**
Sample I	4.80	87 600	
Sample I (Ten Months Later)	4.84	52 000	40.6
Sample I (Ten Months Later with Adding HCl)	2.0	28 000	68.0

Besides this, acid cracking and centrifugation were applied on Sample V one after the other. In this experiment pH was decreased from 5.14 to 2 with the addition of 12 mL HCl (50 % pure). COD valued was decreased from 136 000 mg/L to 54 000 mg / L with 60.3 % removal efficiency. Results were given in Table 3.27.

Table 3.27 COD removal efficiencies with acid cracking and centrifugation

	pH	**COD (mg / L)**	**COD Removal Efficiency (%)**
Sample V	5.14	136 000	-
Sample V + Acid Cracking	2.0	88 000	35.3
Sample V + Acid Cracking + Centrifugation	2.25	54 000	60.3

When acid cracking and centrifugation applied together, 60.3 % COD removal efficiency and magnificent solid – liquid separation were obtained. After the centrifugation, 80 % upper media and 20 % sludge were observed. After acid cracking, sludge's solid matter percentage was increased from 3.4 % to 7.8 % and after the centrifugation, solid matter percentage were increased 7.8 % to 24.5 %. Results were given in Table 3.28.

Table 3.28 Solid matter percentages chancing after acid cracking and centrifugation

	Raw Wastewater	**After Acid Cracking**	**After Acid Cracking + Centrifugation**
Solid Matter Percentage	3.4	7.8	24.5

Solid matter content for 24.5 % could be stored in olive oil factory and would send sludge drying bed. After these procedures, it could be fired with olive cakes in water boiler to warmed process water.

3.2.2.2 Experimental Studies with Ca (OH) $_2$

In these experiments, Ca $(OH)_2$ was applied itself and combination with other physical and chemical treatment applications. Firstly, only Ca $(OH)_2$ was applied on Sample V. In this application 10 g / L Ca $(OH)_2$ dosage was applied and pH value was increased from 5.14 to 8.90. Powdered Ca $(OH)_2$ was used in this experiment. Five minutes rapid mixing and 15 minutes slow mixing was done. After 2 hours settling, COD value was measured. It was seen that; COD values were decreased from 136 000 mg / L to 104 000 mg / L with 23.5 % COD removal efficiency. After treatment, color of sample was turned dark brown. After 2 hours solid – liquid phase separation was observed that; 75% supernatant and 25 % sludge, but 20 % of supernatant was mixed media. Results are given in Table 3.29.

Table 3.29 COD removal efficiency obtained that Ca $(OH)_2$ additional

	pH	**COD (mg / L)**	**COD Removal Efficiency (%)**
Raw Wastewater	5.14	136 000	-
After Treated with 10 g / L Ca $(OH)_2$	8.90	104 000	23.5

After this experiment, treatment combinations were applied. Firstly, combination of acid cracking at pH=2 and Ca $(OH)_2$ dosages at pH=10 were applied one after the other. With 12 ml / L HCl (50 % pure) dosage, pH was decreased from 5.14 to 2. Five minutes rapid mixing, 15 minutes slow mixing and 3 hours settling were applied respectively. After acid cracking process, COD was decreased from 136 000 mg / L to 88 000 mg / L with 35.3 % removal efficiency. Solid – liquid phase separation were observed that 20 % sludge and 80 % supernatant. After acid cracking, supernatant was taken and 10 g / L Ca $(OH)_2$ was added. Five minutes rapid mixing, 15 minutes slow mixing and 3 hours settling were applied respectively. As a result, COD was decreased from 88 000 mg/ L to 56 000 mg / L with % 36 of removal efficiency. Total removal efficiency was observed 58,8 %. After two treatment steps, centrifugation process was applied. 10 ml supernatant which was taken from output of treatment with Ca $(OH)_2$ was taken to centrifugation. 7000 rpm for 25 minutes centrifugation time were applied. 2 ml sludge and 8 ml supernatant were obtained. COD concentration was decreased from 56 000 mg / L to 36 000 mg / L with 35.7 % removal efficiency. Totally 73.5 % removal efficiency was obtained after three steps. Results were given in Table 3.30.

Table 3.30 Treatment combination with acid cracking, $Ca(OH)_2$ and centrifugation processes respectively

	Raw Wastewater	Acid Cracking (pH =2)	$Ca(OH)_2$ Treatment (pH = 10)	Centrifugation (7000 rpm)
COD (mg / L)	136 000	88 000	56 000	36 000
Removal Efficiency of Each Process (%)	-	35.3	36.0	35.0
Total COD Removal Efficiency (%)	-	35.3	58.8	73.5

3.2.2.3 Experimental Studies with Powdered Zeolite

Zeolite is an adsorbant and coagulant material and using vide variety of treatment stages for odour removal, oil separation, absorption etc. Chemical name of zeolite was hydrated aluminosilicate of alkali metals and metals of alkali earths. Color of zeolite was grey – green. Other properties of zeolite were given in Table 2.2. In this experimental study, the aim of zeolite was applied to make use of solid-liquid separation, adsorbsion ability and COD removal efficiency. In this experiment, powdered zeolite was applied.

Firstly, to find the effective zeolite dosages, jar test was done. 5, 10, 15, 20, 25 g / L powdered zeolite dosages were applied to the treated wastewater with HCl addition. 1.5 liters of sample VII were used for these experiments. 20 ml of HCl were used to decrease pH form 4.96 to 2. Five minutes rapid mixing, 10 minutes slow mixing and 2 hours settling were applied respectively. After settling, five 200 ml of beakers was filled with supernatant which was come from acid output of acid cracking process. Respectively, 5, 10, 15, 20, 25 g /L zeolite dosages were applied and taken in jar test mechanism. Five minutes rapid mixing, 10 minutes slow mixing and 2 hours settling were applied respectively. After two hours later, COD values were measured and results were given in Table 3.31. As a result, a best and economical zeolite dosage was obtained at 15 g / L. In spite of at 20 g / L zeolite dosage COD removal efficiency were better than 15 g / L dosage' s percentages, although, we select the 15 g / L dosage. Because, differences for per 5 g / L was not gave a big difference of removal efficiency. At 15 g / L zeolite dosage 62.5 % COD removal efficiency were obtained.

Table 3.31 Effect of zeolite on COD removal efficiency (After acid cracking)

	Raw Ww.	**After Acid Cracking**	**5 g / L zeolite**	**10 g / L zeolite**	**15 g / L zeolite**	**20 g / L zeolite**	**25 g / L zeolite**
COD (mg / L)	96 000	64 000	56 000	48 000	36 000	32 000	30 000
COD Remov. Effc. After Acid Cracking (%)	-	33.3	41.7	50.0	62.5	66.7	68.8
COD Rem.Eff. of Each Dosage (%)	-	-	12.5	25.0	43.8	50.0	53.1

After treatment with acid cracking, lime treatment ($Ca(OH)_2$) and zeolite dosages (15 g / L), centrifugation process was applied. With this combination 83.2 % removal efficiency was obtained. Results about these experiments were given in Table 3.32.

Table 3.32 COD removal efficiency of acid cracking + lime treatment + zeolite + Centrifugation

	Raw Waste Water	**After Treatment**
COD (mg / L)	96 000	16 000
COD removal Efficiency (%)	-	83.3

Another experiment of zeolite application was applied on Sample V. 5, 10 and 15 g / L zeolite dosages were applied on raw wastewater. COD concentrations were decreased from 136 000 mg / L to 124 000 mg / L, 108 000 mg / L, 84 000 mg / L respectively. Best result obtained with 15 mg / L zeolite dosage. Results of these experiments were given in Table 3.33. After treatment with 15 g / L zeolite dosage 38.3% COD removal efficiency were obtained.

Table 3.33 Treatment with zeolite on raw wastewater

	COD (mg / L)	**COD Removal Efficiency (%)**
Raw Wastewater	136 000	-
5 g / L zeolite dosage	124 000	8.8
10 g / L zeolite dosage	108 000	20.6
15 g / L zeolite dosage	84 000	38.3

After treatment with zeolite, centrifugation process was applied. 15 g / L zeolite dosage was selected for this experiment. Firstly, 15 g / L zeolite dosage was applied on raw wastewater. 5 minutes rapid mixing, 20 minutes slow mixing and 2 hours sedimentation were applied respectively. After than, supernatant was taken and centrifugation process were applied. After treatment with zeolite, COD value was decreased from 136 000 mg / L to 84 000 mg / L with 38.3 % removal efficiency. after centrifugation, COD value decreased from 84 000 mg / L to 48 000 mg / L with 64.7 % total removal efficiency. Results were given in Table 3.34.

Table 3.34 COD concentrations and removal efficiencies after treatment by using zeolite and centrifugation.

	COD (mg / L)	**COD Removal Efficiency (%)**
Raw Wastewater	136 000	-
15 g / L zeolite dosage	84 000	38.3
After Centrifugation	48 000	64.7

3.2.2.4. General Evaluations for Chemical Treatability experiments

At chemical treatability studies, maximum COD reduction was found with acid cracking (at pH = 2), lime treatment (Ca $(OH)_2$ (at pH = 10) and centrifugation (at 7000 rpm) combination such as 73.5 %. At the same time, after treatment with HCl (at pH = 2), 15 g / L zeolite dosages were applied and COD removal efficiency was obtained removal efficiency 62.5 %. In same experiment, with 25 g / L zeolite dosages 68.8 % COD removal efficiency were observed. If we thought that economical way of the treatment, then 15 g / L zeolite dosages must select. Another treatment experiment was zeolite (15 g / L) and centrifugation applying. With this experiment, 64.7 % COD removal efficiency was obtained. Applied acid cracking on ten months waited samples were give 68 % removal efficiency .We were seen that; all of the best results could be obtained with combinations of different treatment methods. Maximum COD removal efficiency of chemical treatability experiments were given in Table 3.35 and in Table 3.36 max removal efficiencies of treatment combinations were given.

Table 3.35 Max COD removal efficiencies of chemical treatability experiments

Chemical Treatment Methods	**COD (mg /L) Before Treatment**	**COD (mg /L) After Treatment**	**COD removal efficiency (%)**
Acid Cracking with HCl at pH = 2	136 000	88 000	35.3
$Ca(OH)_2$ at pH =10	136 000	104 000	23.5
Zeolite 15 g / L	136 000	84 000	38.3

Table 3.36 Max COD removal efficiencies of treatment combinations

Treatment Combinations	**COD Removal Efficiency (%)**
10 Month Waited Sample + Acid Cracking (HCl)	68
Acid Cracking + Centrifugation	60.3
Acid cracking + Ca $(OH)_2$ + Centrifugation	73.5
Zeolite (15 g/L) + Centrifugation	64.7
Acid Cracking + Lime + Zeolite + Centrifugation	83.3

3.3. Olive Oil Cake and Treatment Sludge Studies

In these studies, sludge samples which were taken bottom of the beakers were investigated. Water content and drying capability of sludge and were measured. At the same time olive oil cakes which were taken from factories and manufactured 2-Phase and 3-Phase extraction were investigated. Olive oil cakes were dried with different conditions.

Firstly, pH of Olive oil mill waste water was decreased to 4 and after 2 hour later, sludge sample, which were settled at bottom of the beaker were taken and dried on drying unit, which had a 25x25x5 cm (W.L.H) dimensions. Drying unit was given in Figure 3.6. Sludge was spread on drying unit with 1.5 cm height for 2 days. Drying unit was made of stainless steel material and there was a filter at the bottom of the unit to filtrate the water of sludge. Filtrate was collected in filtrate tray.

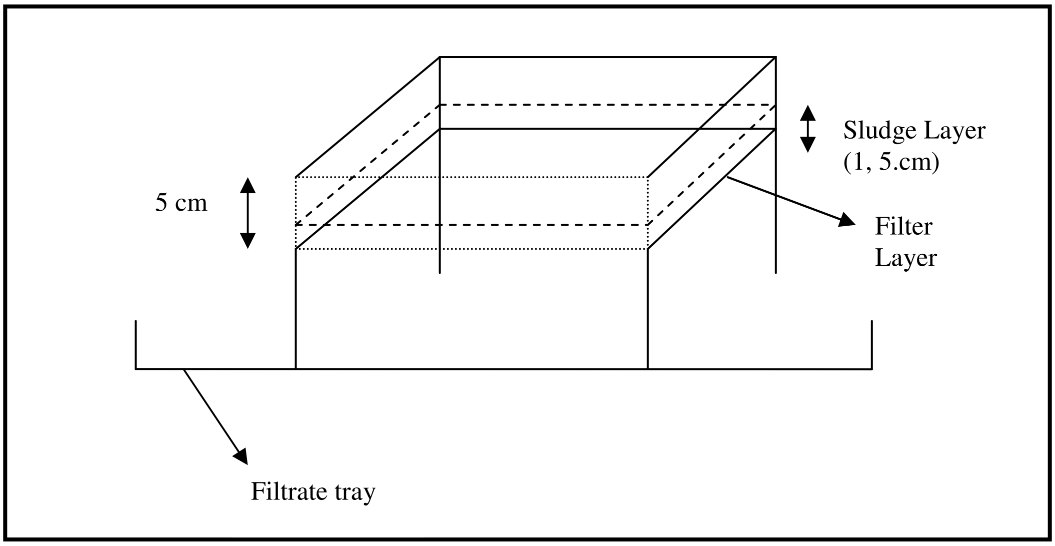

Figure 3.6 Designed sludge drying unit

At the beginning of this experiment, solid matter content was 7 %. At the end of 2 days, solid matter content was increased from 7% to 23%. This experiment was done with 19 liter of sample. After pH was decreased to 4, then 9.5 liter of sludge were obtained. If we calculate minimum area requirement to drying;

Total area of sludge drying unit was 25 cm x 25 cm = 625 cm^2 and height of the sludge layer was 1.5 cm. total volume of filtrated sludge 625 cm^2 x 1.5 cm =937.5 cm^3.

Change of solid matter percentage was 23 % - 7 % = 16 %
937.5 cm^3 x 0.16 = 150 cm^3 water were filtrated and evaporated.
150 cm^3 / 625 cm^2 = 0.24 cm sludge layer were reduced.
After dried for two days, new sludge layer height was 1.26 cm.
After treatment 1 m^3 of olive oil mill wastewater, 0.5 m^3 sludge was formed.

$$0.5\ m^3 \times 0.07 = V_2 \times 0.23$$

$$V_2 = 0.152\ cm^3$$

Observed that, this method was not a economical solution for sludge drying. In order to this method faster and more economical drying unit such as belt press filter could be used.

Another study was investigated of olive oil cake's solid matter contents and water giving capacity. To this study olive oil cakes samples were taken from 2-Phase and 3-Phase producing factories. Firstly, solid matter content was measured. Water contents of 2-Phase and 3-Phase were 34 %, 46 % respectively. Results are given in Table 3.37. According to literature survey solid matter content of 2-Phase were 30 % - 35 % and at 3-Phase 50 – 54 (Improlive, 2000). After measured, dried produce were applied. Drying procedures were applied in two ways. 50 g of each samples were taken to the ceramic disc and dried in room temperature (26 ^{0}C) and in incubator at 105 ^{0}C. solid matter content chancing of 2 and 3 phase samples so; in incubator at the end of the 3 days, 2 phase samples solid matter content was increased form 34 % to 51 % and same time at incubator solid matter content of 3 phase sample's was increased 46 % to 62 %.

At room temperatures (26 ^{0}C), solid matter content of 2-Phase increased form 34 % to 48 and at 3-Phase samples solid matter content was increased from 46% to 58. Results are given in Table 3.37.

Table 3.37 Solid matter content of 2 and 3 phase extraction methods after drying procedure at incubator and room temperature

	Starting Solid Matter Content (%)	**After Dried in Room Temperature at 26 C^{0} (%)**	**Reduced Liquid At Room Temp. (%)**	**After Dried in Incubator At 105 C^{0} (%)**	**Reduced Liquid At Incubator (%)**
2-Phase	34	48	14	51	17
3-Phase	46	58	12	62	16

With applied centrifugation process after acid cracking process, sludge solid content was increased from 3, 4 to 24, and this results are given in Table 3.28.

However, investigation of high COD concentrations source, COD concentration of olive oil was measured. Result was very confusing and surprising. This surprised result were given in Table 3.38

Table 3.38 COD concentrations of olive oil

	Olive Oil (3-Pase extraction)
COD (mg/L)	792 000

CHAPTER FOUR
CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusion

The aim of this study was to investigate the characterization and treatability of the olive mill wastewater which were taken from different time of harvesting seasons of olive oil industry. For the treatability examinations, several unit operations and process performed using different samples. Pollution parameters were chancing depending on harvesting year and in different times of the same harvesting seasons. At the same time, degree of olive ripening, olive's storage time and storage time of wastewater before treatment changes wastewater characteristics substantially. According to amount of olive oil in olive oil mill wastewater pollution parameters chanced between very large intervals.

The main pollutants in this type wastewater are COD, SS, Oil and Grease and pH. Different physical and chemical treatment methods were applied to the effluent samples to find the most suitable pretreatment methods for olive oil mill wastewater. The removal efficiencies obtained from different treatment systems were variable. The reduction of pollution depends on flow diagram of the treatment. Generally, better treatment efficiencies obtained with methods using more steps. All of experimental studies aimed to achieve the discharge limits according to the Water Pollution Control Regulation in Turkey (Table 2.1). Therefore, treatment efficiencies such as 95 % is not sufficient to fulfill the discharge limits. Actually, 95 % is successful treatment efficiency for treatment, but olive oil mill waste has very high pollution parameters such as 120 000 mg/L COD concentration. With applied treatment methods, COD concentrations can be lowered from 96 000 mg/L to 16 000 mg/L which was above the discharge limits.

To observe the clearly, pilot plant were installed in selected olive oil factory which was a produced with tree-phase extraction. We see that, doing experiments in laboratory were not gave a same results of pilot scale. These results showed that, obtained results were not a real reduction value. In pilot scale experiments, every time, reduction values were lover than laboratory scale experiments. Because, treatment conditions such as homogenous, solid-liquid separation etc. were not provided. Therefore, obtained removal efficiency must be calculated with decreasing of its value.

In the first part of this thesis, different physical methods such as sedimentation, filtration and centrifugation were applied to the wastewater. At sedimentation experiment, with two weeks retention time 42 % max COD removal efficient were obtained. In filtration experiment which was filtrated with cartridge filter and four different filter clothes max 35.3% and in centrifugation experiment (7000 rpm) max 58.8 % COD removal efficiency were obtained. Same time, in filtration oil and grease was decreased from 2870 mg/L to 1110 mg/L with 61.3 %. Applied physical treatment methods were not sufficient to fulfill the discharge limits, but, centrifugation processes was successful for pretreatment, it might be used for to be physical pretreatment of treatment combinations.

In the second part, chemical coagulation – flocculation experiments were tried. HCl, $Ca(OH)_2$, and zeolite were used for this purpose. Maximum COD removal efficiencies of these coagulants were 35.3 %, 23.5 %, 38.3 %, respectively. Best chemical treatment efficiency was obtained with zeolite (15 g/L). However, the COD concentration of treated effluent with zeolite was still very high as about 84 000 mg/L.

In the third part of this thesis, different physical and chemical treatment methods were applied in sequence. Results of these combinations were given in Table 3.36. Maximum COD removal efficiency was obtained with acid cracking + lime ($Ca(OH)_2$) + zeolite + centrifugation combination. With this four steps flow diagram

83.3 % COD removal efficiency was obtained. With this combination, COD was decreased 96 000 to 16 000 mg/L. Another successful treatment combination was Acid cracking + lime ($Ca(OH)_2$) + Centrifugation combination. With this combination, 73.5% removal efficiency was obtained. COD concentration was decreased 136 000 mg/L to 36 000 mg/L. These results are not sufficient to fulfill the discharge limits (Table 2.1).

In studies of olive cakes and treatment sludge, 3 and 2 phase olives cakes were investigated. To increase their solid matter contents, drying experiments were applied. at the end of two days, olive cakes sample's which were in incubator (105 C^o) for two days, solid matter contents were increased from 34 % to 51 % and 46 % to 62 % for 2 and 3 phase extraction methods, respectively. At the same time, drying studies were done at normal air temperature (26 ^0C) for two days, in this experiments obtained results of 2 and 3 phase were 48 % and 58 %, respectively. These results showed that; solar energy could be used instead of electricity to drying units. For this aim, solar panels could be designed. However, less drying time would be handled. Drying of treatment sludge were not give an efficient results, because end of the two days sludge's solid matter content increased from 7 % to 23 % in spite of height of spreading sludge on designed drying unit (Figure 3.6) about 1.5 cm. If we calculate the total drying area of treatment sludge, we find very big area requirements. Therefore, this method was not economical and useful.

As a result of all experimental studies, it was impossible to achieve the discharge standards with these methods, since the remaining COD concentration was the minimum of around 16 000 mg/L. Therefore further treatment is needed to reduce the COD concentrations. In literature survey, distillation- evaporation unit was obtained that 90 % COD removal efficiency (Oktav, 2001). According to this result, after distillation process, reached minimum concentration will decrease from 16 000 mg/L to 1600 mg/L. after distillation, biological treatment will apply. According to literature survey, in biological treatment with anaerobic biological treatment, COD removal efficiency was obtained 85 % - 93 % (Ergüder et al., 2000, p 243). According to suggested flow diagram, after biological treatment COD concentration was decreased from 1600 mg/L to 240 mg/L – 112 mg/L. With suggested flow diagram discharge limits should be achieved. Suggested flow diagram was given in Figure 4.1.

Acid cracking (HCl)

↓

Lime ($Ca(OH)_2$)

↓

Zeolite

↓

Centrifugation

↓

Distillation

↓

Anaerobic Biological Treatment

↓

Discharge

Figure 4.1 Suggested treatment combinations

4.2. Recommendations

Suggested combination (at Figure 4.1) would be increased the unit cost of olive oil. In this flow diagram, distillation process's investment and maintenances costs were very high. Instead of distillation, solar energy would be used. Usage is solar energy is very promising solutions Aegean Region. Thermal treatment contains evaporation and distillation processes, either by solar energy (natural evaporation) or by using electricity or natural gas firing. This is the only group of alternative methods that can be defended on economic grounds. This kind of treatment requires storage of the olive mill wastewaters produced during the wet winter season.

If we want to eliminate pollution, we should solve the problem at source. Source means extraction methods such as press, 2 and 3 phase extraction methods. Switching from press and three-phase to two-phase production methods, olive oil mill wastewater problem was eliminated. Two-phase technologies result in a watery olive cake, which is not necessarily easier to treat and dispose of safely. Therefore, although less water is used compared to the three-phase process, two-phase processes do not completely eliminate the environmental problems.

Olive oil mill waste water contains olive oil which has a high COD value about 792 000 mg/L (Table 3.38). Olive oil percentages in olive oil mill wastewater are about 1% to 6% (Table 1.2). An important part of OWM concentrations comes from containing of olive quantities. Beginning of the treatment combinations, olive reducing systems should be planted.

Olive mill solid wastes must be processed to recover the residual oils they contain. Recovered oil from olive mill solid wastes may be used in soap-stock manufacturing, or if the quality allows it can be blended with high-quality oils and sold as edible oil. De-oiled solids may be composted together with other agricultural wastes, or used as biomass fuel or raw material for biotechnology.

Olive oil mill waste water would be diluted with municipal wastewater, and then discharge standards (Table 2.1) were provided easily. Because, founded result at laboratory was not same with application of real treatment systems. Real application's removal efficiencies are as few as 5 % - 10 % as laboratory studies.

Although olive oil mill wastewater has a high pollution parameters, its discharging limits are very low. According to Water Pollution Control Regulation in Turkey discharge limit of some industries is 1000 mg/L such as paper, pulp industry and metal finishing industry. Water Pollution Control Regulation in Turkey should be evaluated and level of COD discharge limit of Olive Oil Mill wastewater can be increased from 250 mg/L to 1 000 mg/L. With this evaluation, discharge limits would be achieved with less step of treatment flow diagram.

Treatment costs are very high, budged of small olive oil factories does not sufficient for this treatment costs. If central treatment systems would be planted more than five olive oil factory could pay treatment costs together. Exactly like this, olive oil factories which were located in same location area were designated and forced to planted treatment system as soon as possible. With each passing day, ground water was polluted because of these wastewaters.

REFERENCES

Aktas, E., Imre, S & Ersoy, L. (2001). Characterization and lime treatment of olive mill wastewater. Water Research, 9, 2336 – 2340.

Al-Malah, K., Azzam, O.J., Abu-Lail, N. I. (2000). Olive mills effluent (OME) wastewater post-treatment using activated clay. Separation and Purification Technology. 20,225-234.

Annesini M.C. & Gironi F. (1991), "Olive Oil Mill Effluent: ageing effects on evaporation behavior", Water Research Vol. 25, No.9, pp. 1157-1160.

Azbar N., Bayram A., Filibeli A., Muezzinoğlu A., Şengül F. & Özer A. (2004). A review of waste management options in olive Oil production. Critical Reviews in Environmental Science and Technology, 34, 209–247

Beltran, F. J., Garcia-Araya, J.F., Frades, J., Alvarez, P. & Gimeno, O. (1999). Effects of single and combined ozonation with hydrogen peroxide or UV radiation on the chemical degradation and biodegradability of debittering table olive industrial wastewaters. Water Research. 33, 723-732.

Beltran-Heredia J., Torregrosa J., Garcia J., Dominguez JR. & Tierno JC (2001), "Degradation of olive oil mill wastewater by the combination of Fenton's reagent and ozonation processes with aerobic biological treatment", Water Science and Technology, 2001, Vol.44, Iss 5, pp.103-108.

Cabrera, F., Lopez, R., Martinez-Bordiu, A., Dupuy de lome, E. & Murilllo, J.M. (1996). Land treatment of olive oil mill wastewater. International, Biodeteriorationa&Biodegradation, 54, 215-225.

Dalis, D., Anagnostidis, K., Lopez, A., Letsiou, I. & Hartmann, L. (1996). Anaerobic digestion of total raw olive-oil wastewater in a two-stage pilot-plant (up-flow and fixed-bed bioreactors). Bioresource Technology, 57, 237-243.

Demicheli, M., & Bontoux, L. *Survey current activity on the valorization of by-products from the olive oil industry*. European Commission Joint Research Centre, Final Report. www.jrc.es/projects/ff/EC/IPTS/IPTSPUBL.html, 1996.

Duarte E.A., Neto I.(1996);"Evaporation Phenomenon as a Waste Management Technology", Water Science and Technology, Vol.33, No.8, pp 53-61, Elsevier Science Ltd. Oxford, UK.

Ergüder, T.H., Guven, E. & Demirer, G.N. (2000). Anaerobic treatment of olive oil mill wastes in batch reactors. Process Biochemistry. 36. 243-248.

European Commission, Universidad Complutense de Madrid (2000). Workshop Improlive 2000. Final Report. Madrid. Aragon, J. M.

Galili, E., & Sharvit, J. 20,000 Olives under the sea. *Archaeol. Hist. Israel Discover* 19(5), 16, 1998.

Garcia, I. G., Pena, P. R. J., Venceslada, J. L. B., Martin, A. M., Santos, M. A. M & Gomez, E. R., (2000). Removal of phenol compounds from olive mill wastewater using *Phanerochaete chrysosporium, Aspergillus niger, Aspergillus terreus* and *Geotrichum candidum.* Process Biochemistry. 35, 751-758.

Gharsallah, N., Labat, M., Aloui, F.& Sayadi, S. (1999). The effect of *Phanerochaete chrysosporiumpretreatment* of olive mill waste waters on anaerobic digestion. Resources, Conservation and Recycling, 27, 187-192.

Gil, M., Haidour, A. & Ramos, J.L. (1998). Two glutaric acid derivatives from bolives. Phvtochemistrv, 49. 1311-1315.

Gonzalez, M.D., Moreno, E., Quevedo, J., & Ramos, A. Studies on antibacterial activity of waste waters from olive oil mills (alpechin): Inhibitory activity of phenolic and fatty acids. *Chemosphere* 20, 432, 1990.

Hamdi, M. (1991). Effects of agitation and pretreatment on the batch anaerobic digestion of olive mill wastewater. Bioresource Technology. 36, 173-178.

Israilides, C.J., Vlyssides, A.G., Mourafeti, V.N., & Karvouni, G. Olive oil wastewater treatment with the use of an electrolysis system. *Bioresource Technol* 61(2), 163, 1997.

Israilides CJ., Vlyssides AG., Mourafeti VN., Karvouni G. (1997), "Olive oil wastewater treatment with the use of an electrolysis system", Bioresource Technology.

Institute for Prospective Technological (1996). Studies Survey on Current Activity on the Valorization of By-Products from Olive Oil Industry. Seville. Demichelli, M. & Bontoux, L.

LED Italia srl. (1998), "LED Italia Technical Report**",** www.leditalia.com, LED Italia Srl.

Lolos, G., Skordilis, A. & Parissakis, G. (1994). Polluting characteristics and lime precipitation of olive mill wastewater. Journal of Environmental Science and Healt, Part A: Environmental Science and Encineering, 29, 1349 – 1356.

Masghouni, M., and Hassairi, M. Energy applications of olive oil industry byproducts:—I. The exhaust foot cake. *Biomass Bioenergy* 18, 257–262, 2000.

Metcalf &Eddy (2003) *Wastewater engineering, treatment and reuse* (4th ed.). New York: Mc Graw-Hill.

Mitrakas, M., Papageorgiou, G., Docoslis, A & Sakellaropoulos, G. (1996) Evaluation of various pretreatment methods for olive oil mill wastewater. European Water Pollution Control, 6, 10 - 16.

Monteoliva-Sanchez, M., Incerti, C, Ramos-Cormenzana, A., Paredes, C, Roig, A.&Cegarra, J. (1996). The study of the aerobic bacterial microbiota and the biotoxicity in various samples of olive mill wastewaters (alpechin) during their composting process. International Biodeterioration&Biodegradation. 53, 211-214.

Official Newspaper of Republic of Italy (1996), law No.547/96, Italy.

Oktav E., 2001. Treatment of Olive Oil Industry Wastewater. DEU, Izmir Master Degree Thesis (P. 79 – 80)

Rozzi, A., & Malpei, F. Treatment and disposal of olive mill effluents. *Int. Biodeterior. Biodegrad.* 38(3–4), 135, 1997.

Samsunlu, A., T¨unay, O., ¨ Oztürk, Z., & Alp, K. Characterization and Treatability of olive oil wastewaters (in Turkish), ˙I.T. ¨ U. 6. *Industrial Pollution Symp. Proc.*, pp. 93–99. Istanbul, 1998.

Scioli C. & Vollaro L. (1997), “The use of Yarrowia Lipolytica to reduce pollution in olive oil mill wastewater “, Water Research Vol.31, No.10, pp 2520-2524.

Sekerratt G., Ammar E. (1999), "The application of redbed treatment technology to the treatment of effluents from olive oil mills", Final report, 1999, Project number:066599003ZH010, Staffordshire University, center for environmental technology, UK.

Şengül F. (1991); "Waste Characteristics and Treatment of Industrial Wastewaters", Section 8, DEU, Izmir.

Tsonis S.P. (1997); “Olive Oil Mill Wastewater as Carbon Source in Post Anoxic Denitrification”, Water Science and Technology, Vol.36, No.2-3, pp.53-60, IWA Publishing.

Tsonis S.P.,Tsola V.P. & Grigoropoulos S.G.(1989). Systematic characterization and chemical treatment of olive oil mill wastewater. Toxicology and Environmental Chemistry. 20., 437 -457.

Ubay, G. & Oztürk, I. (1997). Anaerobic treatment of olive mill effluents. Water Science and Technology. 35. 287-294.

Universities of Milan, Bologna, Florence;(1997, 1998, 1999)” Neutral Antioxidants from Olive Oil Processing Wastewater”, Project EU n.CT973039, Bologna.

Vlyssides, G. A., Bouranis, D.L., Loizidou, M.&Karvouni, G. (1996). Study of demonstration plant for co-composting of olive-oil-processing wastewater and solid residue. Bioresource Technology. 56. 187-193.

Vossen, P. (2001) CORPINI ARTE OLEARIA " Interest to Small Farmers". California, Patent.