

**TREATMENT OF OLIVE OIL INDUSTRY
WASTEWATER**



by
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July, 2001
İZMİR

TREATMENT OF OLIVE OIL INDUSTRY WASTEWATER

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**by
Ezgi OKTAV**

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Ms.Sc. THESIS EXAMINATION RESULT FORM

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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 an important component of Mediterranean cuisine, because of its energy, its satisfying special taste and vitamins that are included. Although, olive oil production which is used little amount of energy and no any other raw material apart from olive oil, seems to be environmentally safe, using organic matter, suspended solids, oil and grease contents of vegetation water are too high. 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 from six olive oil processing industries. For the treatability examinations, several unit operations and processes performed using different samples. The efficiencies obtained from the same unit operation were quite different for different samples. These differences mainly due to the wide variability of olive oil mill wastewater characteristics.

In the first part of experimental studies, different physical methods such as filtration, shaking, aeration, sedimentation, and distillation were applied to the wastewater. In filtration experiments, maximum COD removal efficiency (41 %) was achieved after filtration through filter paper Maximum COD removal efficiency in shaking experiment was 49% and it was obtained at the end of the eleventh day. In aeration experiment, COD removal efficiency achieved 43 % after 7 hours aeration. COD removal efficiency of 26 % was achieved after sedimentation experiment. Therefore plane sedimentation is not promising method as pretreatment step of olive mill wastewater. Distillation process after coagulation as a pretreatment step was the most effective method for the treatment of olive oil industry wastewater. 99% COD removal efficiency was achieved on the distillate.

In the second part, chemical treatment studies were done. Coagulation-flocculation-precipitation and chemical oxidation methods were applied. After chemical coagulation and flocculation experiment with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 32% COD removal efficiency was achieved. Efficiency of chemical precipitation study with $\text{Ca}(\text{OH})_2$ didn't give sufficient result (13%). In acidic condition better results were obtained. After precipitation with HCl, 38 % COD removal efficiency was achieved. Maximum removal efficiency was obtained first acidic and then alkali condition with 55% COD removal efficiency. In chemical oxidation experiments, catalytic oxidation, oxidation using KMnO_4 , H_2O_2 , NaOCl , and Fenton Reagent ($\text{H}_2\text{O}_2 + \text{FeSO}_4$) were applied. Chemical oxidation with Fenton Reagent was the most effective oxidation method on the removal of COD. Approximately 65 % and 70 % COD removal efficiencies were obtained for olive mill wastewaters. However, the COD concentration of treated effluent was still very high as about 32 000 mg/L.

In biological treatment experiments, Oil Gator Bacteria were used in batch reactor and this reactor was aerated continuously. 60 000 mg/L COD concentration and 52% COD removal efficiency in treated water were achieved at the end of the 22nd day.

As a result of all experimental studies, it was impossible to achieve the discharge standards with these methods, since the remaining COD concentration was approximately 1 000 mg/L. Therefore, further treatment is needed to reduce the COD concentration. When physicochemical, chemical or biological methods were applied alone, significant improvement in COD reduction was not observed. 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. Physical treatment, chemical oxidation, and biological treatment alternatives should be applied sequentially for achieving wastewater discharge standards for olive mill wastewater.

ÖZET

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 ögesi konumuna gelmiştir. Zeytinyağı üretimi, hiçbir kimyasal madde kullanılmaması ve büyük miktarda enerjiye ihtiyaç duyulmaması nedeniyle çevre dostu olarak görülse de, üretim sonrasında açığa çıkan atıksuyun (karasu) organik madde, askıda katı madde, yağ ve gres içeriği oldukça yüksektir. Bu sebeple, karasuyun arıtımı, önemli çevre problemleri arasında yer almaktadır.

Bu çalışmanın amacı, farklı endüstrilerden gelen karasuyun karakterizasyonunun ve arıtılabilirliğinin incelenmesidir. Arıtılabilirlik çalışmaları kapsamında, altı farklı karasu örneği incelenmiş, değişik arıtım yöntemleri denenmiştir. Aynı arıtım yönteminin uygulandığı iki farklı karasu numunesiyle yapılan çalışmalarda çok farklı sonuçlar elde edilmiştir.

Deneysel çalışmaların ilk kısmında karasuyun filtrasyon, çalkalama, havalandırma, çöktürme ve distilasyon gibi fiziksel yöntemlerle arıtılabilirliği incelenmiştir. Filtre kağıdından filtrasyon sonrasında %41 KOİ giderme verimi elde edilmiştir. Çalkalayıcıda 11 gün bekletilen atıksuda %49 KOİ giderme verimine ulaşılmıştır. Havalandırma deneylerinde maksimum verim (%43) 7 saat havalandırma sonrasında elde edilmiştir. Çöktürme deneyinde elde edilen KOİ giderme verimi ise sadece %26'dır. Bu sonuç karasu arıtımında çöktürmenin ön arıtım adımı olarak kullanılamayacağını göstermektedir. Tüm fiziksel arıtım yöntemlerinde maksimum KOİ giderme verimi (%99) kimyasal arıtmadan geçmiş atıksuyun distilasyonu ile elde edilmiştir.

Kimyasal arıtım çalışmalarında, kimyasal çöktürme ve kimyasal oksidasyon denemeleri yapılmıştır. Kimyasal çöktürmede koagulant olarak $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ kullanıldığında %32 KOİ giderme verimi elde edilmiştir. Kireç $[\text{Ca}(\text{OH})_2]$ ile çöktürmede elde edilen KOİ giderme verimi %13, HCl ile çöktürmede ise %38'dir. Bu durum asidik koşullarda daha iyi sonuçlara ulaşıldığını göstermektedir. Kimyasal çöktürme çalışmalarında maksimum KOİ giderme verimi (%55) atıksuyun önce asidik sonra bazik hale getirilmesiyle elde edilmiştir. Kimyasal oksidasyon deneylerinde ise MnSO_4 katalizliğinde havalandırma, KMnO_4 , NaOCl , H_2O_2 ve Fenton reaktifi ile oksidasyon alternatifleri incelenmiştir. En yüksek KOİ giderme verimlerine (%65-%70) Fenton reaktifi ile oksidasyon sonrasında ulaşılmıştır. Ancak çıkış suyunun KOİ konsantrasyonu hala 32 000 mg/L gibi yüksek bir değerdedir.

Biyolojik arıtım çalışmalarında ise Oil Gator bakterisi kesikli biyolojik reaktörde kullanılmıştır. Reaktör 3 hafta boyunca sürekli havalandırılmış, günlük olarak KOİ giderme verimleri incelenmiştir. 22 gün sonunda ulaşılan KOİ konsantrasyonu 60 000 mg/L ve KOİ giderme verimi %52'dir.

Tez kapsamında yapılan deneysel çalışmalar sonucunda ulaşılan en düşük KOİ değeri 1 000 mg/L'dir. Bu koşullarda alıcı ortama deşarj standartlarını sağlamak mümkün değildir. Fizikokimyasal, kimyasal veya biyolojik arıtım yöntemlerinin tek başına uygulanması durumunda istenen giderme verimlerine ulaşılamamaktadır. Birden fazla kademede yapılan arıtılabilirlik çalışmalarıyla daha iyi sonuçlar elde edilmektedir. Zeytinyağı üretimi atıksularının arıtımında, fiziksel arıtma, kimyasal oksidasyon ve biyolojik arıtma alternatiflerinin ardışık olarak uygulanmasıyla alıcı ortama deşarj standartları sağlanabilir.

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CHAPTER ONE

INTRODUCTION

1.1. LITERATURE SURVEY

1.1.1. General

The expansion of the agro-industry has grown enormously over the last decades. Therefore, production of organic wastes has decreased day by day. One of these agro-industrial wastes is the olive mill wastewater (Monteoliva-Sanchez et al., 1996). Olive mill wastewater constitute an important environmental pollution problem in Mediterranean countries such as Greece, Italy, Lebanon, Portugal, Spain, Syria, Tunisia and Turkey (Ergüder et al., 2000). In these countries about 11 million tons of olives are produced per year from which about 1.7 million tons of olive oil are extracted. The seasonal polluting load of olive-oil production is equivalent to about that of 22 million people per year since the COD value of the wastewater is about 80 g / L and its volume produced from 1 ton olive is about 0.8 m³ (Aktaş et al., 2001).

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. 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 (bioremediation), 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).

1.1.2. Treatment and Utilization Methods of Olive Mill Wastewater

1.1.2.1. 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. 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.

1.1.2.2. Chemical Treatment Methods of Olive Mill Wastewater

1.1.2.2.1. 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).

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 H₂SO₄) 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%) (Mittrakas et al., 1996, p 10).

1.1.2.2.2. 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 10⁻³ 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).

1.1.2.3. Biological Treatment of Olive Mill Wastewater

1.1.2.3.1. 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 behaviour 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*\Aspergillus niger\Aspergillus terreus.

1.1.2.3.2. 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/m³d. 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 conversion rate of 0.35 m³ per kg COD removed was achieved during the study (Ubay&Öztürk, 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 lignolytic 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 1.1.

Table 1.1. Studies on Anaerobic Treatment of Olive Mill Wastewater

Retention Time	Influent Concentration (g/L as COD)	Loading Rate (kg COD /m³.day)	COD Removal Efficiency (%)	Reference
1 day		5-18	75	Ubay&Öztürk, 1997
	10	5.25-18.65	70-80	Beccari et al., 1996
	8-27		85	Ergüder 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

1.1.2.4. 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, CO₂, 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 m³ wastewater in total, which means an average rate of 11.4 m³/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).

1.1.2.5. Electrolysis System

Olive mill wastewater, which is a toxic liquid, was treated by an electrochemical method using Ti/Pt as anode and Stainless Steel 304 as cathode. In this technique, NaCl 4% (w/v) 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 chemical produced (chlorine, oxygen, hydroxyl radicals and other oxidants) the organic pollutants were wet oxidized carbon dioxide and water. After 1 and 10 h of electrolysis at 0.26 A/cm², total COD was reduced by 41 and 93%, respectively, total TOC was reduced by 20 and 80.4%, VSS were reduced by 1 and 98.7%, and total phenolic compounds were reduced by 50 and 99.4%. Also, the mean energy consumption was 1.273 kwh per kg of COD removed for 1 h and 12.3 kwh per kg of COD removed for 10 h. These results indicate that this electrolytic method of total oxidation of olive oil effluent is not feasible (Israilides et al., 1997, p 163).

1.1.2.6. Evaporation / Distillation

Evaporation and distillation processes have been often used to treat olive mill wastewater. Annesini & Gironi (1991) performed some distillation tests on centrifuged olive mill wastewater, in order to analyze the effect of storage time on the evaporation behavior of this waste. Their experimental data show that the ageing processes cause an increase in the concentrations of volatile compounds. Such behavior can be described in terms of a chemical and a biochemical reaction between a few pseudo-compounds, according to their preliminary model.

Most Mediterranean countries dispose of olive mill wastewater in artificial evaporation ponds. In a study, the qualitative and quantitative evaluation of the phenolic content and the antibacterial properties of these residues are performed during evaporation in simulated evaporation ponds. No antibacterial effect was detectable in subsequent evaporation for 90 days. The evaporation of olive mill vegetation waters permits to pull down the polluting load to an extent superior to the 90% in terms of COD (Di Giacomo et al., 1991, p 249).

In another study, samples of vegetation water from olive mills were separated by evaporation into an aqueous liquid (80-90% of the initial volume), a traditional biological process could then purify that, and a residue in which about 98% of the organic load was concentrated. The properties of the concentrated vegetation water residue and of the olive husk suggested the possibility of using a mixture of the two as an efficient fuel to provide the heat for the evaporation stage (Saez et al., 1992, p 1261).

1.1.2.7. Land Treatment

Direct irrigation of soil with olive mill wastewater to save water and fertilizer has long been proposed. Normally less than 800 m³/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 N₂ 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 odours, insect proliferation, leakages, infiltration and silting with sludges. However, the main problem with evaporation ponds is their insufficient capacity (Cabrera et al., 1996, pp 217-218).

1.1.2.8. Using as Carbon Source

Olive mill wastewater was applied 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 in the treated effluent. Addition of olive mill wastewater was found acceptable only up to 50 mg COD of mill waste/L of wastewater fed to system because at higher additions color problems in the treated effluent were encountered. The required dosage of olive mill wastewater was found to be in the range 4.6-5.4 mg COD/mg N-NO₃ removed. Operation with the olive mill wastewater effects at the same time higher removal of phosphorus (Tsonis, 1997, p 53).

1.1.2.9. Fermentation

Castro & Brenes (2001) studied fermentation of the olive mill wastewaters under acidic conditions throughout a year. When the pH was initially lowered to 3, only yeasts grew and a significant concentration of ethanol was generated. The concentration of phenolic compounds decreased slightly during the fermentation process. Fermentation of vegetation waters under certain conditions may give rise to solutions with no off-odours and a high concentration of lactic acid and hydroxytyrosol, which are economically interesting products.

1.1.2.10. Activated Carbon

In an integrated research program seeking at new materials, stones and a synthetic resin (e.g. phenolic resin) are mixed, then pyrolyzed and activated to use as activated carbon or carbonaceous adsorbent. The research includes the study of pyrolysis, adsorption properties and structure of the carbonaceous products (Demichelli & Bontoux, 1996).

In another study, producing activated carbon from acorns and olive seeds was investigated. *The starting materials are low in cost and they are the cause of solid waste pollution problems in Jordan. A chemical procedure is used to produce the required activated carbon. The results indicate that activated carbon produced from acorns compares favorably with that from olive seeds which rank second, along side commercial type activated carbon which comes last with respect to adsorption capacity. However, the optimum activation temperature is 800 °C and the optimum regeneration temperature is also 800 °C (Lafi, 2001, p 57).*

1.1.2.11. 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 biotransformation products from olive mill wastewater has already been achieved ” (Demichelli&Bontoux, 1996, p 18).

1.1.2.12. 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-[1-(hydroxymethyl)-(E)1-propenyl] glutaric acid and 3-[1-(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).

1.1.2.13. 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).

1.1.2.14. 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. OBJECTIVES 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 follows:

1. To select an effective physical treatment alternative as a pre-treatment method of olive mill wastewater.
2. To select an effective chemical coagulant, acid and alkali for chemical precipitation of olive mill wastewater.
3. To investigate the effects of chemical oxidation methods on olive mill wastewater.
4. To investigate the effects of a new bacteria culture on the treatment of olive mill wastewater.
5. To select the most appropriate wastewater treatment option.

History of olive, olive oil extraction process, and olive oil production amounts in the World and in Turkey are given in Appendix. Characterization study of olive mill wastewater was done and materials and methods, which were applied during experimental studies, are given in Chapter II. Experimental studies and obtained results are given in Chapter III.

In the light of above-mentioned aims, laboratory works for, especially, COD tests were carried out using wastewater produced in six different olive oil mills. Different physical, chemical and biological treatment techniques were applied to wastewater. Experimental studies on treatment alternatives were given.

In the first part of the experimental studies, physical treatment experiments were done. Applied physical treatment studies were filtration experiments, shaker studies, distillation process, aeration and sedimentation experiments. Filtration experiment has not been usually applied for olive mill wastewater. In this thesis, different filter media such as sand filter in 0.85 mm particle diameter, wood shavings filter, filter cloths, and filter paper in 0.80 mm pore diameter were used. The shake flask experiments were carried out in an incubator shaker at 35°C for two weeks without addition of any chemical material. As a third physicochemical treatment study, distillation process was applied to wastewater. A laboratory scale distillation unit was set up in DEU laboratory for experimental studies. The samples were raw wastewater and pretreated wastewater. Samples were boiled until the liquid phase completely evaporated and the vapor was collected after cooled in a condenser unit. In aeration studies, different aeration times were applied to wastewater. In sedimentation experiment, raw wastewater was precipitated without any chemical addition after an hour slow mixing. After all physical treatment experiments, samples were taken to apply COD analysis and then the COD removal efficiencies were calculated for each one.

In chemical precipitation experiments, FeCl_3 , H_2SO_4 , HCl and $\text{Ca}(\text{OH})_2$ were used as coagulant, acid and alkali to treat the raw wastewater. Jar tests were done to

determine the dose of the used chemicals. The most effective chemical and suitable dosages were chosen after chemical treatability studies.

Chemical oxidation is used to convert pollutants to end products or to intermediate products that are more readily biodegradable or removed more readily by adsorption. Application of chemical oxidation methods for treatment of olive mill wastewater has not usually been used. For this reason chemical oxidation experiments were done. In these experiments, manganese sulphate ($MnSO_4$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), sodium hypochlorite ($NaOCl$) were used. Fenton Reagent that is a combination of hydrogen peroxide and ferrous ions was also used in treatability studies.

An inexperienced bacteria species (Oil Gator bacteria), which has not been used in Turkey so far, was examined in bioabsorption experiments. Activity, microbiological behavior and affects on waste removal efficiency of Oil Gator bacteria were unknown parameters. Bacteria were used in experimental studies for different laboratory conditions such as alteration of mixing, aeration and amounts of bacteria. During the biological treatment experiments, Oil Gator bacteria were used in a batch biological reactor for 3 weeks with continues aeration and daily COD measurements were carried out.

CHAPTER TWO

MATERIALS AND METHODS

2.1. Materials

Characterization and treatability studies of the olive mill wastewater from different olive oil processing industries were the main concept of this thesis. The samples were taken between January 1999 and May 2001 time period when the olive oil harvesting and processing season from six olive oil mills. COD, pH, color, oil and grease, suspended solid, nitrogen and phosphorous measurements were carried out on the influent for the characterization studies. Different physical, chemical and biological treatment methods were applied to the effluent samples to find the most suitable treatment method for olive mill wastewater. All 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. Wastewater Discharge Standards of Olive Oil Manufacturing Industry in Turkey are given in Table 2.1.

Table 2.1. Wastewater Discharge Standards of Olive Oil Manufacturing Industry in Turkey

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

2.2. Methods

Physical, chemical and biological treatment experiments were applied to the raw olive oil industry wastewater.

2.2.1. Physical Treatability Experiments

The applied physical treatment methods were filtration, shaking, distillation, aeration and sedimentation.

2.2.1.1. Filtration Experiment

The samples of olive mill effluents from various industries which have different wastewater characteristics were filtered through different kinds of filter materials such as sand filter with 0.85 mm particle diameter, wood shavings with various size, filter clothes and filter paper in 0.80 mm pore diameter. COD and SS concentrations of samples were measured after and before filtration. 1 liter of wastewater was filtered in each filtration methods. No dilution was made to the samples.

2.2.1.2. Shaking Experiment Carried out in Shaker

The shake flask experiments were carried out in an incubator shaker at 35°C and at 100 rpm for two weeks. 500 ml erlenmeyer flasks were filled with raw wastewater without addition of any chemical material. Samples withdrawn everyday were filtered through filter clothe. COD concentration of filtrate was measured.

2.2.1.3. Distillation Experiment

Distillation is the most common separation technique based on the separation of a liquid or vapour mixture of two or more substances to its component fractions of desired purity, by the application and removal of heat, was applied to wastewater. In engineering terminology, the separation of a liquid from a solid by vaporisation is considered evaporation, and the term distillation is reserved for the separation of two or more liquids by vaporisation and condensation.

Distillation process concentrates the organic and inorganic contents of olive mill wastewater by evaporation of the water. The energy to evaporate the water can be provided either by a man-made heat source or by natural source. The more concentrated are the olive mill wastewater, the more economical is the distillation treatment per unit mass of concentrated COD. Several distillation processes, which are already used in desalination and in the chemical and food industries, have been tested on olive mill wastewater: vacuum, multiple effect (to reduce energy requirements); and flash evaporation. The main drawbacks of these processes are related to the post-treatment and disposal of the produced emissions. Disposal of the concentrated paste can be a problem. It can be used as animal feed by taking into consideration of its potassium content. Concentrated paste can be also used to feed the boiler which provides the thermal energy to the distillation plant, but its combustion induces air pollution which has to be dealt with by post-treatment of the gases. The distillate is not made of pure water but carries away appreciable fraction of volatile compounds found in olive mill wastewater such as volatile acids and

alcohols. These compounds are the reason of the high COD of the condensate, which can reach 3 g COD/l, and make necessary an additional treatment of the distillate prior to discharge or reuse. Distillate has to be treated by the most suitable advanced treatment technology (Rozzi & Malpei, 1996).

As a third physicochemical treatment study, distillation process was applied to wastewater. A laboratory scale distillation unit was set up in DEU laboratory for experimental studies. The samples were raw wastewater, pH of wastewater was adjusted to pH = 2 with HCl and pH = 10 with lime and samples was filtered through filter cloth. About 0.6 – 1 L samples were boiled until the liquid phase completely evaporated and the vapor was collected after cooled in a condenser unit. COD concentration was measured in distillate.

2.2.1.4. Aeration

Wastewater samples with 1 L volume were aerated in beakers for 7 hours. An air pump was used for aeration. Samples were collected with 2 hours intervals. No pretreatment was applied to samples before aeration and COD measurements.

2.2.1.5. Sedimentation

Wastewater sample with 2 L volume was precipitated itself after an hour slow mixing. No other chemicals were added to wastewater before and after mixing operation. Supernatant was taken after sedimentation and COD and SS concentrations of supernatant were measured.

2.2.2. Chemical Treatability Experiments

Chemical treatability experiments were carried out on raw wastewater. Following chemical treatment methods were applied:

- Coagulation and flocculation
- Chemical oxidation

2.2.2.1. Coagulation and Flocculation

FeCl_3 , H_2SO_4 , HCl and $\text{Ca}(\text{OH})_2$ were used for coagulation and flocculation to treat the raw wastewater. Jar tests were done to determine the dose of the chemicals.

2.2.2.2. Chemical Oxidation

Chemical oxidation is used to convert pollutants to end products or to intermediate products that are more readily biodegradable or removed more readily by adsorption.

The aim of the chemical oxidation is to transform to a state of harmless of the chemical substances, which is not wanted in the water and in the wastewater treatment.

Chemical oxidation process can be used:

- To remove ammonia,
- To oxidize cyanides,
- To reduce the concentration of residual organics,
- To reduce the bacterial and viral content of the wastewater,
- To destroy residual organics in the wastewater such as phenols, amines, mercaptans, chlorophenols,
- To provide disinfection,
- To potable water treatment,
- To treat toxic organics at low concentrations in groundwater,
- To treat low volume high strength wastewater for detoxification and to enhance biodegradability.

However some organics are resistant to oxidation by most oxidation agents under ambient temperature and pressures and may be required increased temperature, use of a catalyst or use of ultraviolet light. Chemical oxidation is frequently depending on pH and presence of catalysts.

There are some common oxidants capable of meeting most of these requirements:

- Oxygen or Air
- Ozone
- Hydrogen Peroxide
- Potassium Permanganate
- Sodium hypochlorite (Eckenfelder, 1989, p 300).

In chemical oxidation experiments, H_2O_2 , iron salts, manganese sulphate ($MnSO_4$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), sodium hypochlorite ($NaOCl$) were used. Fenton Reagent that is a combination of hydrogen peroxide and ferrous ions was also used in treatability studies.

2.2.3. Biological Treatment Experiments

During the biological treatability studies, Oil Gator bacteria were used.

2.2.3.1. Oil Gator Bacteria

Oil Gator bacteria were discovered in petroleum well at South America. Natural Oil Gator Bacteria were located at 3200-meter depth of petroleum well. Its genetic characterization was changed to be powered via adding waste fiber of cotton plant so those Oil Gator Bacteria were produced. The fibers consisted cellulose materials too.

This bacterium was used for different aims. It is considered that:

- ✓ To adsorb all organic wastes such as high hydrocarbon which has petroleum products,
- ✓ To digest and biodegrade this organic waste,
- ✓ To use in all pH range,
- ✓ To treat the wastewater which has high salinity concentration such as sea water,
- ✓ To reduce as a biological itself after consuming all organic wastes in wastewater.

Oil Gator, which is in cellulose fibers, contains nitrogen and phosphorus that are necessary for natural bacterial living. Bacteria groups, which are incubated to cellulose tubes, are in egg form. When they are inoculated to water, they become activated and increased their number by multiplying rapidly.

The population of bacteria can live with or without oxygen (aerobic and anaerobic conditions). Salinity, low or high pH values of media do not affect to Oil Gator. They can live in all atmospheric conditions. Decreasing heat reduces the activity of Oil Gator but they do not die and freeze.

Oil Gator bacteria covers hydrocarbons to prevent spread of them around and increases biodegradability of hydrocarbons in biological period and converts them into natural manure in a short time (Ptx Petrotex Ind. Inc., USA, 1998).

2.2.3.2. Bioabsorption Experiment with Oil Gator Bacteria

An innovative bacteria species (Oil Gator bacteria), which has not been used in Turkey so far, was examined in bioabsorption experiments. Different amounts of bacteria and different aeration times were applied during bioabsorption studies. The amount of Oil Gator bacteria that would be added into the wastewater was determined according to suspended solid concentration of raw wastewater. Oil Gator concentration was as $\frac{1}{2}$ of suspended solid concentration raw wastewater in all

experiments. No pretreatment and nutrient addition was applied to the raw wastewater. The organisms were directly added into the wastewater sample and then the mixture was mixed approximately 15 minutes. After that it was aerated for 1 and 3 hours. Samples withdrawn at the end of aeration period were filtered through filter paper and COD analyses were done on clear filtrate

2.2.3.3. Biological Treatability Experiment with Oil Gator Bacteria

COD removal performance of Oil Gator bacteria from olive mill effluents was examined in a batch pilot plant unit in the laboratory. The system was aerated continuously for three weeks and daily COD measurements were carried out on the samples.

2.3. Sampling

The quality and quantity of wastewater originating from olive oil production changes depending on technology used in the olive oil production, the age of the olive oil tree and the season of harvest. Therefore, the sampling time and olive oil production process are very important. Sampling date, oil extraction process and location of olive oil producing industries are given in Table 2.2.

Table 2.2. Date, Extraction Process and Location of all Samples which were Taken from Olive Oil Mills

Sample Number	Date	Olive Oil Extraction Processes	Factory Location
I	26.01.1999	Centrifuge	İzmir-Torbalı
II	21.10.1999	Press	İzmir-Bornova
III	09.11.1999	Centrifuge	İzmir-Bornova
IV	23.12.1999	Centrifuge	İzmir-Bornova
V	07.03.2000	Centrifuge	İzmir- Torbalı
VI	27.11.2000	Centrifuge	İzmir- Torbalı

Effluent samples were taken from centrifugation unit of olive oil extraction process of Studied Plant. 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 °C and no pH adjustment was made to keep the samples for a long time, since pH value of samples was around pH = 4.

2.4. Analytical Methods

COD, TOC, pH, color, oil and grease, suspended solid, nitrogen and phosphorous 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 Dichromat Reflux Method according to APHA Standard Methods. Because of high COD value of olive oil wastewater, samples were 1/50 or 1/100 diluted before measurements. 5 ml H₂SO₄ 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 sulphuric acid were added. COD bottles were heated for 2 hours and then cooled to room temperature. Then 80 ml distilled 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 following equation.

$$\text{COD (mg/L)} = \frac{(\text{used FAS for sample} - \text{used FAS for blank}) \times 8000 \times \text{dilution factor}}{\text{ml sample}}$$

2.4.2. TOC Analysis

DOHRMANN DC-190 High Temperature TOC Analyzer was used for TOC measurements.

2.4.3. pH Analysis

pH measurement was done by using 890 MD pH METER.

2.4.4. Suspended Solids Analysis

It was applied by gravimetric method in 0.45 μm pore diameter filter paper model according to 2450 D of Standard Methods (APHA, AWWA, 1992).

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. Nitrogen Analysis

Total Nitrogen was measured by using spectroquant cell test obtained from Merck. For photometric measurement, “Merck Photometer SQ 300 kit” was used.

2.4.7. Phosphorus Analysis

PO₄-P was analysed by using spectroquant cell test obtained from Merck. For photometric measurement, “Merck Photometer SQ 300 kit” was used.

2.4.8. Color Analysis

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

CHAPTER THREE

EXPERIMENTAL RESULTS AND DISCUSSIONS

It was very difficult to characterize olive mill wastewater. Because the wastewater which were used during experimental studies was collected from different mills. With each methods of treatment technology, olive mill wastewater in different characteristics were used. Then different results were achieved after treatability studies, which were done with two different olive mill wastewater using same methods. The samples were taken from different six olive oil mills and numbered from I to VI. Production technology of five plants was centrifuge and the last one was press. Characterization experiments were done for all raw wastewater samples. At the end of characterization of wastewater, it was seen that the COD concentration of wastewater was very high. Therefore in experimental studies, mainly COD tests were carried out and COD removal efficiencies were examined to find the treatability.

3.1. Wastewater Characteristics

Each of the samples has been analysed and wastewater characteristics of these samples are presented in Table 3.1.

COD concentrations of olive mill samples which were used in experimental studies changed from 57 600 mg/L (from centrifuge process) to 168 000 mg/L (from press process). Average value of COD concentration was 120 000 mg/L. pH value of all samples were 3.7 – 5.4. The main characteristics of olive mill wastewater were high COD concentration and low pH value.



Suspended solid concentrations of wastewater were also high. They changed from 8 443 mg/L (from centrifuge process) to 65 536 mg/L (from press process). SS concentration of wastewater from classical olive oil production process was quite higher than from centrifuged process. Oil and grease concentrations of wastewaters were between 1 488 - 2 740 mg/L. All samples had dark brown color. Color value of samples changed from 20 600 to 65 000 Pt-Co unit.

3.2. Treatability Experiments

3.2.1. Physical Treatability Experiments

Application of filtration, centrifugation, adsorption, sedimentation and evaporation on olive mill wastewater as physical treatment methods has been reported (Al-Malah et al., 2000). The effect of filtration, shaking, distillation, aeration, and sedimentation on COD removal was considered as physical and physicochemical treatment of olive oil mill in this study.

3.2.1.1. Effect of Filtration on COD Removal

Filtration processes were applied to only sample II, III, and VI. Different filtration materials such as filter paper, filter cloth, sand filter and wood shavings were used for each sample. COD and suspended solid removal efficiencies were determined.

As a first series of study, sample II was filtered from filter paper in 0.80 mm pore diameter. After filtration, COD concentration of the filtrate was determined, as seen from Table 3.2. The initial COD concentration was 168 000 mg/L and it was decreased to 48 000 mg/L with 71% COD removal efficiency. The main reason of this COD decrease after filtration could be SS concentration in raw wastewater.

Table 3.2. The Treatability Results of Filtration Experiment with Filter Paper

Sample II	COD Concentration (mg / L)	COD Removal Efficiency (%)
Raw wastewater	168 000	-
Wastewater filtered from filter paper	48 000	71

The second sample, on which filtration was applied was sample III. Raw wastewater was filtered through filter paper in 0.80 mm pore diameter, wood shavings and sand filter in 0.85 mm particle diameter. The experimental results are given in Table 3.3. The influent COD concentration of the sample was 124 000 mg/L. The sample was first filtered through 0.45 μm pore size filter paper. However, suspended solids plugged the pores and filtrate was couldn't obtain. This result indicates that the diameter of suspended solid in wastewater is larger than 0.45 μm . After that 0.80 mm pore size filter paper was used. As a result of filtration only 19% COD removal efficiency was obtained with final COD concentration of 100 000 mg/L. This COD removal efficiency is different from first experimental study because of the waste characteristic of raw wastewater. The similar result was observed with filtration through wood shaving. COD removal efficiency was 11 %. The best result was obtained with sand filtration. COD decreased to 84 000 mg/L resulting in 32 % removal efficiency.

Table 3.3. The Treatability Results in Terms of COD of Filtration Experiments that were Carried out with Different Filter Media

Sample III	COD Concentration (mg / L)	COD Removal Efficiency (%)
Raw wastewater	124 000	-
Wastewater filtered from filter paper	100 000	19
Wastewater filtered from wood shavings	110 000	11
Wastewater filtered from sand filter	84 000	32

The effect of filtration technique and centrifugation on suspended solid removal was also investigated on the same sample. The results of experimental studies are depicted in Table 3.4. Raw wastewater was filtered from wood shavings and sand filter in 0.85 mm particle diameter. Suspended solid concentration in raw wastewater was 8 443 mg/L. After application of centrifugation SS concentration decreased to 5 403 mg SS/L. Filtration from sand filter resulted in 8 021 mg/L suspended solid in the filtrate. Similarly using wood shavings as filter material gave around 8 105 mg SS/L for first passage of sample through filter media and 7 599 mg/L SS concentration for the second time resulting in 4% and 10% SS removal efficiency, respectively. Although maximum SS removal efficiency was achieved by centrifugation method (36%), this result does not satisfy Turkish Wastewater Discharge Standards. Further suspended solid removal should be achieved by using advanced treatment techniques.

Table 3.4. The Treatability Results in Terms of SS of Filtration Experiments, which were Carried out with Different Filter Materials

Sample III	SS Concentration (mg / L)	SS Removal Efficiency (%)
Raw wastewater	8 443	-
Centrifuged sample	5 403	36
Wastewater filtered from sand filter	8 021	5
Single filtration through wood shavings	8 105	4
Double filtration through wood shavings	7 599	10

The last sample was sample VI. The effect of several consecutive filtrations through the same filter materials on COD removal was investigated. Although sand filtration resulted the best COD removal efficiency, filter paper was used in this experiment. Because, sand filter plugged with sample VI and no filtrate was collected at all. The filter paper was not changed during filtration and filtrate was filtered again as collected. This procedure was done three times. The decreases in

COD concentration are given in Table 3.5. The COD concentration in the first filtrate was 58 000 mg/L with 37% COD removal efficiency. After the second and third filtration, it was decreased to 56 000 mg/L and 54 000 mg/L giving 39% and 41% removal efficiency, respectively. The results indicated that filtering the samples several times through the same filter media doesn't make a significant decrease in COD concentration.

Table 3.5. COD Concentration and COD Removal Efficiency of Wastewater After Filtration from the Same Filtrate Paper Several Times

Sample VI	COD Concentration (mg / L)	COD Removal Efficiency (%)
Raw wastewater	92 000	-
Wastewater filtered from filter paper once	58 000	37
Wastewater filtered from filter paper twice	56 000	39
Wastewater filtered from filter paper three times	54 000	41

As a last filtration study, sample VI, which had been waiting two months in wastewater laboratory, was filtered from filter paper in 0.80 mm pore diameter and filter clothes, which consist of three clothes. The results of experimental studies are given in Table 3.6. COD concentration in raw wastewater was 80 000 mg/L. Filtration from filter paper resulted in 58 000 mg/L COD concentration in the filtrate with 28% COD removal efficiency. As a result of filtration through filter cloth, 30% COD removal efficiency was obtained with final COD concentration of 56 000 mg/L.

Table 3.6. COD Concentrations of Filtered Wastewaters (sixty days aged) by Using Different Filter Materials

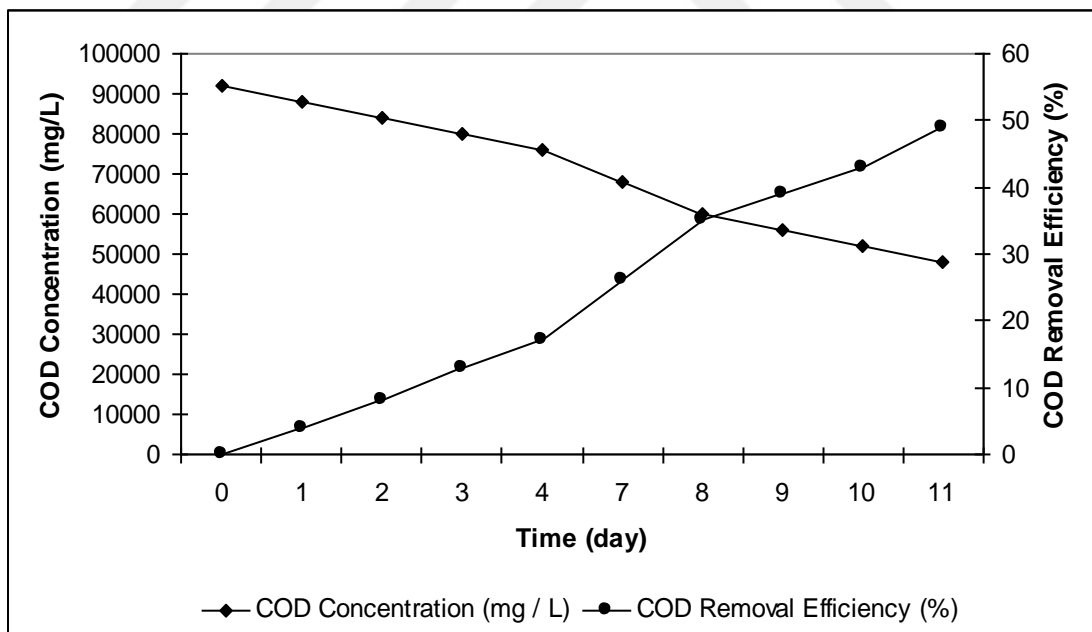
Sample VI	COD Concentration (mg / L)	COD Removal Efficiency (%)
Raw wastewater	80 000	-
Wastewater filtered from filter paper	58 000	28
Wastewater filtered from clothes	56 000	30

3.2.1.2. Experiment Carried out in Shaker

Raw wastewater sample was stayed in the laboratory for two months at room temperature without any operation. It was observed that the wastewater spoiled that is decrease in pH, formation of VOC, flotation of solid materials etc. In the light of these results, effect of shaking on COD removal efficiency was investigated in shake flask experiments. These experiments were carried out with only sample VI in an incubator shaker at 35°C. 500 ml erlenmeyer flasks were filled with raw wastewater and no chemical material was added to flasks. They were shaken for eleven days. Daily samples were taken and filtered through filter cloth to analyze COD concentration. At the beginning, COD concentration of raw wastewater was 92 000 mg/L. There were regular decrease in COD concentration and it reached to 48 000 mg/L with 49 % COD removal efficiency at eleventh day. Dissolved oxygen concentration of sample in shaker was measured as 0.1 mg/L by using DO-meter at the end of the eleventh day. The results of these experiments are given in Table 3.7.

Table 3.7. Daily COD Removal Efficiencies of the Shake Flask Experiments

Time (day)	COD Concentration (mg / L)	COD Removal Efficiency (%)
0	92 000	-
1	88 000	4
2	84 000	8
3	80 000	13
4	76 000	17
7	68 000	26
8	60 000	35
9	56 000	39
10	52 000	43
11	48 000	49

**Figure 3.1. Daily COD Concentration Variation and COD Removal Efficiencies in the Shake Flask Experiments**

3.2.1.3. Distillation Process

Evaporation and distillation processes have been often used to treat wastewater from olive mill effluent (Annesini & Groni, 1991; Rozzi, & Malpei, 1996).

As another physicochemical treatment experiment, distillation unit operation was applied to wastewater. A distillation unit, which was set up in DEU Wastewater Laboratory, was used in experimental studies. Distillation process was applied to samples in number I, III, and VI. About 0.6 –1 L samples were boiled until the liquid phase completely evaporated and the vapor was collected after cooled in a condenser unit. COD concentration was measured in distillate.

As a first distillation study, 600 ml of olive oil industry wastewater from sample number III was distilled in the distillation unit. At the beginning of heating, raw wastewater was boiled at 80-83⁰C. The thermometer always controlled and temperature wasn't changed approximately for an hour. Then suddenly, the temperature increased up to 97-98⁰C and at this point distillation was finished. It took 2.5 hours to finish up the distillation process. The water condensed in the glass flask that is called as distillate was colorless but the residues in distillation unit had a dark brown colour. COD removal efficiency of distillation experiment is given in Table 3.8. COD concentration of raw wastewater was 124 000 mg/L and it reduced to 16 000 mg/L after distillation process resulted in 89% COD removal efficiency. This is the highest COD removal efficiency obtained compared to other pre-treatment methods applied to olive mill wastewaters. That's why, distillation process was used for other olive mill wastewaters collected from different olive oil mills.

Table 3.8. Results of Distillation Experiment in Terms of COD Removal

Temperature °C	Amount of Distillate (ml)	COD Before Distillation (mg/L)	COD After Distillation (mg/L)	COD Removal Efficiency (%)
<80	500	124 000	16 000	87
83-97	440-450			
>97	460			

In another distillation experiment, sample III was concentrated until 30% of the initial volume was obtained as final volume. The 50 ml of distillate was collected throughout the evaporation periodically and COD/TOC concentration of each 50 ml distillate was determined and compared with the composite which was 400 ml. In Table 3.9 and Figure 3.2 COD and TOC values of these collected volumes are reported. COD concentration of raw wastewater was 124 000 mg/L, while TOC concentration was 31 000 mg/L. The COD and TOC values of the first volumes of condensate were quite high. However, in the next volumes these values tended to decrease as the evaporation proceeded. Finally COD and TOC values reached to 6 000 mg/L and 1 475 mg/L, respectively. Almost 95 % removal efficiencies (COD and TOC) were achieved with last four samples.

Table 3.9. COD or TOC Concentrations and COD or TOC Removal Efficiencies of the Distillation Process

Volumes of Distillate (ml)	COD Concentration (mg/L)	COD Removal Efficiency (%)	TOC Concentration (mg/L)	TOC Removal Efficiency (%)
Raw wastewater	124 000	-	31 000	-
0 – 50	43 000	65	10 500	66
50 – 100	20 310	84	5 250	83
100 – 150	10 830	91	2 620	92
150 – 200	7 300	94	1 800	94
200 – 250	6 620	95	1 610	95
250 – 300	6 580	95	1 580	95
300 – 350	6 120	95	1 430	95
350 – 400	6 210	95	1 475	95

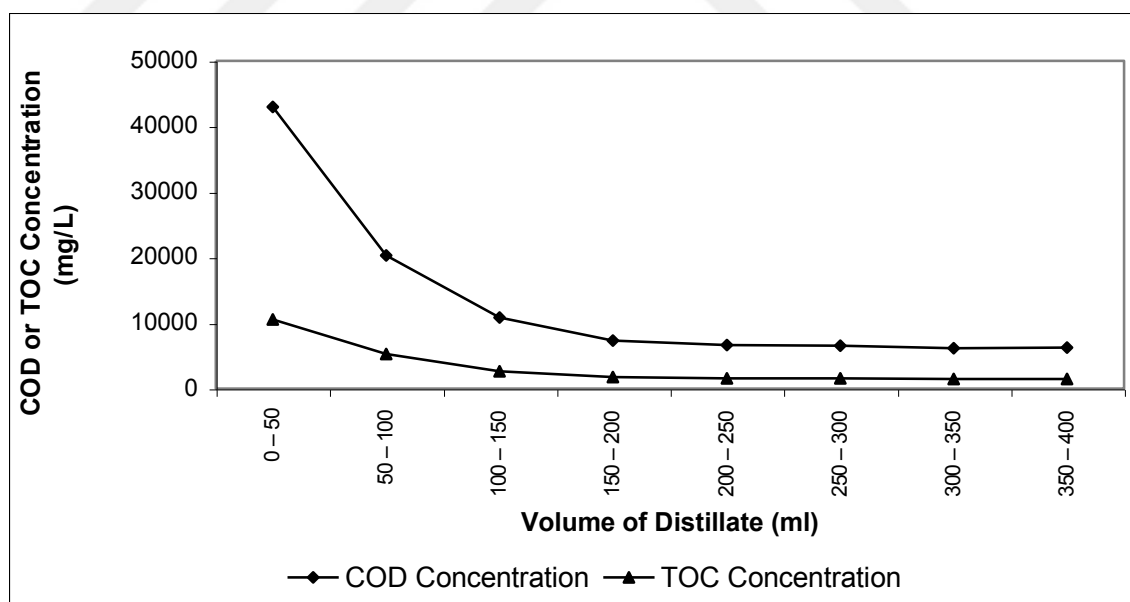


Figure 3.2. COD and TOC Concentrations of the Distillate Obtained from Distillation Process (COD₀=124 000 mg/L; TOC₀=31 000 mg/L)

In another study, 600 ml sample was taken from sample I and distillation process was applied. This sample was boiled at 80°C and first distillate was obtained at 97°C. Distillate was collected in 50 ml volumes. This operation had been continued, when 400 ml of distillate was collected. The TOC values of collected volumes are reported in Table 3.10 and in Figure 3.3. TOC value of raw wastewater was 20 600 mg/L. The TOC value of the first 50 ml volume of distillate was quite high, which was 17 040 mg/L, and then slightly decreased with the consecutive 50 ml samples like 8 130 mg/L, 4 330 mg/L, and 2 940 mg/L. TOC concentration of sample in last volumes was around 2400 mg/L, which means TOC removal efficiencies were up to 88%.

Sample VI was used in another distillation experiment. 600 ml sample was taken from raw wastewater which has 92 000 mg/L COD concentration, and distillation process was applied. While distillation process occurred, 0-100 ml, 100-200 ml and 200-400 ml distillate was taken in different times. Results obtained from distillation experiment are given in Table 3.11 and in Figure 3.4. COD concentration of first 100 ml distillate was 34 000 mg/L, and it was 6 000 mg/L in the next one. Finally, 10 000 mg/L of COD concentration was achieved with 89% COD removal efficiency for the last sample. This increase in COD in the last volume could be because of degradation occurring in the concentrated residue, leading to release of additional organic compounds into the vapors.

Table 3.10. TOC Concentration and TOC Removal Efficiency of Collected Distillates during Distillation Process

Volumes of Distillate (ml)	TOC Concentration (mg/L)	TOC Removal Efficiency (%)
Raw wastewater	20 600	-
0 – 50	17 040	17
50 – 100	8 130	61
100 – 150	4 330	79
150 – 200	2 940	86
200 – 250	2 630	87
250 – 300	2 500	88
300 – 350	2 400	88
350 – 400	2 400	88

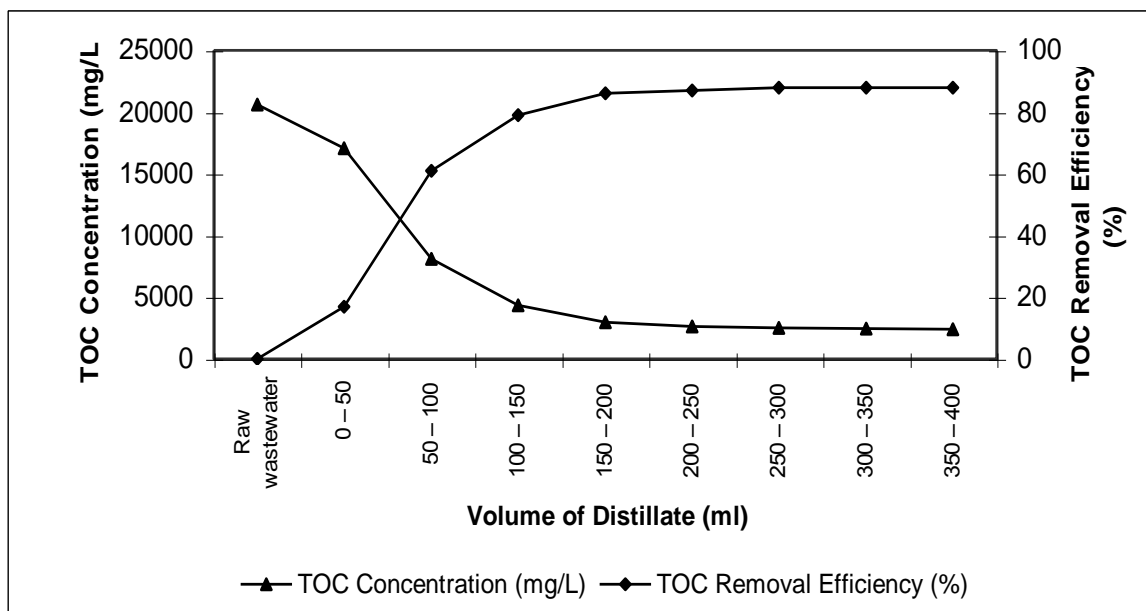


Figure 3.3. TOC Concentration and TOC Removal Efficiencies of Distillates

Table 3.11. COD Concentration and COD Removal Efficiencies of Collected Distillates during Distillation Process

Volumes of Distillate (ml)	COD Concentration (mg/L)	COD Removal Efficiency (%)
Raw wastewater	92 000	-
0 – 100	34 000	63
100 – 200	6 000	93
200 – 400	10 000	89

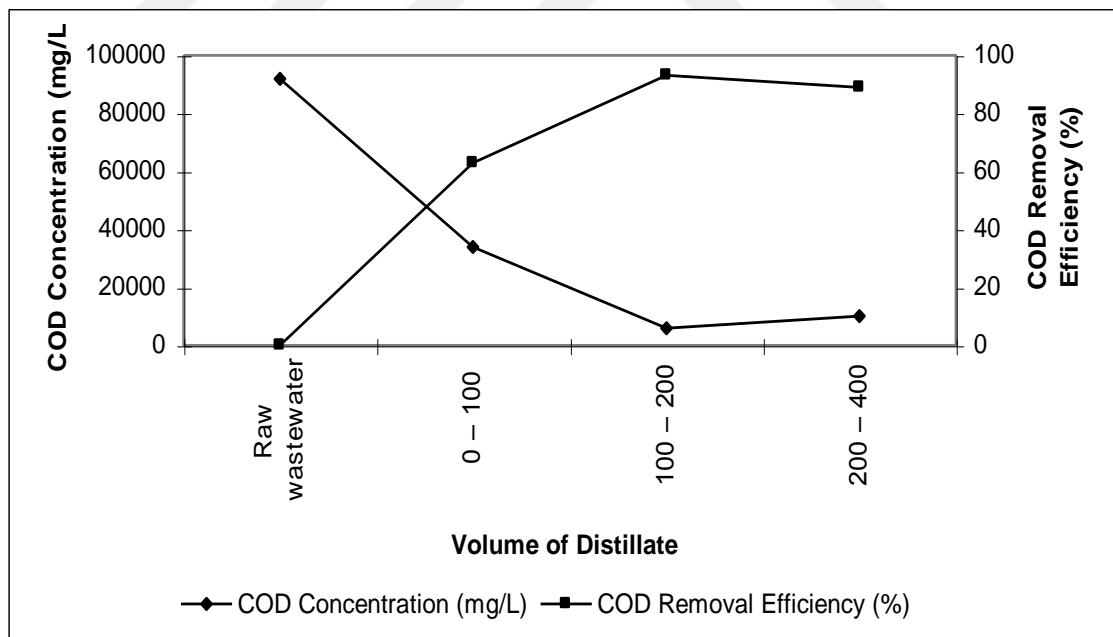


Figure 3.4. COD Concentration and COD Removal Efficiencies of Distillates

In another study with sample VI, the raw wastewater was filtered by filter paper in 0.80 mm pore diameter until 400 ml filtrate was obtained. Distillation process was applied to this filtrate. Two times 100 ml distillate was taken. Initial COD concentration was 92 000 mg/L, after filtration it decreased to 80 000 mg/L. Distillation process was more effective than filtration. After distillation, COD concentration decreased to 40 000 mg/L in the first one and dropped to 24 000 mg/L in the second 100 ml distillate. COD removal efficiencies for distillation were 57% and 74%, respectively. The COD concentration and COD removal efficiencies of the distillate are given in Table 3.12.

Table 3.12. COD Concentration and COD Removal Efficiencies of Filtrated Wastewater and Each Distillate

Sample VI	COD Concentration (mg/L)	COD Removal Efficiency (%)
Raw wastewater	92 000	-
Filtrate	80 000	13
0 – 100 ml distillate	40 000	57
100 – 200 ml distillate	24 000	74

In order to see the effects of acidic condition on distillation process, 2 L sample was taken from sample VI. pH of raw wastewater was pH = 4.5 and it was adjusted to pH=2 by using 50% HCl. Then jar tests were carried out. First, three minutes rapid mixing and then thirty minutes slow mixing were applied. After two hours settling time, the supernatant of sample was taken. Distillation process was applied to this sample and each 50 ml sample of distillate was taken from distillation process. Initial COD concentration was 92 000 mg/L, but it was decreased to 56 000 mg/L by pH adjustment. In the last fraction of distillate, COD was measured between 1 600 – 2 000 mg/L. Experimental results are given in Table 3.13 and Figure 3.5.

Table 3.13. COD Concentration and COD Removal Efficiencies of Wastewater and Each Part of Distillate at pH 2

Sample VI	COD Concentration (mg/L)	COD Removal Efficiency (%)
Raw wastewater	92 000	-
pH = 2	56 000	39
0 – 50 ml distillate	4 200	95
50 – 100 ml distillate	3 600	96
100 – 150 ml distillate	3 100	97
150 – 200 ml distillate	2 500	97
200 – 250 ml distillate	2 100	97
250 – 300 ml distillate	1 600	98
300 – 350 ml distillate	2 000	97
350 – 400 ml distillate	2 000	97

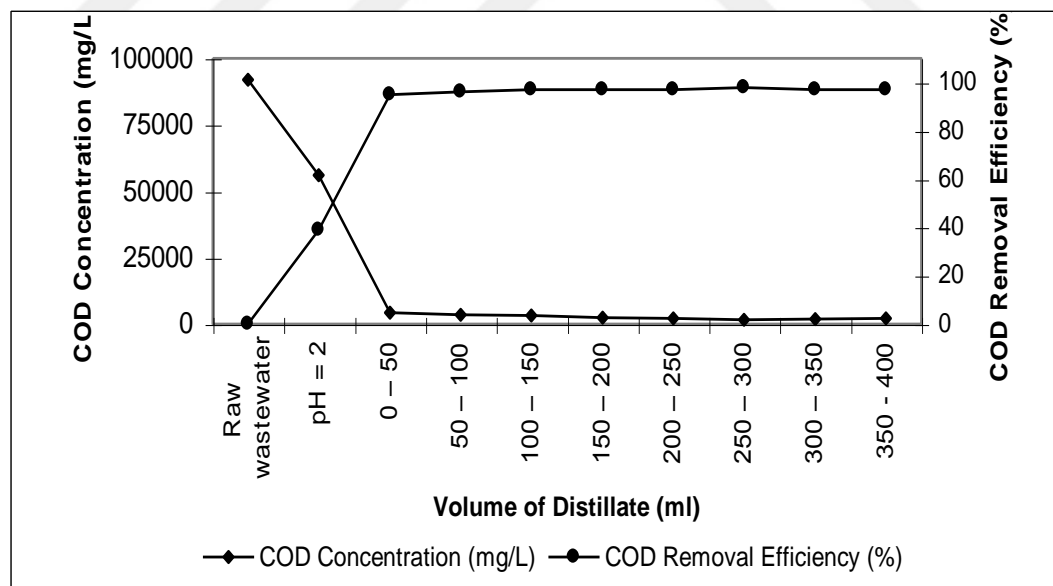


Figure 3.5. COD Concentration and COD Removal Efficiencies of Wastewater and Each Distillate at pH 2

In another distillation experiments with sample VI, pH of the raw wastewater was adjusted from 4.5 to 2 by adding 18 ml /L HCl solution. The raw wastewater was mixed rapidly three minutes and slowly forty-five minutes. After these operations, wastewater was settled for two hours. The supernatant was taken and it was filtered by filter paper in 0.80 mm pore diameter. Distillation tests were performed on filtrated samples in order to separate suspended solids and avoid their cracking during distillation, which may results production of light compounds that affect the distillation. Each 75 ml distillate was taken while distillation was going on. After pH adjustment and filtration, TOC concentration of wastewater was 20 395 mg/L. During the distillation experiment TOC concentration of distillate reduced and finally reached to 470 mg/L. The results of this experiment are presented in Table 3.14 and Figure 3.6.

In the last distillation experiment, sample VI which has 92 000 mg/L COD concentration was used and seeing the effects of acidic and then basic condition on distillation process was aimed. 2 L sample was taken. pH was adjusted from 4.5 to 2 by adding 18 ml/L HCl (1:1 concentrated solution) then jar test was carried out and supernatant of sample was taken. COD concentration of supernatant was 56 000 mg/L. Then, pH was adjusted to 10 by adding 10 % (w/v) $\text{Ca}(\text{OH})_2$. No settling was observed at pH=7, 8, and 9. Therefore experiments was conducted at pH=10. After these adjustments, three minutes rapid mixing and then an hour slow mixing were applied. After mixing, sample was settled for two hours. Distillation process was carried out with the supernatant of sample that was taken from settling tank and has 32 000 mg/L COD concentration. During the distillation process COD concentration of distillate changed from 2 400 mg/L to around 1 500 mg/L. Obtained results are given in Table 3.15 and Figure 3.7.

Table 3.14. TOC Concentration and TOC Removal Efficiencies of Filtered Wastewater and Each Part of Distillate at pH 2

Sample VI	TOC Concentration (mg/L)	TOC Removal Efficiency (%)
Filtrate	20 395	-
0 – 75 ml distillate	16 905	17
75 – 150 ml distillate	4 520	78
150 – 225 ml distillate	910	96
225 – 300 ml distillate	470	98

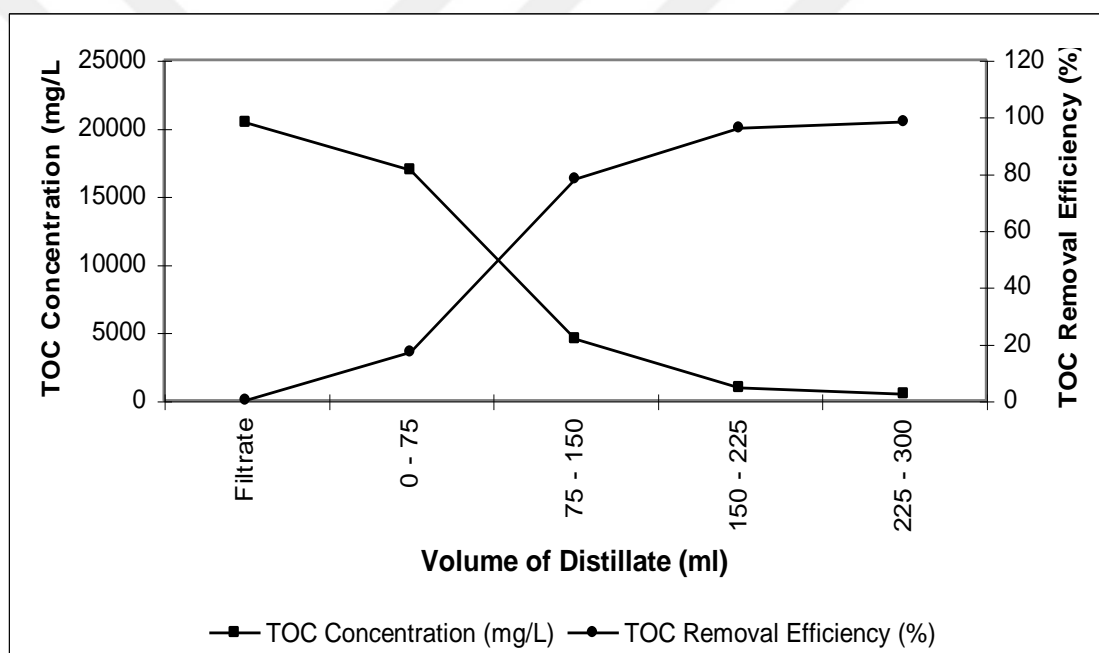


Figure 3.6. TOC Concentration and TOC Removal Efficiencies of Filtered Wastewater and Each Part of Distillate at pH 2

Table 3.15. COD Concentrations of Filtrate Which has pH=2 and pH=10 Values and Each Part of Distillate

Sample VI	COD Concentration (mg/L)	COD Removal Efficiency (%)
Raw wastewater	92 000	-
pH=2	56 000	39
pH=10	32 000	65
0 – 50 ml distillate	2 400	97
50 – 100 ml distillate	2 100	98
100 – 150 ml distillate	1 800	98
150 – 200 ml distillate	1 500	98
200 – 250 ml distillate	1 200	99
250 – 300 ml distillate	1 000	99
300 – 350 ml distillate	1 100	99
350 – 400 ml distillate	1 500	98

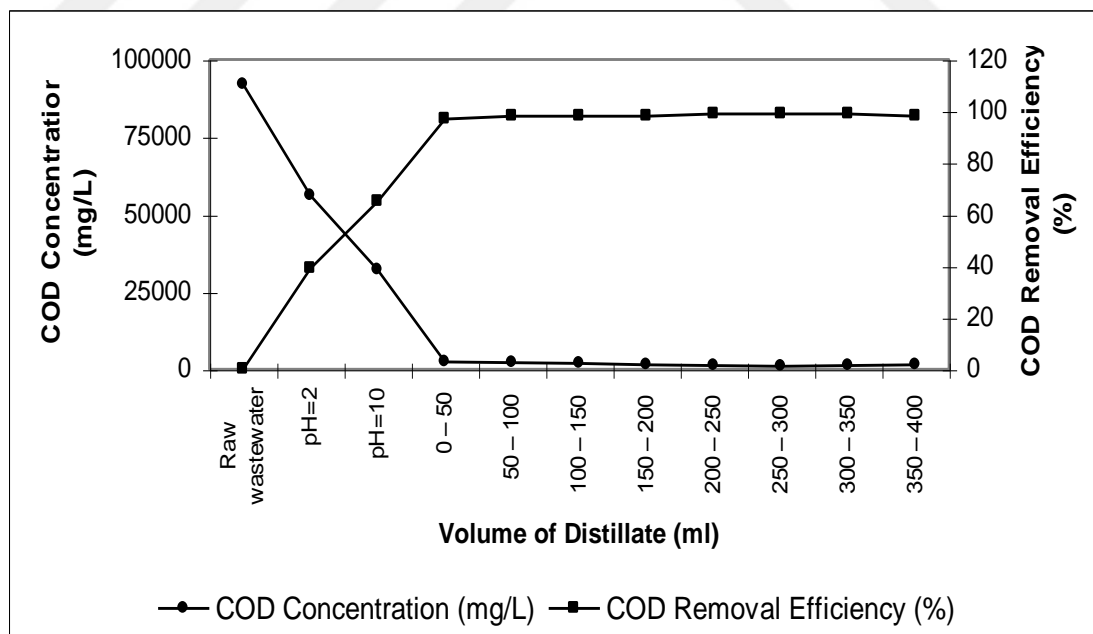


Figure 3.7. COD Concentrations of Filtrate which has pH=2 and pH=10 Values and Each Part of Distillate

Energy Consumption in Distillation Process

- ✓ Power of the heater, which was used during distillation process, was 600 watt and distillation process was kept on 2.5 hours for 2 L wastewater sample.
- ✓ At the end of distillation process, energy consumption of distillation process was calculated as follows;

Energy Consumption of Distillation Process (EC) =

Power of the heater * Reaction Time

$$EC = 600 \text{ watt} * 2.5 \text{ hours} = 1500 \text{ Wh} = 1.5 \text{ kWh} / 2 \text{ L sample}$$

- ✓ Unit price of electric, which was used, for distillation process was 0.0768 cent/kWh, so price of electric consumption in this process was calculated as follows;

Total Price of Electric Consumption (TP) = Unit price of electric *

Energy consumption of distillation process

$$TP = 0.0768 \text{ cent} / \text{kW hour} * 1.5 \text{ kW hour} * (1 / 2 \text{ L}) * 10^{+3} \text{ (L/m}^3\text{)}$$

$$TP = 57.5 \text{ \$} / 1 \text{ m}^3 \text{ wastewater}$$

During olive oil production, 1 m³ olive mill wastewater raises from 1 m³ olive oil. Price of 1 L olive oil is 2 \$. It is equivalent to 2000 \$ for 1 m³ olive oil. Treatment cost of 1 m³ olive mill wastewater is approximately 58 \$ when distillation method is used. While 2000 \$ are obtained by sale of 1 m³ olive oil, 58 \$, which are used for the treatment of 1 m³ olive mill wastewater, are quietly seemed to be cheap and preferable.

3.2.1.4. Effect of Aeration on COD Removal

Since COD removal by distillation technique gave efficient results, effect of aeration, which may provide evaporation of some VOC, was applied. pH of sample V was increased from 3.5 to 7 with the addition of 10 % Ca(OH)₂ solution in order to achieve neutral pH. The wastewater was aerated between 1 and 5 hours and samples were collected at the end of aeration period. Initial COD concentration was 108 000 mg/L. Up to 3 hours aeration, COD concentration of treated wastewater was obtained around 80 000 mg/L. As the aeration period was extended 5 hours, COD concentration decreased to around 72 000 mg/L with maximum COD removal efficiency of 33%. Increasing the aeration time was slightly increased COD removal efficiency (Table 3.16).

Table 3.16. COD Removal Efficiency of Aeration Obtained by Sample V

Aeration Time (h)	Initial pH	Treated Water pH	COD Before Treatment (mg/L)	COD After Aeration(mg/L)	COD Removal Efficiency (%)
1	3.5	7	108 000	84 000	22
2	3.5	7	108 000	84 000	22
3	3.5	7	108 000	80 000	26
4	3.5	7	108 000	76 000	30
5	3.5	7	108 000	72 000	33

Sample VI was also aerated. pH value of raw wastewater was increased from 4.5 to 7 with the addition of 10 % Ca(OH)₂ solution. Different aeration times were applied to wastewater. Samples were taken in each two hours and COD concentrations of these samples were measured. Results are given in Table 3.17. COD concentration of raw wastewater was 92 000 mg/L. After two hours aeration period, it didn't change significantly. But at the end of the seventh hours it decreased to 52 000 mg/L resulting in 43% COD removal efficiency. Compared to previous

experiment better COD removal efficiency was obtained. This difference could be because of different raw wastewater characteristics.

Table 3.17. COD Removal Efficiency of Aeration Obtained by Sample VI

Aeration Time (h)	Initial pH	Treated Water pH	COD Before Aeration (mg/L)	COD After Aeration (mg/L)	COD Removal Efficiency (%)
2	4.5	7	92 000	92 000	-
4	4.5	7	92 000	87 000	5
6	4.5	7	92 000	76 000	17
7	4.5	7	92 000	52 000	43

3.2.1.5. Sedimentation

Sample I was used in sedimentation experiment. Wastewater precipitated itself after an hour slow mixing and two hours settlement. No other chemical was added before and after mixing. Supernatant was taken and COD and SS analyses were carried out. The results are given in Table 3.18. COD concentration of wastewater reduced to 42 400 mg/L with 26% COD removal efficiency. SS concentration also decreased. Initial SS concentration was 12 950 mg/L and it decreased to 7 950 mg/L after sedimentation. Lower COD removal efficiencies were obtained than that of other physicochemical treatment methods studied.

Table 3.18. Wastewater Characteristic of First Sample After Sedimentation Experiment

Parameter	Before Treatment	After Treatment	COD Removal Efficiency (%)
COD (mg/L)	57 600	42 400	26
SS (mg/L)	12 950	7 950	39

General Evaluations for Physical and Physicochemical Treatment Methods

Sample VI was tested with all physical and physicochemical treatment methods. Therefore the results are given in Table 3.19 and in Figure 3.8 for comparison purpose. Only sample I was used in sedimentation experiment. As seen from Table 3.19, the maximum COD removal efficiency was obtained by pH correction, and then distillation process (99 %). COD removal efficiency was around 41- 49 % with filtration, aeration and shaking experiments. The lowest treatment efficiency was 26 %, and obtained from sedimentation. As a result of all physical and physicochemical experiments, it can be said that, distillation process could be applied to olive mill wastewaters for COD removal.

Table 3.19. Maximum Removal Efficiencies after Physical and Physico-Chemical Treatment Experiments

Method	Explanation	COD Removal Efficiency (%)
Filtration (for sample VI)	Through filter paper in 0.80 mm pore diameter	41
Shaking (for sample VI)	At the end of the eleventh day	49
Distillation (for sample VI)	Flow diagram: pH correction to 2 +pH correction to 10 + distillation	99
Aeration (for sample VI)	After 7 hours aeration	43
Sedimentation (for sample I)	After coagulation-flocculation and precipitation	26

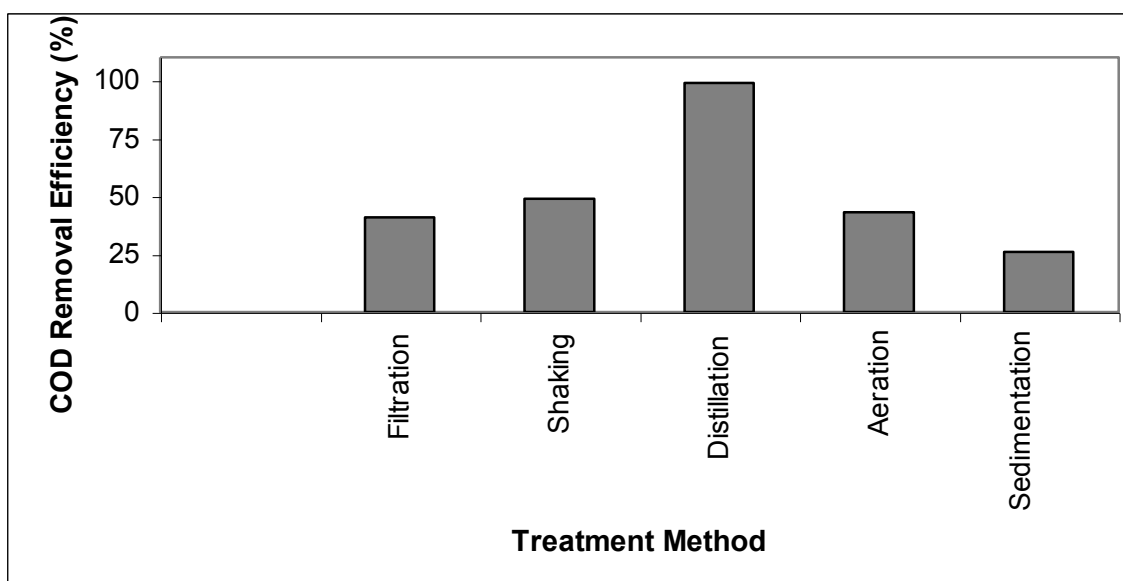


Figure 3.8. Maximum Removal Efficiencies Obtained from Different Physical and Physicochemical Treatment Experiments

3.2.2. Chemical Treatability Experiments

Chemical treatment, especially chemical precipitation is applied for olive mill wastewater as a pre-treatment method. (Aktas et al., 2001; Lolos et al., 1994).

Chemical treatability experiments were carried out on raw wastewater. Applied chemical treatment processes were; chemical oxidation, coagulation and flocculation.

3.2.2.1. Coagulation and Flocculation Experiments

Generally calcium hydroxide, magnesium sulfate, aluminum sulfate, ferrus ions, and sulphuric acid are used for coagulation and flocculation.(Tsonis et al., 1989). FeCl_3 , H_2SO_4 , HCl and $\text{Ca}(\text{OH})_2$ were used as coagulant, acid and alkali to treat the raw wastewater.

3.2.2.1.1. Experimental Studies with $[\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}]$

FeCl_3 was added to sample V as a coagulant in different doses between 300-500 mg/L. pH value of wastewater was increased from 3.5 to 9 with the addition of 10 % $\text{Ca}(\text{OH})_2$ solution. $\text{Ca}(\text{OH})_2$ consumption was 300 ml/L of wastewater. Then jar tests were carried out. First, three minutes rapid mixing and then thirty minutes slow mixing were applied. After two hours settling, COD tests were made on the supernatant. Results of this experiment are given in Table 3.20. The removal efficiency of FeCl_3 was increased with increasing FeCl_3 doses. Initial COD concentration was 108 000 mg/L for sample VI. COD concentration of wastewater after adding 300 mg/L FeCl_3 was 95 000 mg/L. It decreased to 86 000 mg/L and 76 000 mg/L by adding 400 mg FeCl_3 /L and 500 mg FeCl_3 /L, respectively. The results indicated that FeCl_3 is an effective coagulant for COD removal from olive mill wastewater at high doses.

Table 3.20. COD Removal Efficiency of Coagulation Experiments with FeCl_3 Carried out with Sample number V

Sample V	Dosage of FeCl_3 (mg/L)	COD (mg/L) Before Treatment	COD (mg/L) After Treatment	COD Removal Efficiency (%)
1	300	108 000	95 000	12
2	400	108 000	86 000	20
3	500	108 000	76 000	30

Because FeCl_3 gave sufficient removal efficiencies at high doses, the same experiment was repeated with the sample VI, only high dosage was added to the raw wastewater (Table 3.20). pH value of the raw wastewater was 4.5 and the first operation was to increase the pH value around 8-9 with the addition of 10 % $\text{Ca}(\text{OH})_2$ solution. $\text{Ca}(\text{OH})_2$ consumption was 250 ml/L of wastewater. Then 500 mg/L $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ was added to wastewater and jar test was carried out. Three

minutes rapid mixing followed by thirty minutes slow mixing, and 2 hours for settling. Then supernatant was taken and analysed. COD concentrations in initial and treated wastewater are given in Table 3.21. COD value of the sample number VI was 92 000 mg/L. After treatment it decreased to 63 000 mg/L. The same result with previous experiment was obtained that COD removal efficiency was about 32%.

Table 3.21. COD Removal Efficiency of Coagulation Experiments with FeCl₃

Sample VI	COD Concentration (mg/L)	COD Removal Efficiency (%)
Raw wastewater	92 000	-
Treated water with the addition of FeCl ₃ .6H ₂ O	63 000	32

As a third study, sample VI, which has 92 000 mg/L COD concentration and 4.5 pH value was filtered from filter paper in 0.80 mm pore diameter. pH value was increased to around pH=6-7 with the addition of 10 % Ca(OH)₂ solution in order to reach neutral pH. Then 500 mg/L FeCl₃.6 H₂O was added to wastewater and jar test was carried out. After settlement, supernatant was taken and COD concentration was measured. As seen from Table 3.22, after filtration, COD concentration was 56 000 mg/L and decreased to 47 000 mg/L after treatment with FeCl₃.6 H₂O. Filtration positively affected COD removal efficiency.

Table 3.22. COD Removal Efficiency of Coagulation Experiments with FeCl₃ on Filtrated Wastewater

Sample VI	COD Concentration (mg/L)	COD Removal Efficiencies (%)
Raw wastewater	92 000	-
Filtrated wastewater	56 000	43
Filtrate with adding FeCl ₃ .6H ₂ O	47 000	50

3.2.2.1.2. Experimental Studies with Ca(OH)₂

Only Ca(OH)₂ itself also made a coagulation effect on wastewater. In order to evaluate the effect of Ca(OH)₂ on COD, SS, oil and grease removal from olive mill effluent, jar test was done with Ca(OH)₂ using Sample I. pH value was increased gradually from 5.4 to 10 with total 4 g/L Ca(OH)₂. Effective settlement was not observed at pH 7, 8 and 9. At pH value 10, precipitation was obtained. Then jar tests were carried out. Three minutes rapid mixing followed by an hour slow mixing, 2 hours for settling. The characteristics of wastewater were analyzed. The results are given in Table 3.23. COD value decreased from 57 600 mg/L to 50 400 mg/L. COD removal was not so effective compare to other pre-treatment methods. SS concentration was reduced from 12 950 mg/L to 8 900 mg/L. Maximum removal efficiency was achieved in SS concentration. Oil-grease concentration was also decreased from 1 488 mg/L to 1 282 mg/L. The results showed that Ca(OH)₂ couldn't be used as coagulant in the treatment of olive oil industry wastewater. Also it can be concluded that single treatment method could not be sufficient enough to meet the standards.

Table 3.23. Removal Efficiencies Obtained with Ca(OH)₂ Addition

Parameter	Before Treatment	After Treatment	Removal Efficiency (%)
pH	5.4	10.00	-
COD (mg/L)	57 600	50 400	13
SS (mg/L)	12 950	8 900	31
Oil and Grease (mg/L)	1 488	1 282	14

3.2.2.1.3. Experimental Studies with HCl

First experiment was carried out with the sample number I that has a 57 600 mg/L COD concentration. pH value of the raw wastewater was 5.4 and the first operation was to decrease the pH value to 2 with the addition of 6 ml/L HCl (50 % pure). Then jar tests were carried out. Three minutes rapid mixing followed by an hour slow mixing, and 2 hours waiting. The colour of wastewater brightened after this study. The results are given in Table 3.24. COD concentration reduced to 36 000 mg/L with 38% COD removal efficiency. In acidic condition, oil emulsion was broken and free oil was collected at the surface of wastewater. This operation increased the removal efficiencies in all parameter studied. SS and oil and grease removal efficiencies were 79 % and 23%, respectively. Maximum removal efficiency was achieved in colour removal.

Table 3.24. Removal Efficiencies Obtained with HCl Addition

Parameter	Before Treatment	After Treatment	Removal Efficiency (%)
pH	5.37	2.00	-
COD (mg/L)	57 600	36 000	38
SS (mg/L)	12 950	2 700	79
Oil and Grease (mg/L)	1 488	1 150	23
Colour (Pt-Co unit)	58 000	9 600	84

Experimental studies with $\text{Ca}(\text{OH})_2$ and HCl showed that removal efficiencies are higher at acidic condition than that at alkali condition. In order to see the effect of lower pH values on the treatment, different pH values such as 4, 3, 2 were applied by adding H_2SO_4 . COD concentration of wastewater was 57 600 mg/L and pH value was 5.37. Then jar test was carried out. Three minutes rapid mixing followed by forty-five minutes slow mixing, and 2 hours waiting. Supernatants were taken and COD concentrations were measured. COD concentration and COD removal efficiencies obtained at different pH values are presented in Table 3.25. Decreasing

the pH value also decreased COD concentration. 52 800 mg/L, 48 800 mg/L, 36 000 mg/L COD concentrations were measured at 4, 3, and 2 pH levels, respectively.

Table 3.25. COD Removal Efficiencies at Different pH

pH	COD (mg/L) Before Treatment	COD (mg/L) After Treatment	COD Removal Efficiency (%)
5.37	57 600	57 600	-
4.00	57 600	52 800	1
3.00	57 600	48 800	15
2.00	57 600	36 000	38

3.2.2.1.4. Experimental Studies Carried out with HCl and Ca(OH)₂

This experiment was carried out with the sixth wastewater sample. pH value of wastewater was decreased from 4.5 to 2 with the addition of HCl (18 ml/L concentrated solution), because maximum removal efficiency was obtained at pH = 2 in the previous experiments. Then jar test was carried out. After the settlement, supernatant was taken. Since at neutral pH level, precipitation was not observed, pH value of sample was increased from 2 to 10 by using of 8 g/L Ca(OH)₂. The results of this experiment can be seen in Table 3.26. Initial COD concentration was 92 000 mg/L. When pH value was 2, the efficiency was 42%, in alkali condition, COD removal efficiency was 55% with 41 000 mg/L COD concentration in effluent.

Table 3.26. Removal Efficiencies with addition of HCl and Ca(OH)₂

pH	COD (mg/L) Before Treatment	COD (mg/L) After Treatment	COD Removal Efficiency (%)
4.6 (raw wastewater)	92 000	92 000	-
2	92 000	53 000	42
10	92 000	41 000	55

General Evaluations for Chemical Coagulation and Flocculation Experiments

Maximum COD removal efficiencies after chemical coagulation, flocculation and precipitation studies with different chemicals were depicted in Table 3.27 and Figure 3.9. After chemical coagulation and flocculation experiment with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 32% COD removal efficiency was achieved. Efficiency of chemical precipitation study with $\text{Ca}(\text{OH})_2$ didn't give sufficient result. In acidic condition better results were obtained. After precipitation with HCl, 38 % COD removal efficiency was achieved. Maximum removal efficiency was obtained first acidic and then alkali condition with 55% COD removal efficiency.

Table 3.27. Maximum COD Removal Efficiencies after Chemical Precipitation Studies with Different Chemicals

Chemicals	pH Level	COD Removal Efficiency (%)
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	8-9	32
$\text{Ca}(\text{OH})_2$	10	13
HCl	2	38
HCl and $\text{Ca}(\text{OH})_2$	Firstly 2 and then 10	55

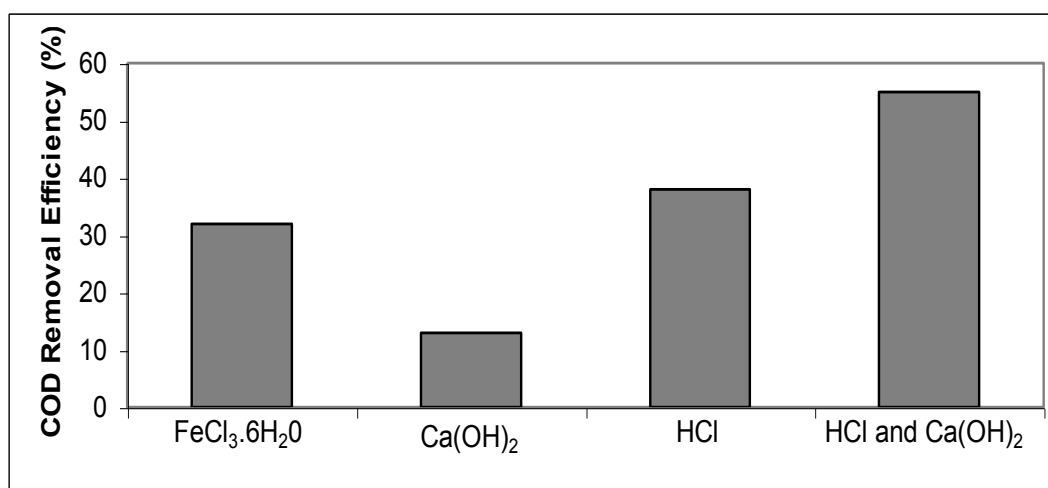


Figure 3.9. Maximum COD Removal Efficiencies after Chemical Precipitation Studies with Different Chemicals

3.2.2.2. Chemical Oxidation Experiments

In chemical oxidation experiments, manganese sulphate (MnSO_4), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl), and Fenton ($\text{H}_2\text{O}_2 + \text{FeSO}_4$) were used. Chemical oxidation experiments were applied to only samples V, and VI.

3.2.2.2.1. Experimental Studies Carried out with Catalytic Oxidation Using MnSO_4 Catalyst

In order to see the effects of catalyst addition during aeration, this experiment was carried out. After pH was increased from 3.5 to 9 with the addition of 300 ml/L, 10% $\text{Ca}(\text{OH})_2$ solution to the wastewater. MnSO_4 was added in different doses, and then the wastewater was aerated for 7 hours and samples were taken with 2 hours interval. Results were not significantly different from aeration experiment. The results are given in Table 3.28. Maximum COD reduction was achieved after 5 hours. The initial COD concentration was 108 000 mg/L and it was decreased to 60 000 mg/L with 44% COD removal efficiency at the end of the 7 hours aeration. The results indicated that increasing in aeration time resulted in increase in COD removal efficiency.

Table 3.28. COD Removal Efficiency of Catalytic Oxidation by Using MnSO_4 Catalyst (with Sample V)

Aeration Time (h)	MnSO_4 Dosage (mg/L)	Initial pH	Treated Water pH	COD Before Treatment (mg/L)	COD After Treatment (mg/L)	COD Removal Efficiency (%)
1	300	3.5	9	108 000	68 000	37
3	300	3.5	9	108 000	64 000	41
5	300	3.5	9	108 000	62 000	43
7	300	3.5	9	108 000	60 000	44

In the same experiment with sample VI, pH was increased from 4.5 to 9 with the addition of 250 ml/L, 10% Ca(OH)₂ solution. MnSO₄ was added in different doses, and then the wastewater was aerated at different durations. The results of experimental studies were depicted in Table 3.29. The COD concentration of raw wastewater was 92 000 mg/L. After application of 7 hour aeration by using MnSO₄ catalyst, COD concentration decreased to 56 000 mg/L with 39% COD removal efficiency. These results were similar with other aeration experiments with or without catalyst addition.

Table 3.29. COD Removal Efficiency of Catalytic Oxidation by Using MnSO₄ Catalyst (with Sample VI)

Aeration Time (h)	MnSO ₄ Dosage (mg/L)	Initial pH	Treated Water pH	COD Before Treatment (mg/L)	COD After Treatment (mg/L)	COD Removal Efficiency (%)
2	300	4.5	9	92 000	72 000	22
4	300	4.5	9	92 000	68 000	26
6	300	4.5	9	92 000	60 000	35
7	300	4.5	9	92 000	56 000	39

3.2.2.2.2. Experimental Studies Carried out with KMnO₄

pH was increased from 3.5 to 9 with the addition of 300 ml/L 10% Ca(OH)₂ solution to the sample number V. 100 or 200 mg/L KMnO₄ and 2 or 4 hours aeration times were applied to raw wastewater. Results are summarized in Table 3.30. Initial COD concentration was 108 000 mg/L. As a result of 4 hours aeration time and 200 mg/L KMnO₄ dosage, 56% COD removal efficiency was obtained with final COD concentration of 48 000 mg/L. After chemical oxidation study with KMnO₄ it could be said that, high aeration time and high KMnO₄ dosage caused high COD removal efficiency.

**Table 3.30. COD Removal Efficiency of Chemical Oxidation with KMnO₄
(with Sample V)**

Aeration Time (h)	KMnO₄ Dosage (mg/L)	Initial pH	Treated Water pH	COD Before Treatment (mg/L)	COD After Treatment (mg/L)	COD Removal Efficiency (%)
2	100	3.5	9	108 000	68 000	37
4	100	3.5	9	108 000	60 000	44
2	200	3.5	9	108 000	65 000	40
4	200	3.5	9	108 000	48 000	56

pH was increased from 4.5 to 9 with the addition of 250 ml/L, 10% Ca(OH)₂ solution to sample VI. 200 mg/L KMnO₄ was added to sample because it was seen from previous study that 200 mg/L KMnO₄ gave better removal efficiency. 2 or 4 hours aeration times were applied. Results are given in Table 3.31. Maximum COD removal efficiency as 52% was obtained after 4 hours aeration with 44 000 mg/L final COD concentration. In this study, increasing aeration time resulted in increase in COD removal efficiency.

Table 3.31. COD Removal Efficiency of Chemical Oxidation with KMnO₄ (with Sample VI)

Aeration Time (h)	KmnO₄ Dosage (mg/L)	Initial pH	Treated Water pH	COD Before Treatment (mg/L)	COD After Treatment (mg/L)	COD Removal Efficiency (%)
2	200	4.5	9	92 000	64 000	30
4	200	4.5	9	92 000	44 000	52

3.2.2.2.3. Experimental Studies with H₂O₂

H₂O₂ is a powerful oxidizing agent generally used to oxidize hardly degradable compounds (Eckenfelder, 1989). Different aeration times and different H₂O₂ doses were used in this experiment. Since H₂O₂ interfere with COD analysis, small amounts of H₂O₂ have to be used in the experiments.

Different doses of H₂O₂ (50-200 mg/L) applied to fifth wastewater sample, which has 3.5 pH value. Then jar tests were carried out for each sample. Three minutes rapid mixing followed by forty-five minutes slow mixing, and 2 hours settling. Then supernatant was taken and COD concentrations of this water were examined. The results are given in Table 3.32. Initial COD was 108 000 mg/L. After 50 mg/L H₂O₂ addition, COD was decreased to 48 000 mg/L with 56% COD removal efficiency. This was maximum COD removal efficiency, which was achieved during chemical oxidation experiments with H₂O₂. When H₂O₂ dose was increased, COD concentration was increased due to interference of H₂O₂ with COD measurement method. Resulting COD concentrations were 60 000 mg/L, 65 000 mg/L, 68 000 mg/L after addition of 100 mg/L, 150 mg/L, 200 mg/L H₂O₂.

Table 3.32. COD Removal Efficiency of Chemical Oxidation with H₂O₂ (with Sample V)

Sample V	H ₂ O ₂ Dosage (mg/L)	Initial pH	Treated Water pH	COD Before Treatment (mg/L)	COD After Treatment (mg/L)	COD Removal Efficiency (%)
1	50	3.5	3.5	108 000	48 000	56
2	100	3.5	3.5	108 000	60 000	44
3	150	3.5	3.5	108 000	65 000	40
4	200	3.5	3.5	108 000	68 000	37

For sample VI, pH was adjusted from 4.5 to 3.5 with HCl (8 ml/L concentrated solution). Since maximum COD removal efficiency was achieved by using 50 mg/L H₂O₂ for first treatment experiments, 50 mg/L H₂O₂ was added to this sample. Then the wastewater was aerated for different periods. The results were given in Table 3.33. Maximum COD removal efficiency was 60 % with 37 000 mg/L COD concentration in effluent was achieved after 6 hours aeration. Using low H₂O₂ doses and long aeration time, high COD removal efficiencies could be obtained.

Table 3.33. COD Removal Efficiency of Chemical Oxidation with H₂O₂ (with Sample VI)

Aeration Time (h)	H ₂ O ₂ Dosage (mg/L)	Initial pH	Treated Water pH	COD Before Treatment (mg/L)	COD After Treatment (mg/L)	COD Removal Efficiency (%)
2	50	4.5	3.5	92 000	48 000	48
4	50	4.5	3.5	92 000	41 000	55
6	50	4.5	3.5	92 000	37 000	60

3.2.2.2.4. Experimental Studies with NaOCl

pH value of the wastewater was increased from 3.5 to 9 with the addition of 300 ml/L, 10 % Ca (OH)₂ solution to the sample V, before starting the experiments. After pH adjustment of sample, different NaOCl doses were added into pH adjusted sample and jar test was carried out. Five minutes rapid mixing was followed by forty-five minutes slow mixing and two hours settling. Then samples were taken and COD analyses were made. COD removal efficiencies were calculated for each sample. Results can be seen in Table 3.34. Initial COD concentration was 108 000 mg/L and maximum COD removal efficiency, which was 45% with 60 000 mg/L COD concentration was achieved after adding 20 mg/L NaOCl. Increasing dosage of NaOCl also increased COD removal efficiency.

Table 3.34. COD Removal Efficiency of Chemical Oxidation with NaOCl (with Sample V)

Sample V	Initial pH	Adjusted pH for NaOCl	NaOCl Dosage (ml/L)	COD Before Treatment (mg/L)	COD After Treatment (mg/L)	COD Removal Efficiency (%)
1	3.5	9	5	108 000	80 000	26
2	3.5	9	10	108 000	72 000	33
3	3.5	9	15	108 000	64 000	41
4	3.5	9	20	108 000	59 000	45

For the sample VI, pH value of the wastewater was adjusted from 4.5 to 9 with the addition of 250 ml/L, 10 % Ca (OH)₂ solution. Then, different doses of NaOCl were added and jar test was carried out. After jar test, samples were taken from supernatant and COD analyses were made. Results are given in Table 3.35. The same results with previous experiment were achieved. Maximum COD removal efficiency (52%) also obtained with 20 mg/L NaOCl dosage.

Table 3.35. COD Removal Efficiency of Chemical Oxidation with NaOCl (with Sample VI)

Sample VI	Initial pH	Adjusted pH for NaOCl	NaOCl Dosage (ml/L)	COD Before Treatment (mg/L)	COD After Treatment (mg/L)	COD Removal Efficiency (%)
1	4.5	9	5	92 000	62 000	33
2	4.5	9	10	92 000	52 000	43
3	4.5	9	15	92 000	48 000	48
4	4.5	9	20	92 000	44 000	52

3.2.2.2.5. Experimental Studies with Fenton Reagent

In this experiment, the treatment efficiency of Fenton Reagent on olive mill wastewater was tested for sample V. pH of sample was not adjusted because it was already 3.5. Then the chemicals (FeSO_4 and H_2O_2) were added to the wastewater and jar test was carried out. Supernatant was taken and pH of it was adjusted to 7 with the addition of 50 ml/L, 10 % $\text{Ca}(\text{OH})_2$ solution. Then it was waited for four hours to let it settle and evaporation of H_2O_2 . Results of this experiment are presented in Table 3.36. In the literature, it was reported that better results were obtained with low FeSO_4 and H_2O_2 (Casero et al., 1997). That's way small amounts were used. However maximum COD removal efficiencies were obtained at low FeSO_4 (50 mg/L) but high H_2O_2 doses (100 mg/L).

Table 3.36. COD Removal Efficiency of Chemical Oxidation with Fenton (with Sample V)

Sample VI	Effluent pH	Dosage FeSO_4 (mg/L)	Dosage H_2O_2 (mg/L)	COD Before Treatment (mg/L)	COD After Treatment (mg/L)	COD Removal Efficiency (%)
1	7	50	50	108 000	64 000	41
2	7	100	100	108 000	56 000	48
3	7	100	50	108 000	48 000	56
4	7	50	100	108 000	32 000	70

For the sample VI, pH was adjusted from 4.5 to 3.5 with the addition of 8 ml/L HCl (concentrated solution). Then the chemicals were added to the wastewater and jar test was carried out. Treated water was taken from upper part and pH was adjusted to 7 by 50 ml/L $\text{Ca}(\text{OH})_2$ (10 % solution). Then it was waited for four hours to settle. Treated water was taken from the upper part and COD analyses were

carried out. Obtained results are given in Table 3.37. The oxidant doses were increased because of the result of previous study. 250 mg H₂O₂ /L was used as the maximum dosage. The increase of doses caused errors in COD measurement. Maximum efficiencies were achieved at 250 mg/L H₂O₂ and 250 mg/L FeSO₄ concentrations.

Table 3.37. COD Removal Efficiency of Chemical Oxidation with Fenton (with Sample VI)

Sample VI	Effluent pH	Dosage FeSO ₄ (mg/L)	Dosage H ₂ O ₂ (mg/L)	COD Before Treatment (mg/L)	COD After Treatment (mg/L)	COD Removal Efficiency (%)
1	7	50	50	92 000	46 000	50
2	7	100	100	92 000	45 000	51
3	7	150	150	92 000	42 000	54
4	7	200	200	92 000	40 000	57
5	7	250	250	92 000	32 000	65

Chemical oxidation with Fenton Reagent was the most effective oxidation method on the removal of COD. 65 % and 70 % COD removal efficiencies were obtained for olive mill wastewaters depending on the sample. However, the COD concentration of treated effluent was still very high such as 32 000 mg/L.

Since maximum COD removal efficiency was obtained with Fenton Reagent, the treatment efficiency of Fenton Reagent on sample VI, which had been waited for 2 months, was examined in another experiment. pH was adjusted to 3.5 for this sample. Then 100 mg/L H₂O₂ and 100 mg/L FeSO₄.7H₂O were added to the wastewater and jar test was carried out. Treated water was taken from upper part and pH was adjusted to 7 by 50 ml/L, 10 % solution Ca (OH)₂. Then it was waited for four hours to settle. Sample was taken from the supernatant at first, second and third days to see

the variation in COD values. Results are given in Table 3.38. Initial COD concentration was 80 000 mg/L. It was reduced to 20 000 mg/L after chemical oxidation with Fenton Reagent in the first day. However, COD concentration was increased at the end of the second and the third day with 48 000 mg/L and 72 000 mg/L, respectively. The ageing processes cause an increase in the concentrations of COD. Chemical reaction between a few pseudo-compounds, and converting to new organic materials may be the reason of increasing the COD concentration.

Table 3.38. Effects of Duration Time on Oxidation with Fenton Reagent

Sample	COD (mg/L)	COD Removal Efficiency (%)
Raw wastewater	80 000	-
First day	20 000	70
Second day	48 000	40
Third day	72 000	10

In another experiment with wastewater sample VI, the treatment efficiency of Fenton Reagent on filtered wastewater was tested. Wastewater was filtered from filter clothes. pH of filtrate was adjusted to 3.5. Then 100 mg/L H₂O₂ and 100 mg/L FeSO₄.7H₂O were added to the wastewater and jar test was carried out. At the end of jar test, four hours settlement was applied to wastewater. Supernatant was taken and pH was adjusted to 7 with the addition of 50 ml/L, 10 % Ca (OH)₂ solution. Then it was waited for four hours to settle. Treated waters were taken from supernatant and COD analyses were carried out. Results are presented in Table 3.39. Initial COD concentration was 92 000 mg/L and it was decreased to 60 000 mg/L with 35% COD removal efficiency after filtration through filter clothes. The result of oxidation study with Fenton Reagent on filtrate was 48% COD removal efficiency.

Table 3.39. Effects of Filtration on Oxidation with Fenton Reagent

Sample	COD (mg/L)	COD Removal Efficiency (%)
Raw wastewater	92 000	-
Filtrate	60 000	35
Oxidation with Fenton Reagent	48 000	48

In another study with the same sample, pH value of raw wastewater was decreased from 4.5 to 2 with the addition of 18 ml/L HCl solution. Then, jar test was carried out. After sedimentation, supernatant was taken and filtrated from filter paper in 0.80 mm diameter. Then, oxidation with Fenton Reagent was applied. 100 mg/L H_2O_2 and 100 mg/L $FeSO_4 \cdot 7H_2O$ were added to the wastewater and jar test was carried out. At the end of jar test, two hours settlement was applied to wastewater. Supernatant was taken and pH was adjusted to 7 with the addition of 50 ml/L, 10 % $Ca(OH)_2$ solution. Then it was waited for four hours to settle. Samples were taken from upper part and COD analyses were done. These results are given in Table 3.40. After pH adjustment following sedimentation and filtration COD concentrations were decreased to 52 000 mg/L and 48 000 mg/L with 43% and 48% COD removal efficiencies, respectively. Oxidation with Fenton Reagent reduced COD concentration to 24 000 mg/L.

Table 3.40. Effects of Acidic Condition and Filtration on Oxidation with Fenton Reagent

Sample	COD Concentration (mg/L)	COD Removal Efficiency (%)
Raw wastewater	92 000	-
Wastewater has 2 pH value	52 000	43
Filtrated wastewater	48 000	48
Oxidation with Fenton Reagent	24 000	74

General Evaluations for Chemical Oxidation Experiments

Results of all chemical oxidation experiments with samples V and VI are given in Table 3.41, Table 3.42, and in Figure 3.10. Different chemical oxidation methods resulted in different COD removal efficiencies because of characteristics of raw wastewater. However, maximum COD removal efficiency was achieved after chemical oxidation experiment with Fenton Reagent for both samples.

Table 3.41. COD Removal Efficiencies after First Set of Chemical Oxidation Experiments with Sample V

Chemical Oxidation Method	COD (mg/L) Before Treatment	COD (mg/L) After Treatment	COD Removal Efficiency (%)
Oxidation by H ₂ O ₂	108 000	64 000	41
Catalytic Oxidation by MnSO ₄	108 000	60 000	44
Oxidation by NaOCl	108 000	60 000	45
Oxidation by KMnO ₄	108 000	48 000	56
Oxidation by Fenton Reagent	108 000	32 000	70

Table 3.42. COD Removal Efficiencies after Second Set of Chemical Oxidation Experiments with Sample VI

Chemical Oxidation Method	COD (mg/L) Before Treatment	COD (mg/L) After Treatment	COD Removal Efficiency (%)
Catalytic Oxidation by MnSO ₄	92 000	60 000	35
Oxidation by KMnO ₄	92 000	44 000	52
Oxidation by NaOCl	92 000	44 000	52
Oxidation by H ₂ O ₂	92 000	37 000	60
Oxidation by Fenton Reagent	92 000	32 000	65

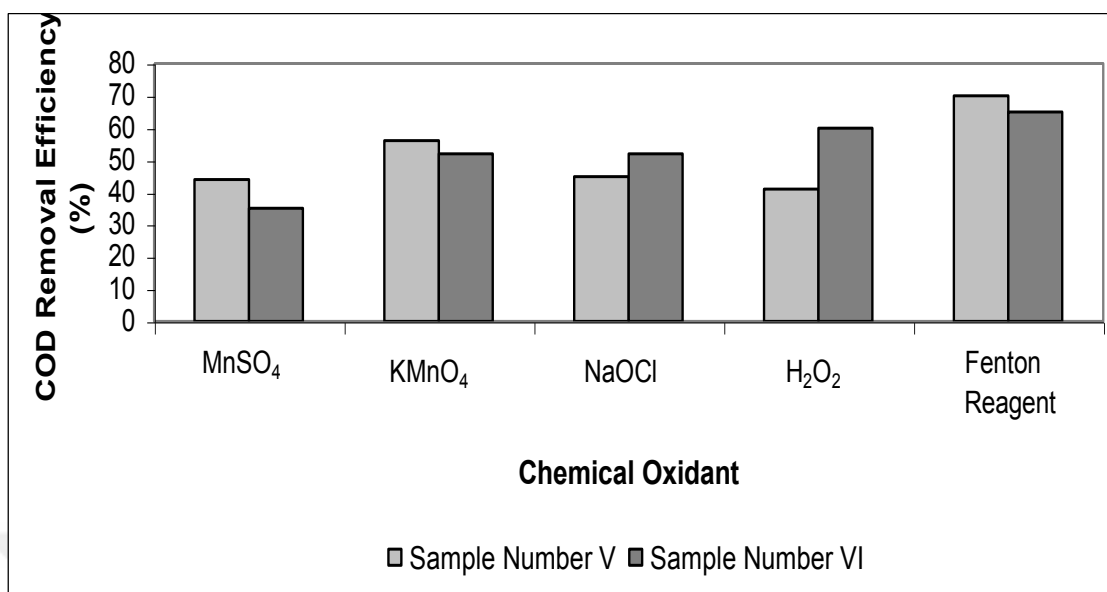


Figure 3.10. COD Removal Efficiencies after Chemical Oxidation Experiments

3.2.3. Biological Treatability Experiments

During the biological treatability studies, Oil Gator bacteria were used. These bacteria were used for different aims such as absorption of all organic wastes especially hydrocarbons; digestion and biodegradation of organic waste; treatment of the wastewater which has high salinity concentration such as seawater etc.

3.2.3.1. Bioabsorption Experiment with Oil Gator Bacteria

First of all, bioabsorption experiments were done. Therefore, different amount of bacteria and aeration time was used.

Oil Gator is a trademark and it is sold in the packs. It is suggested that the amount of bacteria would be added into the wastewater should be half of suspended solid concentration of raw wastewater. The suspended solid concentration in sample II was

65 536 mg/L, so 33 g/L Oil Gator bacteria were added to the sample. The sample was mixed slowly at 30 minutes after bacteria addition for activation of culture. Then, different aeration times were applied to bacteria-wastewater mixture. Finally, wastewater was filtered from filter paper in 0.80 mm pore diameter and COD concentrations were measured. Table 3.43 gives variation of COD removal efficiencies with aeration time. Initial COD concentration was 168 000 mg/L. It was decreased to 80 000 mg/L and 72 000 mg/L after aeration for 1 and 3 hours and the resulting efficiencies were 63% and 67% as COD removal efficiency, respectively. Experimental results indicated that COD removal efficiency increased with increasing aeration time.

Table 3.43. Effects of Aeration Time on COD Removal Efficiency during Bioabsorption Experiment

Amount of Bacteria (g/L)	Aeration Time (h)	COD Concentration (mg / L)	COD Removal Efficiency (%)
Raw wastewater	-	168 000	-
30	1	80 000	63
30	3	72 000	67

In order to see the effect of initial bacteria concentration on COD removal efficiency, different amounts of bacteria were added into sample III. The amount of bacteria were related with suspended solid concentration of raw wastewater which was 8 443 mg/L. Therefore the bacteria concentration should have been 4 g/L, but 8 g/L and 16 g/L bacteria concentrations were also examined. The bacteria added wastewater was mixed slowly for 30 minutes and then aerated for 1 hour. After this operation, wastewater was filtered from filter paper in 0.80 mm pore diameter and COD values of treated wastewaters were determined. Obtained results are given in Table 3.44. Initial COD concentration was 120 000 mg/L. 106 000 mg/L, 91 000 mg/L, and 78 000 mg/L COD concentrations were achieved after adding 4 g/L, 8 g/L, and 16 g/L Oil Gator Bacteria, respectively. Increase in the Oil Gator bacteria amount provided decreasing in COD concentration.

Table 3.44. Effects of Bacteria Amount on COD Removal Efficiency during Bioabsorption Experiment with Sample III

The Amount of Bacteria (g/L)	Aeration Time (h)	COD Concentration (mg / L)	COD Removal Efficiency (%)
Raw wastewater	-	120 000	-
4	1	106 000	12
8	1	91 000	24
16	1	78 000	35

In another experiment with the sample IV, which has 124 000 mg/L COD concentration and 16 376 mg/L SS concentration, different bacteria amounts were applied. The same steps, which were explained in previous experiment, were carried out. pH value of wastewater decreased after addition of bacteria. Obtained results are given in Table 3.45. 109 000 mg/L, 94 000 mg/L, and 80 000 mg/L COD concentration and 4.02, 3.95, and 3.89 pH value were obtained after adding 4 g/L, 8 g/L, and 16 g/L Oil Gator Bacteria, respectively. The same COD removal efficiencies were obtained during last two bioabsorption experiments. Increasing in the Oil Gator Bacteria amount also resulted in increase in COD removal efficiencies.

Table 3.45. Effects of Bacteria Amount on COD Removal Efficiency during Bioabsorption Experiment with Sample IV

Amount of Bacteria (g/L)	Aeration Time (h)	pH	COD Concentration (mg / L)	COD Removal Efficiency (%)
Raw wastewater	-	5.00	124 000	-
4	1	4.02	109 000	12
8	1	3.95	94 000	24
16	1	3.89	80 000	36

3.2.3.2. Biological Treatability Study with Oil Gator Bacteria

It was tried to adapt Oil Gator bacteria to the activated sludge process in batch reactor. For this reason, an 80 g bacterium, which was half amount of the suspended solid concentration of wastewater, was added to sample IV. Reactor was aerated continuously and sample was taken daily. COD concentrations of each sample were measured and COD removal efficiencies were calculated. Variation of COD removal efficiency with time is given in Table 3.46 and in Figure 3.11. Initial COD concentration was 124 000 mg/L. It decreased day by day and reached to 60 000 mg/L at the end of the 22nd day with 52% COD removal efficiency.

Table 3.46. COD Removal Efficiency of Continuously Aerated Batch Reactor

Time (day)	COD Concentration of Effluent (mg / L)	COD Removal Efficiency (%)
0	124 000	-
6	96 000	23
7	95 000	23
8	92 000	26
11	89 000	28
12	86 000	31
13	84 000	32
14	80 000	36
15	76 000	39
18	74 000	40
19	72 000	42
20	70 000	44
21	64 000	48
22	60 000	52

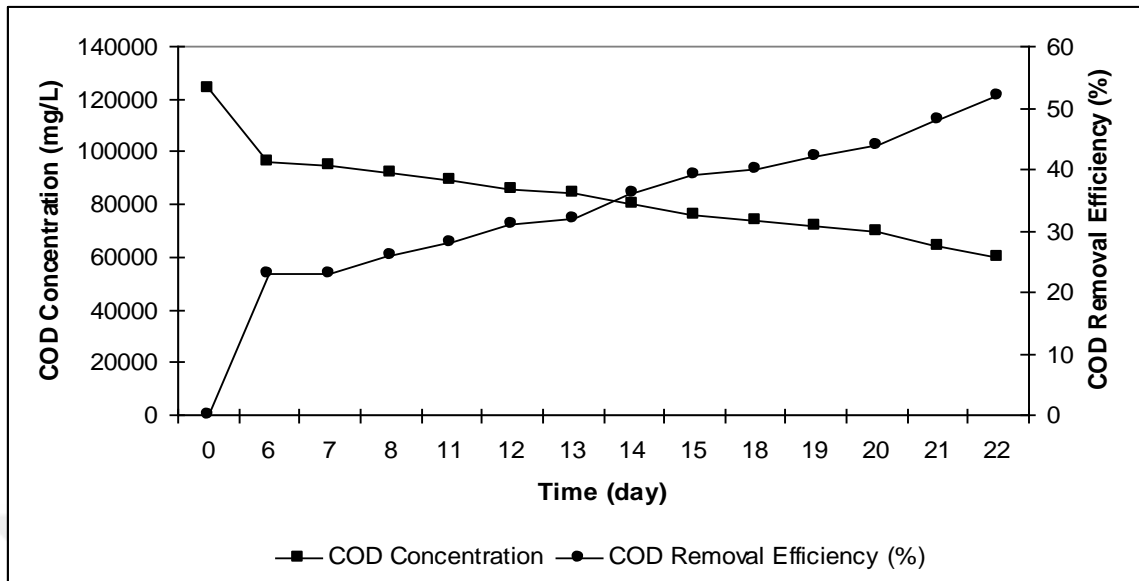


Figure 3.11. COD Removal Efficiency of Aerobic Batch Reactor

Biological treatability experiments with Oil Gator bacteria showed that, these bacteria were very effective in long retention time without any pre-treatment. If physicochemical treatment methods were applied before biological treatment with Oil Gator bacteria, retention time could be decreased.

CHAPTER FOUR

CONCLUSIONS

The aim of this study was to investigate the characterization and treatability of the olive mill wastewater from different olive oil processing industries. For the treatability examinations, several unit operations and processes performed using different samples. The efficiencies obtained from the same unit operation were quite different for different samples. These differences mainly due to the wide variability of olive oil mill wastewater characteristics. Depending on the extraction process, degree of olive ripening, storage time of olives before milling or storage time of wastewater before treatment, wastewater characteristics changes substantially.

The main pollutants in these type wastewaters are COD, SS, Oil and Grease, and pH. Different physical, chemical and biological treatment methods were applied to the effluent samples to find the most suitable treatment method 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. Because inlet concentration as high as 120 000 mg/L can be lowered to 1000 mg/L which was well above the discharge limits.

In the first part of this thesis, different physical and physicochemical methods such as filtration, shaking, aeration, sedimentation, and distillation were applied to the wastewater. Distillation process after coagulation as a pretreatment step was found the most effective method with 99% COD removal efficiency for the treatment of olive mill wastewater.

Maximum COD removal efficiencies were achieved with methods using distillation process. The distillation process increases the unit cost of olive oil as high as 10%. This cost estimation is based on least efficient distillation method. If more efficient methods are applied the cost of distillation decreases ten folds. Furthermore usage of solar energy is very promising solution for Aegean Region. In addition, concentrated paste, which was obtained after distillation process can be used as animal feed by taking into consideration of its potassium content. Concentrated paste can be also used burned to feed the boiler which provides the thermal energy to the distillation plant, but its combustion induces air pollution which has to be dealt with by post-treatment of the gases. These operations will be brought additional profits. As another profit, distillate can be used several times. The taste of olive oil problem can be examined. Evaluation of all these position showed that distillation is not too expensive treatment method for olive mill wastewaters.

In the second part, chemical precipitation and chemical oxidation methods were applied to olive mill wastewater. Maximum removal efficiencies were 55% and 70%, respectively. However, the COD concentration of treated effluent was still very high as about 32 000 mg/L.

In biological treatment experiments, Oil Gator Bacteria were used in batch reactor and this reactor was aerated continuously. 60 000 mg/L COD concentration and 52% COD removal efficiency in treated water were achieved at the end of the 22nd day. Biological treatability experiments with Oil Gator bacteria showed that, these bacteria were very effective in long retention time without any pre-treatment. If

physicochemical treatment methods were applied before biological treatment with Oil Gator bacteria, retention time could be decreased.

All experimental results are summarized in Table 4.1.

Table 4.1. Maximum Removal Efficiencies after all Treatment Experiments

Method	COD Removal Efficiency (%)
<i>PHYSICAL AND PHYSICOCHEMICAL TREATMENT</i>	
Filtration	41
Shaking	49
Distillation	99
Aeration	43
Sedimentation	26
<i>CHEMICAL COAGULATION AND FLOCCULATION</i>	
With FeCl ₃ .6H ₂ O	32
With Ca(OH) ₂	13
With HCl	38
With HCl and Ca(OH) ₂	55
<i>CHEMICAL OXIDATION</i>	
Oxidation by H ₂ O ₂	41
Catalytic Oxidation by MnSO ₄	44
Oxidation by NaOCl	45
Oxidation by KMnO ₄	56
Oxidation by Fenton Reagent	70
<i>BIOLOGICAL TREATMENT</i>	
With Oil Gator bacteria in batch reactor	52

Decrease in COD concentration during the chemical oxidation experiments, especially in Fenton oxidation, indicated that phenol removal was occurred. Aerobic biological treatment step could be applied after chemical oxidation process in order to achieve higher COD removal efficiencies.

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 1 000 mg/L. Therefore, further treatment is needed to reduce the COD concentration. When physico-chemical or biological methods were applied alone, significant improvement in COD reduction was not observed. On the other hand, the combination of different methods could be resulted in effective COD removal efficiencies.

According to Water Pollution Control Regulation in Turkey, COD discharge limit of some industries is 1000 mg/L (for Paper and Pulp Industry, 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, which was obtained from effluent of distillation process.

Physical treatment, chemical oxidation, and biological treatment alternatives should be applied sequentially for achieving wastewater discharge standards for olive mill wastewater.

REFERENCES

- 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.
- Aktas, E., Imre, S. & Ersoy, L. (2001). Characterization and lime treatment of olive mill wastewater. Water Research, 9, 2336-2340.
- Annesini, M.C.&Gironi,F. (1991). Olive oil mill effluent: ageing effects on evaporation behaviour. Water Research, 25, 1157-1160.
- American Public Health Association, American Water Works Association, Water Pollution Control Federation (1992). Standart Methods for the Examination of Waster and Wastewater, 18th Edition, Washington.
- Beccari, M., Bonemazzi, E., Majone, M., Riccardi, C. (1996). Interactions between acidogenesis and methanogenesisi in the anaerobic treatment of olive mill effluents. Water Research, 30, 183-190.
- 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.
- Boda, R., Alba, I., Banks,CI. (1996). Anaerobic digestion of wash waters derived from purification of virgin olive oil using a hybrid reactor combining a filter and a sludge blanket. Process Chemistry, 31, 219-224.
- Borges (2001). Spanish Olive Oil Experts, [http:// www.aceitesborges.es](http://www.aceitesborges.es).
- Burr, M. (2001). Tandara Grove Olives,<http://www.tandaragrove.com.au>.
- Cabrera, F., Lopez, R., Martinez-Bordiu, A., Dupuy de Lome, E. & Murillo, J.M. (1996). Land treatment of olive oil mill wastewater. International, Biodeterioration&Biodegradation, 54, 215-225.

- Casero, I., Sicilla, D., Rubio, S. & Bendito, D. (1997). Chemical degradation of aromatic amines by fenton's reagent. Water Research, 31, 1985-1995.
- Castro, A. & Brenes, M (2001). Fermentation of washing waters of Spanish-style green olive processing. Process Biochemistry, 36, 797-802.
- 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.
- Di Giacomo, G., Brandani, V. & Del Re, G. (1991). Evaporation of olive oil mill vegetation waters. Desalination, 81, 249-259.
- Eckenfelder, W. W. (1989). Industrial water pollution control. 2nd Edition), Mc-Graw Hill, New York.
- Ege Birlik Organization (2001). www.egebirlik.org.tr/PRODUCTION.htm.
- Ergüder, T.H., Güven, 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.
- 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 chrysosporium* pretreatment 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 olives. Phytochemistry, 49, 1311-1315.
- Hamdi, M. (1991). Effects of agitation and pretreatment on the batch anaerobic digestion of olive mill wastewater. Bioresource Technology, 36, 173-178.
- 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.

- Institute for Prospective Technological (1996). Euro-Mediterranean Policies and Olive Oil: Competition or Job Sharing?. Seville. Bonazzi, M.
- Israilides, C.J., Vlyssides, A.G., Mourafeti, V.N. & Karvouni, G. (1997). Olive oil wastewater treatment with the use of an electrolysis system. Bioresource Technology, 61, 163-170.
- Lafi, W. K. (2001). Production of activated carbon from acorns and olive seeds. Biomass and Bioenergy, 20, 57-62.
- Lolos, G., Skordilis, A. & Parissakis, G. (1994). Polluting characteristics and lime precipitation of olive mill wastewater. Journal of Environmental Science and Health, Part A: Environmental Science and Engineering, 29, 1349-1356.
- Martin, A., Boda, R. & Chica, A. (1993). Kinetic study of an anaerobic fluidized bed system used for the purification of fermented olive mill wastewater. Chemical Technology and Biotechnology, 56, 155-162.
- Masghouni, M. & Hassairi, M. (2000). Energy applications of olive-oil industry by-products: - I. The exhaust foot cake, Biomass and Bioenergy, 18, 257-262.
- Mitrakas, M., Papageorgiou, G., Docoslis, A. & Sakellariopoulos, G. (1996). Evaluation of various pretreatment methods for olive oil mill wastewaters. 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.
- Ptx Petrotex Ind (1998). http://www.bwnow.com/petrotex_gator.
- Rozzi, A., Limoni, N., Menegatti, S., Boari, G., Liberti, L. & Passino, R. (1988). Influence of Na and Ca alkalinity on UASB treatment of olive mill effluents. Part I: Preliminary results. Process Chemistry, 23, 86-90.
- Rozzi, A. Malpei, F. (1996). Treatment and disposal of olive mill effluents. International Biodeterioration Biodegradation, 38, 135-144.

- 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.
- Tsonis, S. P. (1997). Olive oil mill wastewaters as carbon source in past anoxic denitrification. Water Science and Technology, 36, 53-60.
- Turkish Water Pollution Control Regulation, 4th September 1988, Official Gazette, Number 19919.
- Ubay, G. & Öztürk, İ. (1997). Anaerobic treatment of olive mill effluents. Water Science and Technology. 35, 287-294.
- 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.

APPENDIX

1. OLIVE OIL PRODUCTION

1.1. History of Olive

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.

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 30th and the 45th 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).

1.2. Production of Olive Oil

Before oil can be made, the olive fruit must be harvested. In the small grove, this is generally done by hand whereas in the bigger plantations efforts to mechanize the process are well under way. Once the olives have been harvested they are crushed whole (as the pits contain a natural preservative) into a paste or pasta (Borges, 2001). All of these processes are explained below.

1.2.1. Harvesting

It is fundamental to obtain an olive oil of quality by harvesting the olive in its right moment of ripeness, when the majority is changing color (begin to look ripe). Hardly are any green or completely ripen ones left in the fields.

The ideal method of harvesting is to strip olives as when milking dry, by hand or with scrapers. The most important is not to harm the olive and transport it as soon as possible to the oil-mill, so the fruit does not deteriorate.



Figure A.1. A Demonstration of Harvesting (Borges, 2001)

Harvested oil contains:

- Oil : 15-20%
- Water : 30-60%

- Sugars : 19%
- Fiber : 5.8%
- Proteins : 1.6%
- Ceneri : 1.5% (Burr, 2001).

1.2.2.The Oil Mill

The olive must be milled on the same day of harvesting, thus being a fruit with vegetable water that ferments and oil that oxidizes, the storing time spoils the final product. In the oil-mills, the olives are cleaned and washed, classified by qualities and/or varieties to obtain the best oils. The following processes are milling, pressing and decanting that are mechanically performed in the mill (Borges, 2001).

Milling

It is done with a hammer crusher or stone molars, which breaks the vegetable tissue and liberates the oil, forming a homogeneous paste. It can be seen in Figure A.2.



Figure A.2. Milling of Olives (Borges, 2001)

Pressing

After milling process, paste is put through a cold press to extract the oil and vegetable water. The best oil is extracted from the first cold pressing paste. Figure A.3. shows a cold press.



Figure A.3. A Cold Press (Borges, 2001)

Decanting

In order to separate the water from the oil, the remainders of vegetable water are separated from the oil by means of natural decanting or through vertical, centrifugal machine to avoid the alteration of the oil's quality.

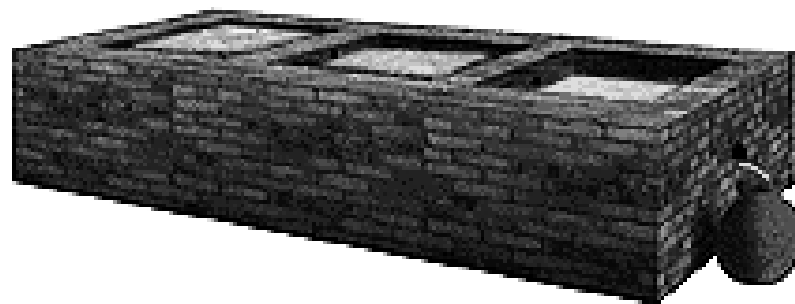


Figure A.4. Decanting of Olive (Borges, 2001)

1.2.3. Olive Oil Extraction Processes

There are three main processes for olive oil extraction which shown in Figure A.5.

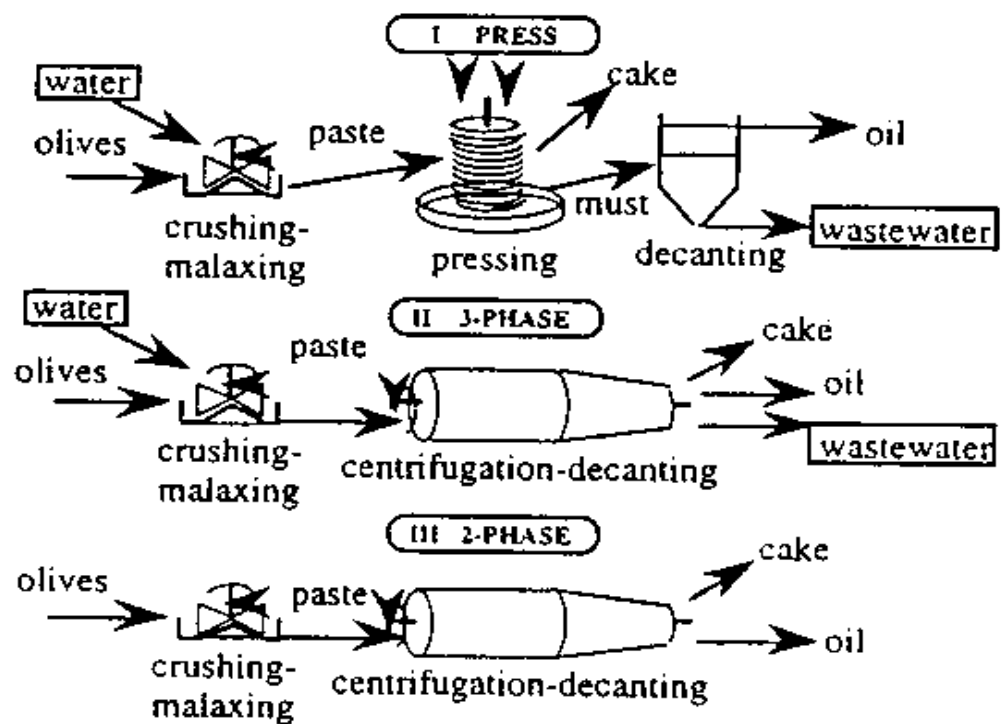


Figure A.5. Olive Oil Extraction Processes (Demichelli&Bontoux, 1996)

1.2.3.1.Press Process

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).

1.2.3.2.Continuous Extraction Process

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 advantages of this process can be given as follows (Demichelli&Bontoux, 1996):

- ◆ This process can operate without hot process water,
- ◆ It saves both energy and water,

- ◆ It produces very small amount of wastewater,
- ◆ It reduces pollution load relatively to the other two processes.

The main advantages and disadvantages of continuous centrifugation technology versus press technology from an industrial point of view are given in Table A.1.

Table A.1. The Main Pros and Cons of Continuous Centrifugation Process vs. Press Technology

Advantages	Disadvantages
<ul style="list-style-type: none"> • A continuous process • Much less labour-intensive • Possibility of “ same day processing” • Higher output • Better quality control (elimination of “mat flavor”) • Requires less room • Improved process control, automatizable 	<ul style="list-style-type: none"> • More capital-intensive • New line of products and by-products (mainly the 2-phase process)

1.3. Olive Oil Productions in the World and in Turkey

1.3.1. Olive Oil Production in the World

Olive oil mills are small agro-industrial units which are located mainly in the vicinity of Mediterranean, Aegean and Marmara Seas (Ergüder et.al., 2000). Percentages of world olive oil production between the years of 1983-1993 are given in Figure A.6.

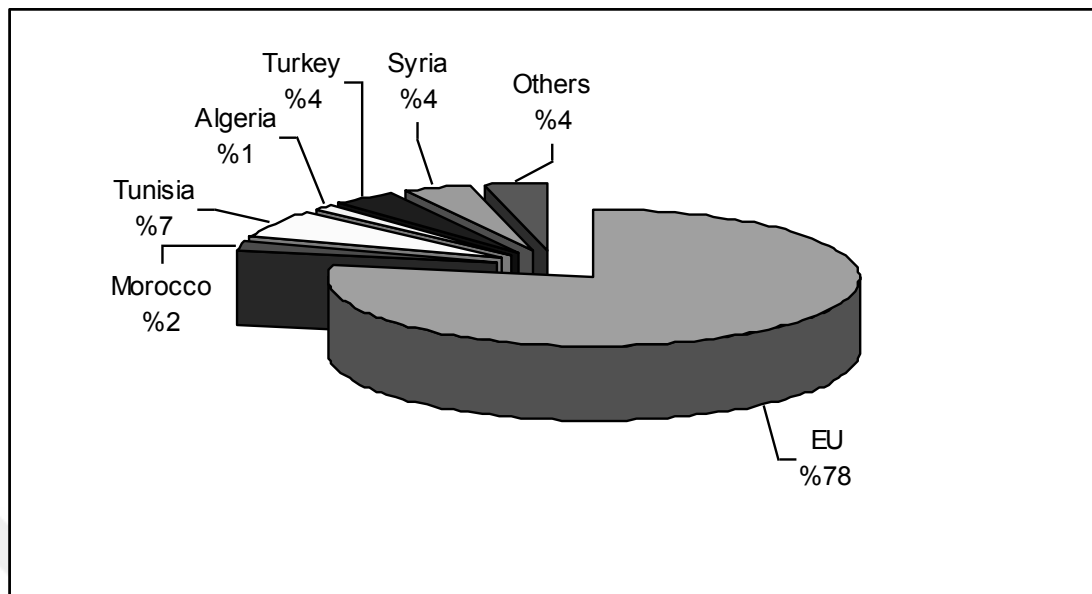


Figure A.6. World Production of Olive Oil (Bonazzi, 1996)

1.3.2. Olive Oil Production in Turkey

Since olive-tree is an alternate bearing plant, each year differs significantly. Due to this fact, Turkish olive oil production reaches up to around 200 000 tons in “on years” and around 80 000 tons in “off years”.

According to the International Olive Oil Council (IOOC), world olive production varied around 1.5-2.5 million tons during the 1992/93-1996/97 seasons. Turkey ranks fifth in the world olive oil production, it has the potential of exporting a great majority of her production, which averages 90-95 000 tons per annum (Egebirlik Org., 2001).

Olive oil production amounts in Turkey vs. in the World are given in Figure A.7.

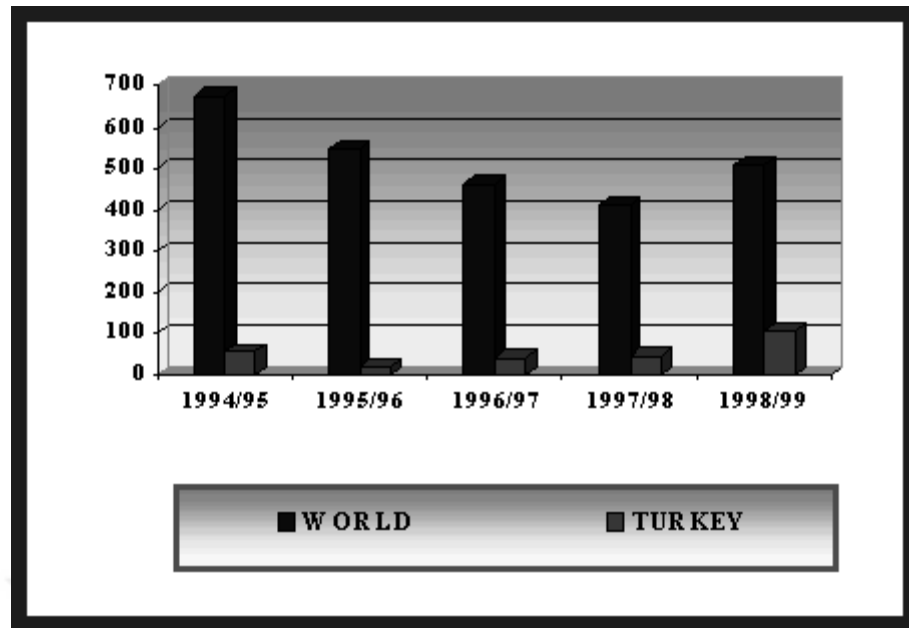


Figure A.7. Olive Oil Production Amounts of Turkey (ton/year)
(Egebirlik Org., 2001)