Süleyman Demirel Üniversitesi,
Fen Bilimleri Enstitüsü Dergisi,
13-3 (2009),271-276

Zeytin Karasuyunun Fiziko-Kimyasal Arıtılabilirliği

Melike YALILI KILIÇ*, Kadir KESTİOĞLU, Gonca KAYA
Uludağ Universitesi, Mühendislik Mimarlık Fakültesi,Çevre Mühendisliği Bölümü / BURSA
Alınış tarihi:30.12.2008, Kabul tarihi:10.06.2009

Özet: Bu çalışmada Balıkesir'in Edremit ilçesinde üç fazlı sisteme göre zeytinyağı üretimi yapan bir fabrikanın atıksularının (karasu) fiziko-kimyasal arıtılabilirliği araştırılmıştır. İncelenen karasuda öncelikle asit kraking işlemi yapılarak yağlı kısmın atıksudan ayrılması sağlanmıştır. Bu işlem sonucunda KOİ'de %53, AKM'de %91, fenolde ise %31 oranlarında giderim sağlanmıştır. Daha sonra asit kraking çıkışından alınan atıksuda, Chitosan, SDS (Sodyum dodesil sülfat) ve $FeCl_3$ kullanılarak kimyasal arıtma yapılmıştır. Kimyasal arıtılabilirlik çalışması neticesinde ise, pH=6'da, 50 mg/L Chitosan, 0,6 g/L SDS ve 2500 mg/L $FeCl_3$ dozlarında, KOİ'de %68 oranında giderme verimi elde edilmiştir. Bu arıtılabilirlik çalışmasına göre, karasuyun KOİ değeri 128000 mg/L'den 19200 mg/L değerine %85'lik bir verimle indirilebilmiştir. Karasuyun SKKY'nde verilen deşarj kriterine kadar (KOİ=230 mg/L) arıtılabilmesi için, fiziko-kimyasal arıtmadan sonra ileri arıtma tekniklerine ihtiyaç duyulduğu düşünülmektedir.

Anahtar Kelimeler: Arıtılabilirlik, Chitosan, $FeCl_3$, Fiziko-Kimyasal Arıtma, Karasu, SDS

Physico-chemical Treatability of Olive Mill Wastewater (OMW)

Abstract: In this study, physico-chemical treatability of olive mill wastewater (OMW) arises from a plant which produces olive oil according to three-phase system in Edremit-Balıkesir has been investigated. First of all, it has been separated fatty parts from OMW with acid cracking and COD, MLSS and phenol removal efficiencies have been determined as 53%, 91%, 31%, respectively. The chemical treatment has been carried out after acid cracking and Chitosan, SDS (sodium dodecyl sulfate) and $FeCl_3$ have been used as a coagulant. The removal efficiency of COD was 68% at pH=6 and the dosages of Chitosan, SDS and $FeCl_3$ are 50 mg/L, 0,6 g/L and 2500 mg/L, respectively in chemical treatment. As a result of this study, the COD has been decreased from 128000 mg/L to 19200 mg/L with a removal efficiency of 85%. It has been considered that advanced treatment technics are necessary after physico-chemical treatment for treatability of OMW until discharge standards (COD=230 mg/L) given in Turkish Water Pollution Control Regulations.

Keywords: Treatability, Chitosan, $FeCl_3$, Physico-Chemical Treatment, Olive Mill Wastewater (OMW), SDS

Introduction

Olive and olive oil production which have important position in agricultural activities, have intensified in the Mediterranean Region and become widespread in the world. It is estimated that the annual world production of olive oil and table olives (black and green) is about $2,5.10^6$ and 10^6 tons, respectively, with Spain, Italy and Greece being the major producers (Brenes et al., 1999). There has been a recent rise though in other countries as well, such as Canada, Australia, Japan and the US. Other important olive-producing countries are Turkey, Tunisia, Morocco, Syria, Portugal, United States, Canada, Australia and Japan (Arvanitoyannis et al., 2007).

Olive oil is produced from olives either by the discontinuous press method or the continuous centrifugation method (three-phase and two-phase) in nowadays. Two by-products such as bagasse and olive mill wastewater (OMW) are obtained from olive oil in these two methods. It is produced 0,4-0,5 m^3 and 1-1,5 m^3 wastewater, respectively for 1 ton olive in discontinuous and continuous methods (Şengül et al., 2002).

OMW has essentially contain materials which are in olive. This wastewater has an important pollute potential due to having high BOD, COD, MLSS, oil&grease, phenol and polyphenole compounds which are phytotoxic (Hamdi, 1993; Kavaklı, 2002). OMW has BOD values in the range of 12-63 g/L (Cossu et al., 1993; Azzam et al., 2004; Al-Malah et al., 2000), COD values in the range of 80-200 g/L (Boari and Mancini, 1990; Tsonis and Girigeropoulos, 1993; Scioli and Vollaro, 1997), phenol values in the range of 0,5-24 g/L (Paraskeva and Diamadopoulos, 2006).

Treatment of OMW is difficult and treatment cost is very high because of having high organic pollution and long-chain fatty acids and phenolic compounds which are hard to biodegrade of OMW, scattering high territorial of small olive oil producers, doing the production of olive oil in three or four months.

It has necessary combination of many treatment methods for treatability of OMW. In treatability studies of OMW in literature have been used a lot of methods such as aerobic treatment (Fadil et al., 2003; Tziotzios et al., 2007), anaerobic treatment (Ergüder et al., 2000), aerobic treatment + fenton oxidation (Kotsou et al., 2004), chemical treatment (Aktaş et al., 2001; Oktav et al., 2003; De Rosa et al., 2005; Sarika et al., 2005; Ginos et al., 2006), distillation (Oktav and Şengül, 2003), chemical+biological treatment (Bressan et al., 2004), land disposal (Kocaer et al., 2004), electrocoagulation (Inan et

* myalili@uludag.edu.tr

al., 2004; Tezcan Ün et al., 2006), adsorption (Al Malah et al., 2000; Azzam et al., 2004), advanced oxidation processes (Canizares et al., 2007), membrane processes (Paraskeva et al., 2007), electrofenton (Khoufi et al., 2004), electrofenton+anaerobic treatment (Khoufi et al., 2006), composting (Vlyssides et al., 1996).

Many studies have been done for treatment of OMW in Turkey and in the world. Oktav et al., (2003) obtained 13% COD removal efficiency by using lime and 38% by using HCl in chemical precipitation. They used $KMnO_4$, NaOCl, H_2O_2 and Fenton's Reagent in chemical oxidation study and obtained 70% COD removal efficiency. Physico-chemical treatment and advanced oxidation processes (H_2O_2/UV and O_3/UV) were carried out by Kestioğlu et al., (2005). They obtained 38% COD and 23% total phenol removal efficiency in acid cracking, 94% COD and 91% total phenol removal efficiency in acid cracking+alume caogulation, 95% COD and 90% total phenol removal efficiency in acid cracking+$FeCl_3$ coagulation, %99 COD and total phenol removal efficiency in the whole processes. Ginos et al., (2006) investigated the pre-treatment of OMW by means of coagulation-flocculation coupling various inorganic materials and organic polyelectrolytes and obtained COD and TP removal varied between about 10-40% and 30-80%, respectively. To enhance organic matter degradation, iron-based coagulation was coupled with H_2O_2 and this increased COD reduction to about 60%.
In this study, OMW from a plant which produces olive oil according to three-phase system in Edremit-Balıkesir has been investigated. Acid cracking and chemical treatment have been carried out in OMW which characterizated and the results of physico-chemical treatability have been explained as COD removal efficiency.

Materials and Methods

In this study the analysis of OMW were done according to Standard Methods (APHA, AWWA, WCPF, 1998). The jar test apparatus was a Velp Scientifica apparatus with six stirrers. MLSS mechanism and pH meter were from Sartorius. Chitosan was solubilized in 50% acetic acid solutions and mixed at a temperature of 50 ^{o}C (Meyssami and Kasaeian, 2005).

For breaking oils, first of all acid cracking were applied to OMW. pH were dropped to 1.3 adding 7 ml 96% H_2SO_4 to 1 L wastewater in acid cracking. The oily parts were peeled off sample and COD, MLSS and phenol were analysed at supernatant.
The Jar Tests were done in wastewater from acid cracking adding $FeCl_3$ (500-2500 mg/L), Chitosan (30-70 mg/L) and SDS (0,2-1 g/L). The pH were increased to 6 with 25% NaOH as study done by Meyssami and Kasaeian, (2005), then amount of two coagulants were constant and amount of other coagulant were changed. After stirring times between 5 and 30 min and stirring speeds between 15 and 90 rpm, the samples were settled 1 hour and COD were analysed at supernatant.

Results and Discussion

The characteristics of OMW used in this study are given in Table 1.

Table 1. *Characteristics of OMW*

Parameter	Unit	Value
pH	-	4.95
Electric conductivity	mS/cm	7.00
COD	mg/L	128000
MLSS	mg/L	27000
Oil&grease	mg/L	10000
Phenol	mg/L	3760

Acid Cracking

COD, MLSS and phenol removal efficiencies after acid cracking were given in Table 2.

Table 2. *The results of acid cracking*

Parameter	Unit	Entry Value	Exit Value	Removal Efficiency (%)
pH	-	4.95	1.3	-
COD	mg/L	128000	60000	53
MLSS	mg/L	27000	2500	91
Phenol	mg/L	3760	2580	31

Chemical Treatability Study

The aim of the coagulation step was to remove COD from OMW using Chitosan, SDS and $FeCl_3$ together. Accordingly the coagulation efficiency was investigated in terms of COD removal.

It was added 50 mg/L Chitosan, 0,6 g/L SDS and 500, 1000, 1500, 2000, 2500 mg / L $FeCl_3$ to vessels for determination of optimum $FeCl_3$ dosages at pH=6 in OMW after acid cracking. Exit COD values in different $FeCl_3$ dosages were shown in Figure 1. The optimum coagulant dosage of $FeCl_3$ was determined as 2500 mg/L as seen in Figure 1.

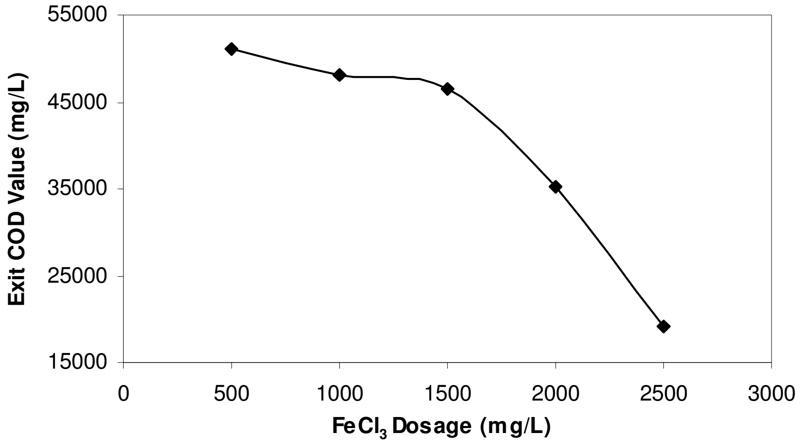

Figure 1. *Exit COD Values in Different $FeCl_3$ Dosages (pH=6; Chitosan=50 mg/L, SDS=0,6 g/L)*

For determination of optimum Chitosan dosages in Jar Tests after acid cracking, it was added 0,6 g/L SDS, 2500 mg/L $FeCl_3$ and 30, 40, 50, 60, 70 mg/L Chitosan to OMW (pH=6) in vessels and exit COD values in different Chitosan dosages were shown in Figure 2.

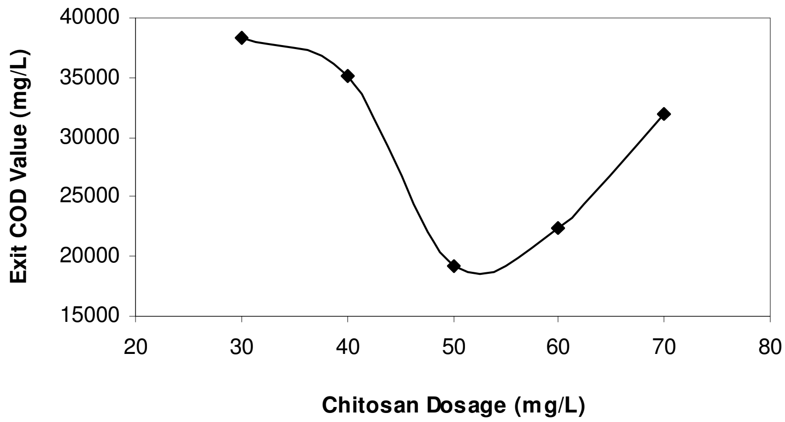

Figure 2. *Exit COD Values in Different Chitosan Dosages (pH=6; SDS=0,6 g/L; $FeCl_3$=2500 mg/ L)*

In OMW (pH=6) 50 mg/L Chitosan, 2500 mg/L $FeCl_3$ and 0,2; 0,4; 0,6; 0,8; 1 g/L SDS was added to vessels after acid cracking for determination of optimum SDS dosages. Exit COD values in different SDS dosages after Jar Test were shown in Figure 3.

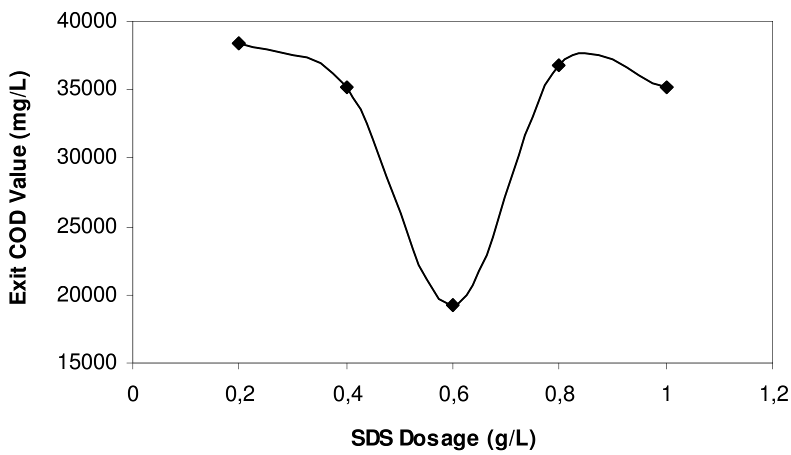

Figure 3. *Exit COD Values in Different SDS Dosages (pH=6; Chitosan=50 mg/L; $FeCl_3$=2500 mg/L)*

The COD values after optimum dosages of Chitosan (50 mg/L) and SDS (0.6 g/L) were increased as seen Figure 2 and 3, because of interference between potassium dichromate and coagulants in COD test.

As a result of chemical treatment, optimum coagulant dosages of Chitosan, SDS and $FeCl_3$ was determined as 50 mg/L, 0,6 g/L, 2500 mg/L, respectively. COD, MLSS and phenol removal efficiencies in these dosages were obtained as 68%, 28% and 25%, respectively and 100 ml/L sludge was obtained at the end of this process. The removal efficiencies determined in this study, are similar to some studies done by Meyssami and Kasaeian (2005), Rizzo et al., (2008) and Ginos et al., (2006).

Meyssami and Kasaeian, (2005) investigated the use of chitosan in the treatment of olive oil wastewater model solutions. In the jar experiments, they used chitosan and alum together at concentrations of 15 and 25 ppm, respectively, at pH 6 and obtained the lowest turbidity values in these conditions. Rizzo et al., (2008) studied coagulation with chitosan and advanced oxidation processes on OMW. They achieved 81% TSS removal at pH 4.3 for 400 mg/L chitosan dosage. Ginos et al., (2006) investigated the OMW treatment by the combined use of coagulants (Fe(III), ferrous sulphate (FS), magnesium sulphate (MS) and PACl), the two OMW samples (W1 and W2) being characterized by higher TSS concentrations (36.7 and 52.7 mg/L) and pH values (5.3 and 5.3) and comparable COD concentrations (61.1 and 29.3 g/L) with respect to OMW sample investigated in the present work. The best TSS removal they detected were 14, 60, 90 and 95% with 1000 mg/L of FC, PACl, MS and FS, respectively.

The cost of chemical materials used in this physico-chemical treatatability study was calculated according to market prices. Total daily chemical material cost was determined as 6807.83 Euro for a flow of 100 m^3/day (Table 3).

Table 3. *The cost of daily chemical material used in treatment plant*

Chemical Material	**Required dosage**	**Daily used dosage**	**Unit Price**	**Total Price**
Technics sulphuric acid	7 ml/L	700 L/d	1.4 Euro/L	980 Euro/d
Chitosan	50 mg/L	5 kg/d	500 Euro/kg	2500 Euro/d
$FeCl_3$	2500 mg/L	250 kg/d	2,27 Euro/kg	567,5 Euro/d
SDS	0.6 g/L	60 kg/d	20.7 Euro/kg	1242 Euro/d
Acetic acid	2.5 L/d	2.5 L/d	3.3 Euro/L	8.25 Euro/d
NaOH	57.2 ml/L	1716 kg/d	0.88 Euro/kg	1510.08 Euro/d
Total cost				**6807.83 Euro/d**

Conclusion

In this study, physico-chemical treatability of OMW arises from a plant which produces olive oil according to three-phase system in Edremit-Balıkesir has been investigated. The oil-grease was removed by acid craking before chemical treatment using Chitosan, SDS (Sodium Dodecly Sulfate) and $FeCl_3$. The optimum dosages of Chitosan, SDS and $FeCl_3$ at pH=6 were found as 50 mg/L, 0.6 mg/L and 2500 mg/L, respectively.

As a result of this study, COD, MLSS and phenol were decreased to 19200 mg/L, 1800 mg/L and 1940 mg/L, respectively with a 85% COD, 93% MLSS and 48% phenol removal efficiencies by the combination of acid craking and chemical treatment in the optimum conditions. The COD was largely removed by physico-chemical treatment, but it wasn't reached to discharge standard given in Table 5.5 in Turkish Water Pollution Control Regulation (Anonymous, 2004). It has required a combination of physico-chemical and advanced treatment methods reaching discharge standarts for receive environment. Also, the chemical material cost has been calculated as 6807.83 Euro for a factory with a flow of 100 m^3 per day. At the end of this study, it has been considered that the physico-chemical treatability with these coagulants of OMW isn't economic. So that, it has been thought that treatability studies with different processes should apply.

Acknowledgement

The authors acknowledge the support of Uludag University Research Projects Department for this project (Project No. M-2008/33).

References

Aktaş, S., Imre, S., Ersoy, L. 2001. Characterization and Lime Treatment of Olive Mill Wastewater. Water Research, 35(9), 2336-2340.

Al-Malah, K., Azzam, M.O.J., Abu-Lail, N.I. 2000. Olive Mills Effluent (OME) Wastewater Post-Treatment Using Activated Clay. Separation and Purification Technology, 20, 225-234.

Anonymous 2004. Water Pollution Control Regulation. 31 December 2004 Date and 25687 Numbered Official Newspaper, Ministry of Environment and Forest, Ankara.

APHA, AWWA, WCPF 1998. Standard Methods for the Examination of Water and Wastewater. 20th Eddition American Public Health Association, Washington D.C., USA.

Arvanitoyannis, I.S., Kassaveti, A., Stefanatos, S. 2007. Olive Oil Waste Treatment: A Comparative and Critical Presentation of Methods, Advantages & Disadvantages. Critical Reviews in Food Science and Nutrition, 47,187-229.

Azzam, M.O.J., Al-Malah, K.I., Abu-Lail, N.I. 2004. Dynamic Post-Treatment Response of Olive Mill Effluent Wastewater Using Activated Carbon, Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering, A39(1), 269-280.

Boari, G., Mancini, I.M. 1990. Combined Treatments of Urban and Olive Mill Effluents in Apulia, Italy, Water Science & Technology, 22, 235-240.

Brenes, M., Garcia, A., Garcia, P., Rios, J.J., Garrido, A. 1999. Phenolic Compounds in Spanish Olive Oils. J. Agric. Food Chem., 47, 3535-3540.

Bressan, M., Liberatore, L., D'Alessandro, N., Tonucci, L., Belli, C., Ranalli, G. 2004. Improved Combined Chemical and Biological Treatments of Olive Oil Mill Wastewaters. J. Agric. Food Chem., 52, 1228-1233.

Canizares, P., Lobato, J., Paz, R., Rodrigo, M.A., Saez, C. 2007. Advanced Oxidation Processes for the Treatment of Olive-Oil Mills Wastewater. Chemosphere, 67, 832-838.

Cossu, R., Blakey, N., Cannas, P. 1993. Influence of Codisposal of Municipal Solid Waste and Olive Vegetation Water on the Anaerobic Digestion of a Sanitary Landfill. Water Science & Technology, 27, 261-271.

De Rosa, S., Giordano, G., Granato, T., Katovic, A., Siciliano, A., Tripicchio, F. 2005. Chemical Pretreatment of Olive Oil Mill Wastewater Using A Metal-Organic Framework Catalyst. J. Agric. Food Chem., 53, 8306-8309.

Ergüder, T.H., Güven, E., Demirer, G.N. 2000. Anaerobic Treatment of Olive Mill Wastes in Batch Reactors. Process Biochemistry, 36, 243-248.

Fadil, K., Chahlaoui, A., Ouahbi, A., Zaid, A., Borja, R. 2003. Aerobic Biodegradation and Detoxication of Wastewaters from the Olive Oil Industry. International Biodeterioration & Biodegradation, 51, 37-41.

Ginos, A., Manios, T., Mantzavinos, D. 2006. Treatment of Olive Mill Effluents by Coagulation–Focculation–Hydrogen Peroxide Oxidation and Effect on Phytotoxicity. Journal of Hazardous Materials B, 133, 135-142.

Hamdi, M. 1993. Thermoacidic Precipitation of Darkly Coloured Polyphenols of Olive Mill Wastewaters. Environmental Technology, 14, 495-500.

Inan, H., Dimoglo, A., Şimşek, H., Karpuzcu, M. 2004. Olive Oil Mill Wastewater Treatment by Means of Electro-Coagulation. Separation and Purification Technology, 36, 23-31.

Kavaklı, M. 2002. Environmental Problems Resulting from Olive Oil Production and Selective Disposal Alternatives. In: Azbar N, Vardar N, Akın M, Cevilan I, editors. Proceedings of the First International Workshop on Environmental Problems in Olive Oil Production and Solutions, 07-09 June 2002, Balıkesir, 109-120.

Kestioğlu, K., Yonar, T., Azbar, N. 2005. Feasibility of Physico-Chemical Treatment and Advanced Oxidation Processes (AOPs) as a Means of Pretreatment of Olive Mill Effluent (OME). Process Biochemistry, 40, 2409-2416.

Khoufi, S., Aouissaoui, H., Penninckx, M., Sayadi, S. 2004. Application of Electro-Fenton Oxidation for the Detoxification of Olive Mill Wastewater Phenolic Compounds. Water Science and Technology, 49(4), 97-102.

Khoufi, S., Aloui, F., Sayadi, S. 2006. Treatment of Olive Oil Mill Wastewater by Combined Process Electro-Fenton Reaction and Anaerobic Digestion. Water Research, 40, 2007-2016.

Kocaer, F.O., Uçaroğlu, S., Başkaya, H.S. 2004. Land Disposal of Olive Oil Vegetation Water. University of Uludag Journal of the Faculty of Engineering and Architecture, 9(2), 69-77.

Kotsou, M., Kyriacou, A., Lasaridi, K., Pilidis, G. 2004. Integrated Aerobic Biological Treatment and Chemical Oxidation with Fenton's Reagent for the Processing of Green Table Olive Wastewater. Process Biochemistry, 39, 1653-1660.

Meyssami, B., Kasaeian, A.B. 2005. Use of Coagulants in Treatment of Olive Oil Wastewater Model Solutions by Induced Air Fotation. Bioresource Technology, 96, 303-307.

Oktav, E., Şengül, F. 2003. Treatment of Olive Oil Mill Wastewaters by Distillation Method. Journal of Water Pollution Control, 13(3), 8-17.

Oktav, E., Çatalkaya, E., Şengül, F. 2003. Treatment of Olive Oil Mill Wastewaters with Chemical Treatment Methods. University of Dokuz Eylül Faculty of Engineering Journal of Science and Engineering, 5(3), 11-21.

Paraskeva, P., Diamadopoulos, E. 2006. Review Technologies for Olive Mill Wastewater (OMW) Treatment: A Review. Journal of Chemical Technology and Biotechnology, 81, 1475-1485.

Paraskeva, C.A., Papadakis, V.G., Tsarouchi, E., Kanellopoulou, D.G., Koutsoukos, P.G. 2007. Membrane Processing for Olive Mill Wastewater Fractionation. Desalination, 213, 218-229.

Rizzo, L., Lofrano, G., Grassi, M., Belgiorno, V. 2008. Pre-treatment of Olive Mill Wastewater by Chitosan Coagulation and Advanced Oxidation Processes. Separation and Purification Technology, 63, 648-653.

Sarika, R., Kalogerakis, N., Mantzavinos, D. 2005. Treatment of Olive Mill Effluents Part II. Complete Removal of Solids by Direct Flocculation with Poly-Electrolytes. Environment International, 31, 297-304.

Scioli, C., Vollaro, L. 1997. Use of Yarrowia Lipolytica to Reduce Pollution in Olive Mill Wastewaters. Water Research, 31(10), 2520-2524.

Şengül, F., Oktav, E., Çokay Çatalkaya, E. 2002. Waste Characteristics of Varius OOM: Treatment and Disposal Technologies of OOMW. In: Azbar N, Vardar N, Akın M, Cevilan I, editors. Proceedings of the First International Workshop on Environmental Problems in Olive Oil Production and Solutions, 07-09 June 2002, Balıkesir, 35-49.

Tezcan Ün, Ü., Uğur, S., Koparal, A.S., Bakır Öğütveren, Ü. 2006. Electrocoagulation of Olive Mill Wastewaters. Separation and Purification Technology, 52, 136-141.

Tsonis, S.P., Girigeropoulos, S.G. 1993. Anaerobic Treatability of Olive Oil Mill Wastewater. Water Science & Technology, 28, 35-44.

Tziotzios, G., Michailakis, S., Vayenas, D.V. 2007. Aerobic Biological Treatment of Olive Mill Wastewater by Olive Pulp Bacteria, International Biodeterioration & Biodegradation, 60, 209-214.