1 Reducing the Environmental Impact of Olive Mill Wastewater in Jordan, Palestine and Israel

Basheer Sobhi, Sabbah Isam, Yazbek Ahmad and Haj Jacob,

Saleeba Ahlam, R&D Center, the Galilee Society,
P.O. BOX 437, Shefa-Amr 20200, Israel.
Tel: +972-4-9504523 Fax: +972-4-9504525
E-mail: sbsheer@gal-soc.org

ABSTRACT[1]

Olive mill wastewater (OMW) generated by the olive oil extraction process is the main waste product of this industry. Approximately 5.4×10^6 m^3 of olive mill wastewater are produced annually worldwide. The majority of it is being produced in the Mediterranean Basin. The uncontrolled disposal of OMW is becoming a serious environmental problem, due to its high organic COD concentration, and because of its high content of microbial growth-inhibiting compounds, such as phenolic compounds and tannins. The improper disposal of OMW to the environment or to domestic wastewater treatment plants is prohibited due to its toxicity to microorganisms, and because of its potential threat to surface and groundwater, due to the current lack of appropriate alternative technologies to properly treat OMW. In the Mediterranean area it is most often discharged directly into sewer systems and water streams or concentrated in cesspools, despite the fact that such disposal methods are prohibited in many Mediterranean countries.

The Research and Development Center of the *Galilee Society* (GS) in Israel is coordinating a joint USAID funded project with partners from Hebron University, Palestine, *The Royal Scientific Society* (RSS) in Jordan, and the Technion - Haifa, Israel. The project aims to investigate industrially feasible physico-chemical and biological treatment systems in order to reduce the environmental impact of OMW. During the last three years, the partners conducted an inclusive survey on location, type of olive mills, production capacity, OMW generation, current practiced methods for the disposal of OMW and data related to the socio-economic situation of the farmers in the region. Furthermore, laboratory and pilot-scale experiments have been conducted in the GS, RSS and the Technion to examine the most effective physico-chemical and biological treatment systems to treat OMW.

The experimental work was conducted to identify the most efficient anaerobic treatment for OMW. It was demonstrated that in the *up-flow anaerobic sludge blanket reactor* (UASB) reactor, COD removal efficiency of 75–85 per cent was reached at a *Hydraulic*

1 The authors thank the US-AID for their financial support (Grant No. TA-MOU-00-M20-091). The authors are also grateful to Prof. Awni Al-Khatib, Eng. Yousef Subuh at the Hebron University, Palestine, Dr. Bassam Al-Hayek, Eng. Mohamad Musa at The Royal Scientific Society, Amman, Jordan, and Prof. Noah Galil at The Technion, Haifa, Israel, for the valuable discussions.

Retention Time (HRT) of 5 days with an influent COD concentration of about 40 gL^{-1} and *Organic Loading Rate* (OLR) = 7–8 g CODL-1.d^{-1}. Based on the results obtained in bench scale experiments, a demonstration pilot scale system was designed and constructed in Hebron district to continuously treat OMW.

Keywords: Anaerobic treatment, biomass, olive mill wastewater, GIS database, upflow anaerobic sludge blanket reactor.

1.1 Introduction

Olive mill wastewater (OMW) generated by the olive oil extraction process is the main waste product of this industry. Approximately, 1.8x106 tons of olive oil are produced annually worldwide, the majority (98 per cent) of it is produced in the Mediterranean basin (Benitez/Beltran-Heredia/Torregrosa/Acero 1997a). It is reported that OMW resulting from the production process surpasses 30 million m^3 per year (Baccari/Bonemazzi/Majone/Riccardi 1996) in the Mediterranean region. Treatment of OMW is becoming a serious environmental problem, due to its high organic COD concentration, and because of its resistance to biodegradation due to its high content of biomass-inhibiting growth, mainly phenolic compounds (Ramos-Comenzana/Monteolica-Sanchez/Lopez 1995). In addition, OMW typically contains polysaccharides, lipids, proteins, a number of monocyclic and polymeric aromatic molecules (Ethaliotis/Papadopoulou/Kotsou/Mari/Balis 1999), which might exhibit inhibition effects towards some specific anaerobic microorganism populations. All chemicals of analytical grade were purchased from Sigma.

The OMW is a significant source of environmental pollution in the Mediterranean countries (Basheer/Sabbah/Marzook 1999; Basheer/Sabbah/Marzook 2004). In general and for economic reasons, OMW is often concentrated in evaporation ponds and left to dry throughout the summer season (Borja/Martin/Maestro/Alba/Fiestas 1992; Benitez/Beltran-Heredia/Torregrosa/Acero/Cercas 1997b). OMW, negatively impacts the regional environment due to its toxicity to microorganisms in domestic wastewater treatment plants, its strong and unpleasant odor after anaerobic digestion, and also due to its potential threat to surface and groundwater sources. The seasonal production and high organic load of OMW make anaerobic treatment a very reasonable treatment option for this type of aqueous waste (Boari/Brunett/Passino/Rozzi 19084).

Within the different anaerobic treatment systems studied so far, up-flow anaerobic sludge blanket reactor (UASB) is considered as one of the most popular bioreactors to treat agro-industrial wastewaters characterized with high organic load. Previous research works show that a very high efficiency of COD removal has been achieved using UASB reactors with an influent organic loading rate of 8 g COD-1d-1 (Erguder/Guven/Demirer 2000). Most research studies in this field report that the major problems of UASB system are the long-term start-up period in addition to the instability of the biological activity as a result of washing out a significant part of the biomass from the reactor. Also, other problems are accounted such as the high toxicity of phenolic compounds, tannins, and adjusting the pH in the medium of the reactor (Sabbah/Marzook/Basheer 2004) when dealing with wastewater generated from the agro-industry.

Suitable sludge source is highly important for both start-up period and overcoming the low biodegradability of toxic compounds typically present in OMW. Therefore, the main goal of this study is to examine the most suitable sludge to be used for OMW in anaerobic treatment systems, mainly UASB reactors. Also, a *geographic information system* (GIS) database to allocate olive mills mainly in Jordan, Palestine and Israel and document their characteristics was prepared in this study.

1.1.1 Geographic Information System (GIS)

In order to successfully manage the OMW generated in Jordan, Palestine and Israel it was necessary to identify the locations most in need of facilities. In particular, analysis of the following was carried out:

- Location of the olive mills
- Availability of wastewater treatment facilities
- Characteristics and quantity of wastewater

A GIS database currently exists mapping many details about olive oil production in Jordan, Palestine and Israel. The database has been divided into three areas. Area 1 covers the Kingdom of Jordan and has been accumulated by the Royal Scientific Society. Area 2 was compiled by the Hebron University team and is subdivided into area 2(a) (West Bank) and area 2(b) (Gaza Strip). The Regional R&D Center at the Galilee

Society collected the data for area 3 (Israel). The following information has been brought together for the database:

- Towns and villages
- Districts
- Main Roads
- Regional Roads
- Local Roads.

There are two comprehensive maps on the database. Each map contains several different layers for Jordan, Palestine and Israel. Layers detailing rivers, districts, roads, towns and villages, and olive mills have been added to a base map. A second map was compiled specifically for area 3. A questionnaire for olive mill owners was produced and the information gathered has been added to the database. This includes tables with the following information:

- General information about the mill, including name, location, type and manufacturing country.
- Numerator – contains information about the data entry.
- Olive mill owner information, including level of education.
- Production capacity of the mill.
- Water consumption and use of other resources.
- Generation of wastewater and solid waste.
- Infrastructure of the mill.
- Characteristics for area 1 – results of tests (quality of waste) carried out for some of the olive mills in Jordan.
- Characteristics for area 2 – results of tests carried out for some of the olive mills in Palestine.

The information in the database allows the relevant stakeholders to assess the requirement for the treatment in different areas, as well as practical considerations such as how to collect the OMW from the olive mills concerned. Any change in local circumstances, such as increase in mill's production capacity or modernization of milling Techniques, can be easily added to the database.

1.2 Materials and Methods

1.2.1 OMW Characterization

OMW for this study was obtained from different olive mills in the Galilee area and was refrigerated at 4 °C. The parameters COD, BOD, TSS, VSS, pH, and alkalinity of the collected OMW samples were determined according to the "Standard Methods for the Examination of Water and Wastewater, 20th Edition 1998". The total polyphenols in OMW were determined according to the Folin-Cioacalteau method (see Hamdi 1995; Kachouri/Hamdi 2004). Table 41.1 shows the typical characteristic parameters of OMW from the region. All chemicals of analytical grade were purchased from Sigma.

1.2.2 Biomass Characterization

The main characteristics of five different types of biomass collected from different sources in Israel are given in table 41.2. The differences in concentrations of *mixed liquor suspended solids* (MLSS) and *mixed liquor volatile suspended solids* (MLVSS) for the tested OMW samples were due to the solid contents of the original biomass collected from the specific source.

Table 1.1: Characteristics of Olive Mill Wastewater Used for the Biomass Selection Study (Batch Systems). **Source**: Basheer/Sabbah/Marzook 2004)

Parameter	Value
pH	5.0
Total alkalinity as CaCO3	1.172 g l^{-1}
Total polyphenols	6.8 g l^{-1}
COD(total)	163.5 g l^{-1}
COD (soluable)	131.5 g l^{-1}
BOD	27.5 g l^{-1}
TSS	86.84 g l^{-1}
VSS	0.503 g l^{-1}
$N_-NH^+_4$	0.11 g l-1

Biomass dry weight for the OMW samples was checked by taking an amount of mixed liquor suspended biomass, which was centrifuged at 5000 rpm for 10 minutes. The two phases obtained after centrifugation, were separated by decantation and then a fixed amount of the accumulated biomass was weighted and considered as wet base biomass. The obtained wet biomass amount was heated in an oven at 110 °C for 24 hours, and the resulting weight was considered as the dry weight of the biomass.

The relatively low MLVSS/MLSS (0.227) of Gadot biomass was due to the presence of an inert carrier material (such as sand and silt), where the high MLVSS/MLSS (0.7260) ratio of the biomass from Pri-

Table 1.2: Characteristics of Five Different Biomass Sources Tested in this Study.

Biomass Type	MLSS ($g\ l^{-1}$)	MLVSS ($g\ l^{-1}$)	MLVSS/ MLSS	Wet Weight (g)	Dry Weight (g)	% Dry/Wet weight
Sakhnin UASB	102.4	69.5	0.678	50.0	7.7	15.4
Haifa (HWTP)	23.3	16.25	0.697	43.6	4.2	9.6
Gadot UASB	411.4	93.6	0.227	49.8	20.0	40.2
OMW-evaporation pond	48.7	35.4	0.726	50.0	5.1	10.2
PriGat UASB	74.05	53.4	0.722	50.0	6.5	13

Gat was due to the high organic content of the distillery wastewater that was absorbed or mixed with the biomass.

1.2.3 Anaerobic Batch Experiments

Anaerobic batch experiments were carried out in 1 l Erlenmeyer flasks connected with tubing to gas measuring tubes of 500 ml in volume. All gas collection tubes were calibrated daily to determine the volume of gas accumulated. For each biomass source OMW with COD concentrations in the range of 993–35,500 mg l^{-1}, was added.

Similar volumes of standard solutions containing trace elements and yeast extract were added to all of the anaerobic batch experiments in addition to a source of carbon (either sodium acetate or OMW). Sucrose solutions (5 per cent of total COD, 700 ml in each flask) were added to two flasks containing OMW, where the first had a COD of 1 g l^{-1} and the second had a COD of 20 g l^{-1}, in order to examine the effect of easy biodegradable compounds on the total efficiency of biodegradation. Each flask was supplemented with 50 g of biomass from a different source and 0.4 g urea as a source of nitrogen. The medium in each flask was adjusted to pH = 7.0 and kept constant at this value by appropriate addition of NaOH or HCl solutions each of 0.1 M. The flasks were immersed in a shaker bath at temperature 37°C and shaken at 50 rpm. Samples were taken daily for COD and pH tests. The COD was determined by taking 5 ml of the flask content, centrifuged at 5000 rpm for 10 minutes, then tested according to the "Standard Methods for the Examination of Water and Wastewater, 20th Edition 1998". The gas collection tubes were monitored to determine the volume of the accumulated gas.

1.3 Results and Discussion

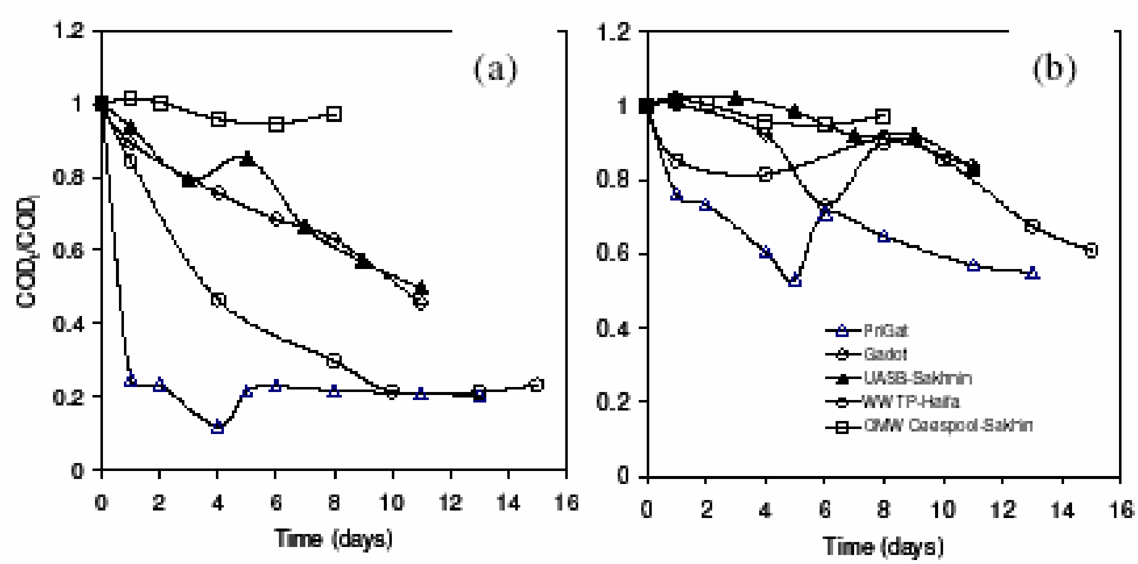
1.3.1 Biomass Activity with OMW

In a preliminary work, the anaerobic activity of the five different sources of biomass was evaluated. Each of the five batch-anaerobic systems containing water-diluted OMW with two various initial COD concentrations, each were inoculated with one of the five different biomass sources. Figure 41.1 shows the rate of the biological activity using the five different sources of biomass with OMW at initial COD concentrations of 1 g l^{-1} (figure 41.1a) and 20 g l^{-1} (Figure 41.1b). Figures 40.1a and 40.1b show obviously that the biomass from PriGat has the highest anaerobic biological activity in the treatment of OMW at both low and high concentration ranges. This result confirms that the PriGat biomass comprised the most appropriate populations of anaerobic microorganisms for the treatment of OMW compared to other sources of biomass used in this study.

1.3.2 Effect of Concentration Range of OMW on the Biomass Activity

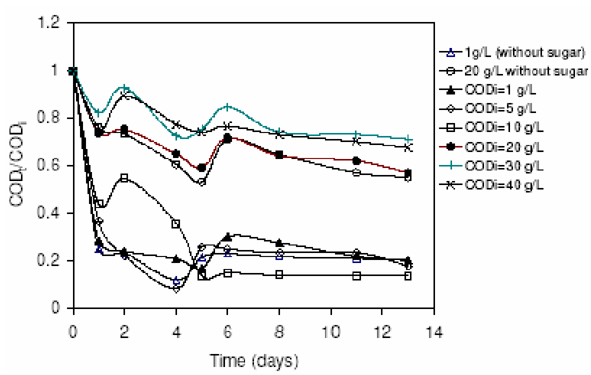
The biomass of Gadot and PriGat were selected for our further study in order to test the effect of a broader COD concentration range on the biological activity of OMW biodegradation under anaerobic conditions. Figure 41.2 presents the results for the effect of initial COD concentrations of OMW on the biological activity of biomass from PriGat. It can be seen from the results that the initial COD concentration of 5 g l^{-1} does not affect the rate of biodegradation of OMW as well as having no effect on the extent of the ultimate removal percentage (80%) obtained after 4 days. However, the (a) (b) results in figure 41.2 show that starting with initial COD concentrations of OMW equal or higher than 20 g l^{-1} caused a major

Figure 1.1: Kinetics of COD (mg/L) Removal of OMW Presented as COD Measured at Different Time Intervals (CODt) per the Initial COD Concentration (CODi). The anaerobic biodegradation conditions: Two sets of five OMW solutions (1l) of CODi 1 g/l (graph a) and of 20 g/l (graph b) were inoculated each with 50 g of sludge from the different sources. The solutions were shaken at 50 rpm, pH 7 and at 35 °C. **Source**: Basheer/Sabbah/Marzook 2004



inhibition effect on the anaerobic biodegradation rate of OMW as well as on the final extent of COD removal. It can also be seen in figure 41.2 that the initial COD concentration of 10 g l^{-1} was observed to be such an 'intermediate' concentration level, where the biodegradation rate was slow in the first three days, but the ultimate degraded organic materials present in OMW was similar to the extent obtained when using lower initial concentration of COD for OMW. Figure 41.2 also shows that 73-85 % of the COD content in the low range (1-10 g l^{-1}) was removed within 4-5 days of contact time compared to about 40 % COD removal obtained when the initial COD concentration of 20 g l^{-1} was used with the PriGat biomass. The results also show that only 25-28 per cent of the COD concentration was removed when the initial COD concentration was of 40 g l^{-1}. These results indicate that the equivalent concentration of the refractory compounds (assumed to be polyphenols) in OMW of 20 g l^{-1} or more as COD has significantly inhibited the biomass anaerobic activity.

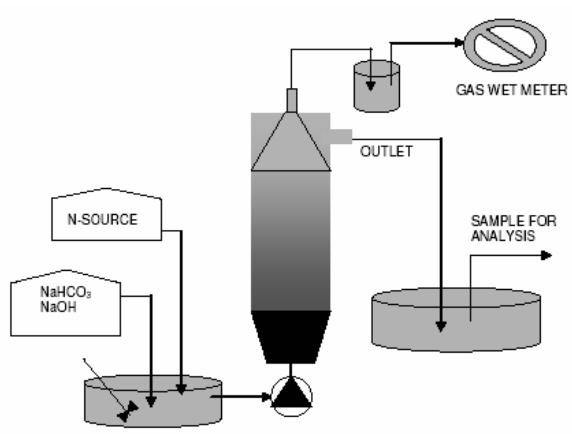
Figure 1.2: The Effect of Initial COD Concentration of OMW on the Kinetic Activity of Biomass from PriGat. The activity profile is presented as COD measured at different time intervals (CODt) per the initial COD concentration (CODi). The anaerobic biodegradation conditions: OMW solutions (1l) of various initial COD concentrations were inoculated each with 50 g of sludge from PriGat. The solutions were shaken at 50 rpm, pH 7 and at 35 °C.



1.3.3 Pilot Plant for the Treatment of OMW

Pilot plant of 4 m^3 in volume was designed and constructed for the treatment of OMW in one olive mill in the region of Hebron (figure 41.3). The concentration of COD in the reactor was 5000 mg/L. The amount of wastewater, which flowed into the reactor was 3m3, and the amount of sludge seeded was 1900L (1.9m^3) with the concentration of 53 g VSS/L. The constructed UASB was fed with diluted OMW with COD content in the range of 2000-5000 mg/L

Figure 1.3: Schematic Drawing for the UASB $4m^3$ in Volume Reactor System. **Source**: Basheer/Sabbah/Marzook 2004



during the start-up period of the continuous reactor. The generation of biogas bubbles in top of the reactor could be observed on the 5^{th} day of operation, indicating anaerobic activity. Anti-foaming agent was used to reduce the scum layer that periodically appeared on top of the liquid phase of the UASB reactor. The pH of the influent was adjusted to the range of 6.8–7.00 with alkaline solution while the pH of the effluent was in the range of 7.5–7.75. The COD applied after two weeks after start-up of the continuous reactor was 6250 mg/L, while the CODout was 1710 mg/L using a Hydraulic Retention Time (HRT) of 5 days. The flow rate was increased from around 980L/d to 1200L/d (HRT=4.2 days) within a one-week period. Depending on the reactor performance the HRT has been decreased down to 3.5 days or less. The work on the pilot station is being continued, with the aim of treating OMW in the constructed UASB system so that the effluents of the system can be disposed directly to the municipal wastewater system.

1.4 Conclusions

A GIS database system was compiled in this study. This system is comprised of three levels representing Jordan, Palestine and Israel. The database contains geographic data, which includes maps and locations for the areas and the mills in the three countries. The compiled database also contains information about the characteristic of olive mills in Jordan, Palestine and Israel.

In our study also, two types of biomass, collected from the wastewater treatment systems of a citrus juice producing company “PriGat” and of citric acid manufacturing factory “Gadot” both located in Israel, were found to be the most efficient sources of microorganisms to anaerobically treat both sodium acetate solution and OMW. The results show that 70–85 % of COD removal was reached using Gadot biomass after 8–10 days when the initial COD concentration of OMW was up to 5 g l^{-1}, while similar removal efficiency was achieved using OMW of initial COD concentration of 10 g l^{-1} in 2–4 days of contact time with the PriGat biomass.

The physico-chemical pretreatment of OMW was found to enhance the anaerobic biodegradation rate for OMW with initial concentration of 20 g l^{-1} using PriGat biomass. A removal efficiency of 80 % was observed when OMW was first physicochemically pretreated, while only 40 per cent of removal efficiency was reached using water-diluted OMW with the same initial COD and biomass concentrations. This finding is attributed to the high removal efficiency of polyphenols and other toxicants by the proposed pretreatment process for OMW.

REFERENCES

Baccari, M.; Bonemazzi, F.; Majone, M.; Riccardi, C., 1996: “Interaction between Acidogenesis and Methanogenesis in the Anaerobic Treatment of Olive Oil Mill Effluents”, in: *Wat. Res.*, 30,1: 183–189.

Basheer, S.; Sabbah, I.; Marzook, T., 1999: “Olive mill wastewater treatment in the Galilee Region”. *Annual Report, Israeli Ministry of Agriculture* ((city: publisher/organization).

Basheer, S.; Sabbah, I.; Marzook, T., 2004: “The effect of pretreatment on anaerobic activity of olive mill wastewater using batch and continuous systems”, in: *Process Biochem*, 39: 1947–1951.

Benitez, F.J.; Beltran-Heredia, J.; Torregrosa, J.; Acero, J.L., 1997[a]: “Aerobic degradation of olive mill wastewater”, in: *Appl. Microbiol. Biotechnol*, 47: 185–188.

Boari, G.; Brunetti, A.; Passino, R.; Rozzi, A., 1974: “Anaerobic digestion of olive mill wastewater2, in: *Agri. Wastes,* 10: 161–175.

Borja, R.; Martin, M.; Maestro, R.; Alba, J.; Fiestas, J.A., 1992: “Enhancement of the anaerobic digestion of olive mill wastewater by the removal of phenolic inhibitors”, in: *Process Biochem*, 27: 231–237.

Cercas, V., 1997b: “Chemical pretreatment by ozone of wastewater from olive oil mills”, in: *Technol. Environ. Chem*, 60: 97–109.

Erguder, T.H.; Guven, E.; Demirer, G.N., 2000: “Anaerobic treatment of olive mill wastes in batch reactors”, in: *Process Biochem*, 36: 243–248.

Ethaliotis, C.; Papadopoulou, K.; Kotsou, M.; Mari, I.; Balis, C., 1999: “Adaptation and population dynamics of Aztobacter vinelandii during aerobic biological treatment of olive mill wastewater", in: *FEMS Microbiol. Ecol.*, 30: 301–311.

Hamdi, M., 1995: "Anaerobic digestion of olive mill wastewater", in: *Process Biochem.*, 31: 105–110.

Kachouri, F.; Hamdi, M., 2004: "Enhancement of polyphenols in olive oil by contact with fermented olive mill wastewater by Lactobacillus plantarum", in: *Process Biochem.*, 39: 841–845.

Ramos-Comenzana, A., 1995: "Monteolica-Sanchez M and Lopez MJ, Bioremediation of alpechin", in: *J. Biodeter. Biodegr*, 35: 249–268.

Sabbah I.; Marzook T.; Basheer S., 2004: "The effect of pretreatment on anaerobic activity of olive mill wastewater using batch and continuous systems", in: *Process Biochem*, 39: 1947–1951.