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# The effect of pretreatment on anaerobic activity of olive mill wastewater using batch and continuous systems

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**Abstract**

This study was focused on several physico-chemical and biological treatment methods that may affect the reduction of the organic load in olive mill wastewater (OMW). In this study, removal of 95% of the phenolic compounds present in OMW was achieved using sand filtration and subsequent treatment with powdered activated carbon in a batch system. This pretreatment for OMW was found to enhance the anaerobic activity of the sludge in the batch system significantly. The efficiency of organic load removal achieved by the anaerobic treatment of untreated OMW in batch reactors with tap water dilution factors below 1:10, reached approximately 65% chemical oxygen demand (COD) removal. However, in the up-flow sludge anaerobic blanket (UASB) reactor, COD removal efficiency of 80–85% was reached at a hydraulic retention time (HRT) of 5 days with an influent COD concentration of $40\,g\,l^{-1}$ and organic loading rate (OLR) $= 8\,g^{-1}\,COD\,l^{-1}$ per day.


*Keywords:* Olive mill wastewater; Anaerobic treatment; OLR; Polyphenol; UASB

## 1. Introduction

Olive mill wastewater (OMW) generated by the olive oil extraction process is the main waste product of this industry. Approximately $1.8 \times 10^6$ t of olive oil are produced annually worldwide where the majority of it is produced in the Mediterranean basin [1]. The average amount of olive mill wastewater produced during the milling process is 1.2–1.8 $m^3\,t^{-1}$ of olives. OMW resulting from the production process surpasses 30 million $m^3$ per year [2] in the Mediterranean region. Treatment of OMW is becoming a serious environmental problem, due to its high organic chemical oxygen demand (COD) concentration, and because of its resistance to biodegradation due to its high content of phenolic compounds [3].

Due to the current lack of appropriate alternative technologies to treat OMW, much of the OMW in the Mediterranean area is 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. Similarly, OMW is often concentrated in ponds and left to dry throughout the summer season [4,5]. OMW, which contains high concentrations of organic materials, such as polyphenols, tannins, and lipids, 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.

OMW is comprised of water (83%), organic compounds (15%), and inorganic chemicals (about 2%). The color of the waste produced ranges from black to dark-red reflecting the presence of phenolic compounds. OMW is acidic and contains high concentrations of total suspended solids (TSS), total dissolved solids (TDS), and phenols. The OMW is characterized by high levels of COD and biochemical oxygen demand (BOD), in addition to having very high concentrations of fat, oil, and grease (FOG) [6]. Maximum BOD and COD concentrations in OMW reach 100,000 and 220,000 $mg\,l^{-1}$, respectively. This is one of the highest organic loads of known concentrated effluents, which is 100–150 times higher than that of domestic wastewater.

Several methods have been proposed for treating OMW, such as evaporation ponds, thermal treatment, physico-chemical and biological treatments. Also, reuse of the OMW

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by distribution in agricultural soils as an organic fertilizer was studied [7]. In the last decade, most of the research conducted on OMW treatment has been focused on the use and development of anaerobic methods and bioreactors that can remove efficiently the high organic load [5,8–11] as well as reduce the toxicity of microorganisms-inhibiting materials present in OMW [7]. It has been reported that anaerobic bacteria decompose organic materials in a three-stage process [4,12,13]. In the first stage, anaerobic bacteria degrade complex organic materials into simpler compounds; namely, polysaccharides and polyphenols are converted to their monomers (monosaccharides and phenols, respectively). During the second stage, acetogenic bacteria convert the phenols and the monosaccharide into organic acids, such as acetic, lactic and formic acids and alcohol. Finally, in the third stage, methanogenic bacteria, which are characterized by their sensitivity to pH, convert the organic acids into biogas (a mixture of 60–80% methane and other gases, mainly carbon dioxide).

This study focuses on several physico-chemical and biological treatment methods that may affect the reduction of organic load of OMW. The physico-chemical methods were examined for the removal of microorganisms-inhibiting compounds (phenolic compounds).

## 2. Materials and methods

### *2.1. Characterization of OMW*

OMW for this study was obtained from the continuous centrifuge of an olive mill in Sakhnin, Israel, located in the Galilee region in the north of the country. Samples were collected and refrigerated at 4 °C. Polyphenols, COD, BOD, TSS, VSS, pH, and alkalinity were determined according to the APHA (1995). Table 1 shows the typical characteristic parameters of OMW from the region. Anaerobic sludge was obtained from the Haifa Wastewater Plant, Israel.

### *2.2. Physico-chemical treatment*

Physical removal of COD present in OMW and its effect on biological treatment were investigated using three different systems: sand filtration, subsequent treatment with activated carbon and filtration through GFA paper (Fig. 1). A multi-layered sand filter 60 cm high with an internal diameter of 8 cm utilized natural sand and gravel materials. The filter consisted of three layers: gravel (grain size 3–5 mm), coarse sand (grain size 1–2 mm) and fine grain sand (grain size 0.5–1 mm). The OMW was filtered first through coarse sand, followed by fine sand, again by coarse sand and finally by gravel. After sand filtration, the OMW was treated by powder activated carbon (PAC)—10 g of activated carbon added to 1 l of OMW solution. Finally, the OMW, pretreated by sand filtration and activated carbon, was subjected to biological treatment for a period of 30 days by anaerobic batch reactors (1 l each) inoculated with anaerobic sludge (10 ml) from the Haifa Wastewater Plant. These two reactors were compared with the GFA filtered OMW. This investigation was conducted under the conditions of pH 7 and 35 °C.

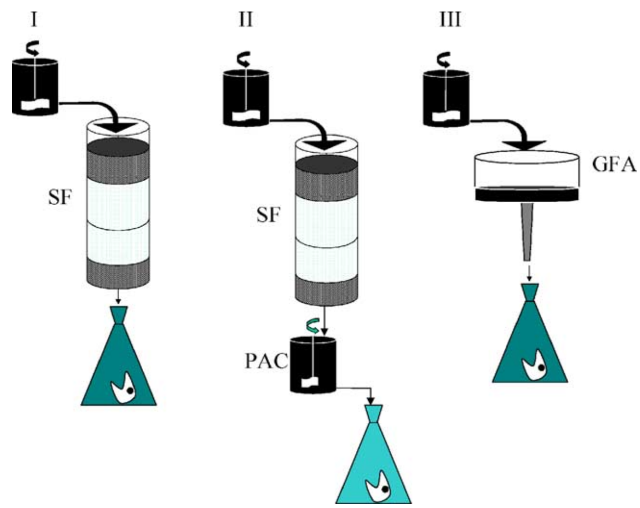


Fig. 1. Scheme of the different physico-chemical treatment processes.

Table 1
Characterization of olive mill wastewater

| Parameter | Value |
|---|---|
| COD (mg $l^{-1}$) | 148000 ± 13300 |
| BOD (mg $l^{-1}$) | 67000 ± 6640 |
| TSS (mg $l^{-1}$) | 14500 ± 1230 |
| VSS (mg $l^{-1}$) | 11000 ± 1120 |
| pH | 5.2 ± 0.08 |
| Phenols (mg $l^{-1}$) | 2210 ± 128 |

### *2.3. Up-flow anaerobic sludge blanket (UASB) reactor system*

A 25 l (active volume) UASB reactor 110 cm high with an internal diameter of 20 cm was constructed of Plexiglas (Fig. 2). The UASB was inoculated with 18 l of sludge inoculum of VSS of 26,240 mg $l^{-1}$. The UASB reactor was operated for 6 months at 35 ± 2 °C and pH 7. The reactor was initially fed with diluted OMW (about 2000 mg $l^{-1}$) and the influent COD concentration was increased gradually (20–30% by reducing the dilution factor with tap water) while the hydraulic retention time (HRT) was kept constant (5 days). The organic loading rate (OLR) was increased according to the COD removal (increasing of 20–30% of the concentration when the removal efficiency reached 60–70%). The OMW was fed into the reactor using a peristaltic pump. Sodium bicarbonate ($NaHCO_3$) and sodium hydroxide (NaOH) solutions were used for pH adjustment to 7 and urea was added as a source of N.

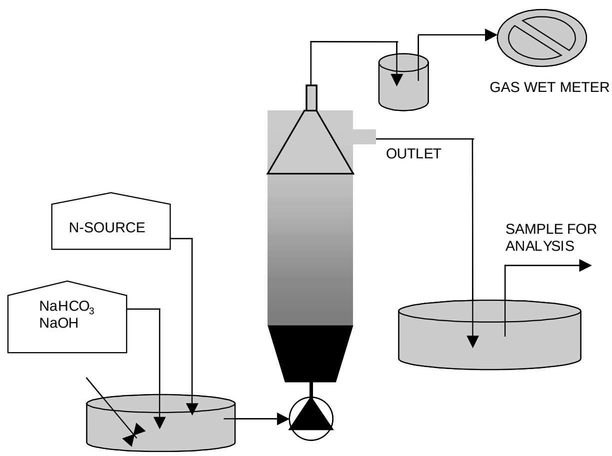


Fig. 2. A schematic drawing for the UASB reactor system.

### 2.4. Anaerobic batch experiments

The batch experiments were conducted with 1 l Erlenmeyer bottles as anaerobic reactors. Inoculums samples of 150 ml of 26,100 mg $l^{-1}$ VSS each were added to 850 ml of OMW diluted with tap water. The reactors were incubated at 35 °C and an initial pH value of 7. The dilution of OMW for five separate initial concentrations were 1219, 25,102, 34,425, 52,100 and 63,300 mg $l^{-1}$ as COD total in the above-mentioned batch reactors. Samples for COD analysis were taken weekly during the experimentation period.

## 3. Results and discussion

Experiments showed that treatment of OMW with activated carbon increased the $BOD_5$/COD ratio from 0.6 to 0.88 in the filtrate resulting from the anaerobic treatment of OMW. Additionally, the concentration of phenols was reduced from 2210 to 285 mg $l^{-1}$ after sand filtration and to 108 mg $l^{-1}$ through the additional step of adsorption on activated carbon. Although the removal efficiency of COD by the three different filtration systems were similar (62–67%) as can be seen in Table 2, the additional treatment with activated carbon removes significantly more phenolic compounds and possibly other toxic pollutants that we believe have toxic effects on the biomass activity. The removal of the phenolic compound and possibly other toxic materials

Table 2
Effect of physico-chemical treatment type on COD removal

| Treatment type | $COD_{in}$ (mg $l^{-1}$) | $COD_{out}$ (mg $l^{-1}$) | COD removal (%) |
|---|---|---|---|
| GFA paper filtration | 148000 | 56000 | 62 |
| Sand filtration | 148000 | 52000 | 65 |
| Sand filtration + adsorption by activated carbon | 148000 | 47000 | 67 |

Table 3
Effect of physico-chemical treatment type on anaerobic digestion efficiency

| Treatment type | COD removal after incubation of 30 days with initial COD = 35 g $l^{-1}$ (%) |
|---|---|
| Without any pretreatment | 40 |
| GFA paper filtration | 45 |
| Sand filtration | 58 |
| Sand filtration + adsorption by activated carbon | 68 |

that inhibit the growth of microorganisms using sand filtration and PAC contributes significantly on increasing the efficiency of anaerobic digestion as can be seen in Table 3. The removal of COD by anaerobic digestion (batch reactor) was increased after sand filtration for the raw OMW from 45 to 58%, and to 68% after treating the filtrated OMW with 10 g $l^{-1}$ of PAC. The increase in COD removal efficiency by about 10% more than the filtrated OMW and 20% more than the raw OMW (diluted) indicate that activated carbon contributes significantly to the removal of polyphenols and therefore led to enhancement of the biological activity. Subsequently, the biogas production increased when the OMW was pretreated with activated carbon in this system. The biogas production can be attributed to enhancement of the anaerobic activity. These results are in good agreement with the results obtained by Al-Malah et al. [14]. It has been reported that filtration of OMW removed more than 55% of the polyphenols while treatment with activated clay removed about 81% of the polyphenols present in OMW.

Biological treatment was conducted using both laboratory scale anaerobic batch reactors and a bench scale UASB reactor. Results demonstrated the benefits of anaerobic treatment of wastewater, specifically a high tolerance for the steep organic load and inhibiting materials present in OMW. Fig. 3 shows the COD removal kinetic as a function of different initial concentrations in batch anaerobic systems. As can be seen in this figure, removal of organic matter has not been observed for initial concentrations of 50,000 and 63,000 mg $l^{-1}$ COD. On the other hand, 40% COD removal was performed with initial concentrations below 35,000 mg $l^{-1}$ COD. Removal of 65% of COD was achieved by the anaerobic treatment of OMW in batch system with tap water dilution factors below 1:10 (reactor 1) where the initial COD concentration was about 12,000 mg $l^{-1}$.

Anaerobic digestion of OMW using a 25 l Plexiglas UASB reactor inoculated with sludge from the Haifa Wastewater Plant was evaluated. At pH 7 and 35 °C, an initial concentration of 2000 mg $l^{-1}$ COD was fed with the mean flow rate of 3–4 ml $min^{-1}$. The concentration of the influent increased when the COD removal efficiency reached 60–70% in order to determine the maximum possible organic loading rate as well as the maximum influent COD concentration

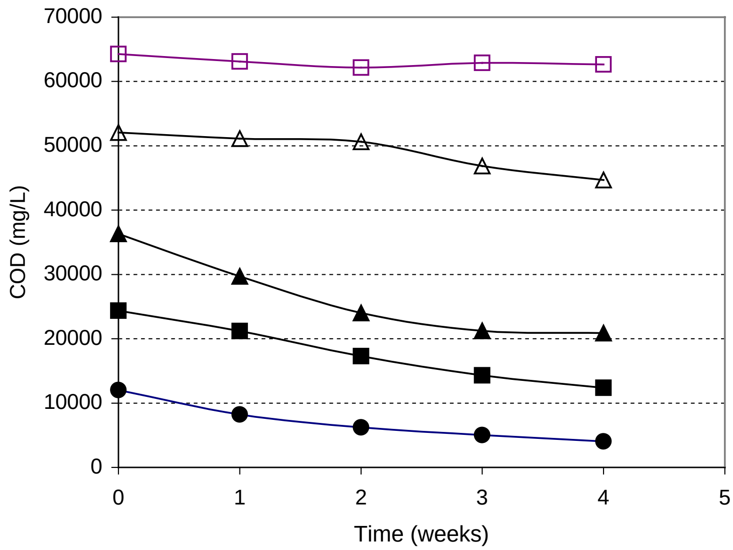


Fig. 3. Kinetics of COD (mg l$^{-1}$) removal vs. initial concentration in the batch systems at 35 °C and pH 7: (●) reactor 1; (■) reactor 2; (▲) reactor 3; (△) reactor 4; (□) reactor 5.

while maintaining satisfactory COD removal. Unlike the batch systems, the UASB removes more than 80% of the COD of the influent OMW with a tap water dilution factor below 1:5, and gas production of 300 l gas kg$^{-1}$ COD removed.

Fig. 4 shows the UASB efficiency as COD removal percentage as well as the organic loading rate during the performance period of the UASB system. As can be seen from this figure, COD removal efficiency of 80–90% was reached even at organic loading rate of 7–8 g COD l$^{-1}$ per day, which is equivalent to COD concentration of about 40 g l$^{-1}$.

The higher tolerance of biomass to high organic loading in the UASB than the batch reactor could be attributed to the fact that the laminar flow reactor was performed in sequences of the three anaerobic activity steps reducing the negative effect of each step onto the next one. This could be an advantage of using UASB reactor to reach better removal efficiency of organic matter without any further expensive pretreatment or with minimum pretreatment. This interpretation should be addressed with future study by developing an analytical method for sampling from different heights in the reactor and analysis of the samples for different metabolites of the organic compounds that could represent the three steps of anaerobic activity of OMW.

Fig. 5 illustrates the production of biogas kg$^{-1}$ COD removed as the OMW initial COD concentration increased. The average production of 200–300 l biogas kg$^{-1}$ COD removed was in accordance with the COD removal. This figure shows that the decreased dilution (inlet concentration of

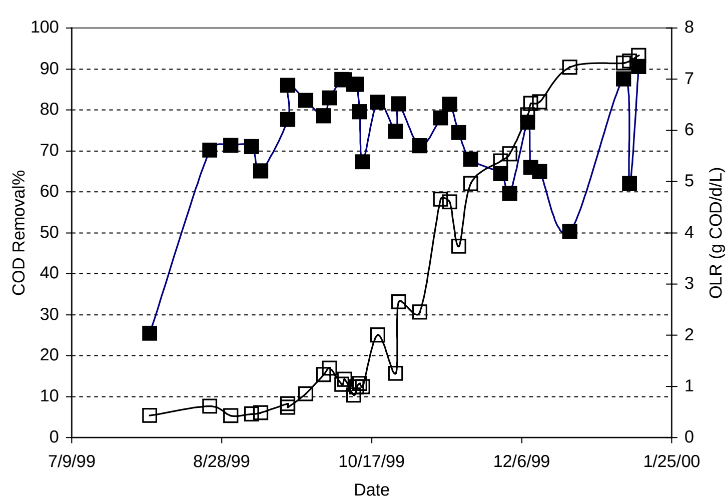


Fig. 4. COD removal (%) and organic loading rate (g COD l$^{-1}$ per day) in the UASB reactor system. Experimental conditions: temperature, 35 °C; pH 7. (■) COD removal (%); (□) OLR.

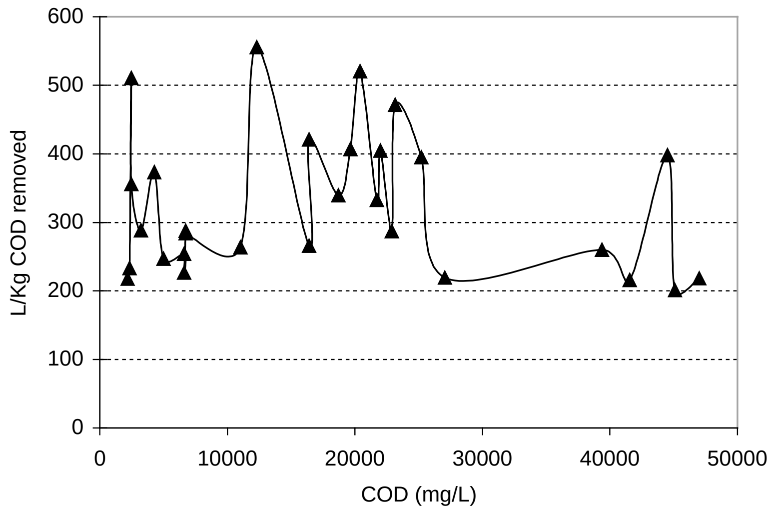


Fig. 5. Biogas production ($l\,kg^{-1}$ COD removed) as a function of COD concentration in the inlet. Experimental conditions: see Fig. 4.

more than 30,000 $mg\,l^{-1}$) caused a decrease in production rate of biogas.

## 4. Conclusions

The efficiency of anaerobic digestion was increased when preceded by a pretreatment step (physico-chemical treatment). The results showed that treatment of OMW with activated carbon, subsequently, after sand filtration resulted in an increase in COD removal of more than 20%. This result indicates that a strong adsorbent, such as activated carbon, could efficiently remove a significant portion of the toxic compounds, such as phenols, present in OMW. The results from the biological treatment experiments show that anaerobic systems have a high potential to tolerate the steep organic load and the toxic compounds present in OMW. This study also shows that the UASB reactor removed more than 80% of the inlet COD concentration of over 40,000 $mg\,l^{-1}$, and produces about 300 l biogas $kg^{-1}$ COD removed. Unlike UASB bioreactor, a maximum removal of about 40% could be reached using a batch bioreactor with initial COD concentration of 35,000 $mg\,l^{-1}$ while COD concentration higher than 40,000 $mg\,l^{-1}$ could not be treated by an anaerobic batch reactor.

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## References

[1] Benitez FJ, Beltran-Heredia J, Torregrosa J, Acero JL. Aerobic degradation of olive mill wastewater. Appl Microbiol Biotechnol 1997;47:185–8.
[2] Baccari M, Bonemazzi F, Majone M, Riccardi C. Interaction between acidogenesis and methanogenesis in the anaerobic treatment of olive oil mill effluents. Water Res 1996;30(1):183–9.
[3] Ramos-Comenzana A, Monteolica-Sanchez M, Lopez MJ. Bioremediation of alpechin. I. Biodeter Biodegr 1995;35:249–68.
[4] Benitez FJ, Beltran-Heredia J, Torregrosa J, Acero JL, Cercas V. Chemical pretreatment by ozone of wastewater from olive oil mills. Technol Environ Chem 1997;60:97–109.
[5] Boari G, Brunetti A, Passino R, Rozzi A. Anaerobic digestion of olive mill wastewater. Agric Wastes 1984;10:161–75.
[6] Benitez FJ, Beltran-Heredia J, Torregrosa J, Acero JL. Improvement of biodegradation of olive mill wastewater by prior ozonation pretreatment. Bioprocess Eng 1997;17:169–75.
[7] Paredes C, Bernal MP, Roig A, Cerarra J. Effect of olive mill wastewater addition in composting of agroindustrial and urban wastes. Biodegradation 2001;12:225–34.
[8] Annual Report, Israeli Ministry of Agriculture, 1997.
[9] Borja R, Martin M, Maestro R, Alba J, Fiestas JA. Enhancement of the anaerobic digestion of olive mill wastewater by the removal of phenolic inhibitors. Process Biochem 1992;27:231–7.
[10] Hamdi M. Anaerobic digestion of olive mill wastewater. Process Biochem 1995;31:105–10.
[11] Andreozzi R, Longo G, Majone M, Modesti G. Integrated treatment of olive oil mill effluents. Water Res 1998;32:2357–64.
[12] Martin M, Borja R, Garcia I, Fiestas JA. Kinetics of methane production from olive mill wastewater. Process Biochem 1991;26:101–7.
[13] Zemman G, Sanders WTM, Wang KY, Lettinga G. Anaerobic treatment for complex wastewater and waste activated sludge-application of an upflow anaerobic solid removal (UASR) reactor for removal and prehydrolyzed of suspended COD. Water Sci Technol 1997;35:121–8.
[14] Al-Malah K, Azzam M, Abu-Lail N. Olive mills effluent wastewater post-treatment using activated clay. Sep Purif Technol 2000;20:225–34.