International Journal of Recycling of Organic Waste in Agriculture (2023)12: 37-45
Doi: 10.30486/IJROWA.2022.1946764.1383

ORIGINAL RESEARCH

Olive mill wastewater treatment using a solar reactor and reuse of the waste as liquid fertilizer

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Received: 07 December 2021 / Accepted: 08 May 2022 / Published online: 19 July 2022

Abstract

Purpose The main aim of this study was to treat olive mill wastewater (OMW) using a photo-Fenton's solar reactor; to investigate its potential use as liquid fertilizer and to evaluate its impact on pepper crop.

Method Olive mill wastewater was collected in a tank 1000 L and supplemented with 2000 gr $FeSO_{4}.{}_7H_2o$. After that, 150 ml H_2O_2 was added to the tank to start Fenton's reactor. The treated OMWwas collected in a container and NaOH with a concentration of 1 M was added to improve the pH of the treated OMW. Pepper seedlings were cultivated on 16 February, 2020 inside the greenhouse for a period of five months. The treated OMW was used as liquid fertilizer and compared with chemical fertilizer as control.

Results The pH and electrical conductivity of treated OMW were 7.5 and 7.6 dS/m, respectively. Furthermore, the control produced the highest yield and fruit number significantly ($p < 0.05$) compared to the other treatments, followed by OMW treated by stabilization bond (SB-OMW100%). Also the treatments fertilized by OMW treated by solar reactor (SR-OMW50%) and stabilization bond (SB-OMW100%) produced the same plant length at the end of the growing period.

Conclusion The concentrations of N, P, and K of treated OMW (0.21, 0.06, and 0.68 respectively) were quite low and supplementary fertilization was necessary to improve the nutrients value of the treated OMW. The solar reactor could be a valuable and useful tool in treatment of olive mill wastewater for agricultural purposes mainly on small scale sites.

Keywords Olive mill, Pepper, Liquid fertilizer, Treatment, Yield production

Introduction

Olive mill wastewater (OMW) is the liquid by-product generated from the olive oil extraction process. The annual production of OMW generated in the Mediterranean countries reached up to 30 MCM of which 700000 CM in Tunisia alone (McNamara et al. 2008; Souilem et al. 2017). In Palestine, there were 295 olive presses in 2016, generating annually about 274000 CM of OMW. Most of OMW (44.3%) is disposed into septic tanks. OMW also spread into agricultural lands and diffuses into surface water bodies, which negatively impacts the physiochemical characteristics of the soil (PCBS 2017). Nowadays, OMW is considered one of the major pollution risks to the environment worldwide. The most common method for disposing OMW is the direct application into the cultivated

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lands as organic liquid fertilizers. Many field investigations indicated a positive impact of OMW on soil fertility as well as crop growth and development and proved that the application of OMW did not cause accumulation of heavy metals in the soil profile (Rinaldi et al. 2003). Other field studies showed that the application of untreated OMW as organic amendment causes undesirable changes in soil properties and the activity of soil microorganisms leading to negative impacts on soil fertility and quality due to phytotoxicity of OMW (Mekki et al. 2007). Moreover, other findings showed that the high values of COD and the high concentration of antibacterial and phytotoxic polyphenols in OMW poses a significant pollution risk to surface and groundwater bodies (EL-Alami and Fattah 2020). The high concentration of phenolic compounds present in OMW makes it highly toxic and undesirable for agricultural purposes (Aggelis et al. 2003). In addition to that, irrigation of plants with untreated OMW might adversely reduce the germination of seeds, plant growth and development of many vegetable crops and may cause fruit and leaf damage (Mekki et al. 2013). The chemical composition of OMW is highly variable due to many factors including olive genotype and variety, olives maturity, climatic conditions, type and amount of fertilizers and pesticides used, and method of extraction (Santi et al. 2008). Additionally, OMW contains organic compounds such as polyphenols, organic acids, sugars, some salts, and large amount of water around 80% (Niaounakis and Halvadakis 2006; Saadi et al. 2007; Negro et al. 2017). Interestingly, the nutritional characteristics of OMW are favorable for agricultural purposes since it contains significant amount of nitrogen, potassium, phosphorous, calcium, magnesium, and iron and some anions like Cl^{-1}, F^{-1}, PO_4^{-2}, and SO_4^{-2} (Lesage-Meesen et al. 2001).

In terms of pollution effect, one cubic meter of OMW is equivalent to 100-200 m^3 of municipal wastewater. Raw OMW has a bad odors and dark color, which prohibits its direct disposal into the environment (Fig. 1). Uncontrolled discharge of OMW into the agricultural lands and water courses leads to undesirable impacts for the environment and has a deleterious effect to the physiochemical properties of soil and can potentially contaminate groundwater aquifers (Rinaldi et al. 2003; Laconi et al. 2007; Santi et al. 2008; Anastasiou et al. 2015).

The physiochemical properties of the soil such as pH and porosity are negatively affected by the application of OMW directly into the soil (Sierra et al. 2001; Niaounakis and Halvadakis 2006).

Fig. 1 Storage of OMW into an open pond (A), and discharging of OMW in the environment (B)

Different chemical and biological methods have been proposed for treatment of OMW (Zyoud et al. 2021; Iwissat et al. 2022). Other methods might produce toxic byproducts and do not alleviate the toxicity or high COD of OMW (Rengaraj et al. 2002; McNamara et al. 2008). Oxidation methods that utilize H_2O_2, O_3 or O_2 oxidants, are very promising techniques for remediation of wastewater that contains non-biodegradable organic pollutants (Scott and Ollis 1995; Gogate and Pandit 2004). These methods involve the generation of the hydroxyl radicals which are reactive intermediate and have high oxidation potential (Sarria et al. 2002). Taking into account the potential value of OMW as a fertilizer, the main objective of this study was to treat the olive mill wastewater using Photo-Fenton's solar reactor method and to investigate its possibility to be used as liquid fertilizer.

Materials and methods

Photo-Fenton process

Olive mill wastewater was treated using a parabolic solar reactor (Fig. 2). The reactor consists of glass tubes fixed on concave aluminum panels reflecting the sunlight. Treatment of OMW by the reactor depends on the Fenton's reaction, which is based on the production of hydroxyl radicals through the catalytic decomposition of hydrogen peroxide promoted by iron ions. In the first step, the ferric ion Fe^{3+} well complexed with organic matter of the OMW.

After irradiation under sun light, Fe^{3+} is reduced into Fe^{2+} (Equ. 1). In the next step, ferrous iron reacts with hydrogen peroxide to produce OH radicals, ferric ions, and hydro-oxide. Finally, the reaction of OH radicals with organic matter will oxidize it, and after several oxidation steps the carbon dioxide and water will be produced (Equ. 2).

$$Fe^{+3} + O.M \rightarrow Fe^{+2} + H_2O_2 \rightarrow OH + Fe^{+2} + OH^- \quad \text{(Equ. 1)}$$

$$O.M + OH^- \rightarrow \text{oxidized } O.M \rightarrow CO_2 + H_2O \quad \text{(Equ. 2)}$$

Treatment process

Olive mill wastewater was collected from a three-phase olive press. The sample was placed in a 1000 L plastic container (Fig. 2). The OMW was supplemented with 2000 gr $FeSO_4.7H_2O$ to make a concentration of 0.1 M that allows iron to dissolve. The pH of OMW was adjusted by application of 1 M HCl to facilitate the solubility of iron. After that, 150 ml of H_2O_2 was added to the tank to start the Fenton's reaction. During the reaction, the OMW was allowed to flow to the reactor over a period of 8 hours, and the treated OMW was collected in another container. The pH of the treated OMW was adjusted to 7 by application of 1 M NaOH.

Fig. 2 The solar reactor which used in the treatment of OMW

Use of the treated OMW as a liquid fertilizer

Pot experiment was carried out at the experimental greenhouse station of Palestine Technical University Kadoorie, Tulkarm, Palestine. Pepper (*Capsicum*) seedlings (variety 209) were used as test plants. The seedlings were cultivated in 7 liters pots filled with clay soil texture (Fig. 3). The seedlings were grown for a period of five months starting from 16 February, 2020. Five replicates for each treatment were used in the experiment. Irrigation water was applied every two days at a rate of 0.5 L per plant during the first two weeks of the growing period, and increased gradually to reach 3 L per plant at the end of the experiment. Compound liquid fertilizer (6:6:6) was applied to the control plants based on the nutrients requirement of pepper plants during the first growth stage for a period of one month, after which compound liquid fertilizer (5:3:8) was added during the rest growing periods (Table 1). Two types of treated OMW were used in the experiment; OMW treated by the solar reactor and OMW treated by sedimentation bond. The treated OMW was applied to the plant as a liquid fertilizer either at 100 or 50% dilutions (Table 2).

Fig. 3 Pepper seedling cultivated in pots during the field experiment

Table 1 Nutrient requirement of pepper plants cultivated inside greenhouse

Growth stages	Nutrient requirement (gr/du/day)		
	TN	**P_2O_5**	**K_2O**
Transplanting – first fruit set	50-100	50-100	50-100
First fruit set – harvesting	200-480	150-400	100-250
Harvesting – end of growing season	250-600	250-500	200-250

Table 2 Type of treated OMW used in the experiment

Treatments	Description	Dilution
*SR-OMW100%	Treated OMW by solar reactor	100% OMW
SR-OMW50%	Treated OMW by solar reactor	50% OMW + 50% water
**SB-OMW100%	Treated OMW by sedimentation bond	100% OMW
SB-OMW50%	Treated OMW by sedimentation bond	50% OMW + 50% water
Control	Compound chemical liquid fertilizer	(6:6:6) and (5:3:8)

*SR: solar reactor
**SB: sedimentation bon

Observations

Total nitrogen, phosphorus, potassium, calcium, magnesium, and sodium as well as the electrical conductivity and pH were analyzed in the treated OMW. Soil samples were collected to analyze the physicochemical properties of the soil at initial conditions. The samples were analyzed for evaluating total nitrogen, phosphorus, potassium calcium, magnesium, sodium, organic matter, soil texture, pH, and electrical conductivity. Total nitrogen was analyzed using Kjeldahl. The phosphorus was determined by a spectrophotometer. Na^{+} and K^{+} were analyzed using a flame-photometer. The soil texture was analyzed using a hydrometer. The soil pH and ECe were determined using the saturation past method. The plant growth index was estimated by measuring the plant height, fruit number per plant, fruit weight per plant, fruit length per plant and total yield.

Data analysis

Statistical analysis of the data was carried out using ElStat Program (version 2021). Significant differences were computed using ANOVA after Tukey's-HSD test at $P < 0.05$. Means with different letters are significantly different.

Result and discussion

Characteristics of the soil and the treated olive mill wastewater

Results of soil analysis (Table 3) indicated that the soil pH (7.96) and ECe (1.2 dS/m) are suitable for cultivation of pepper plants. The nutrient concentrations of nitrogen, phosphorus and potassium were quite low and supplementary fertilization was added to support pepper growth.

Table 3 Physicochemical properties of the soil at initial condition

Parameter	Unit	Results
pH		7.96
ECe	dS/m	1.2
Ca^{+2}	ppm	280
Mg^{+2}	ppm	160
Na^{+1}	ppm	93
TN	%	0.03
P	%	0.01
K^{+}	%	0.02
OM	%	2.3
Texture		Clay soil

The treated OMW was analyzed to evaluate the possibility of using it as liquid fertilizers (Table 4). The results indicated that the pH (7.5) of the treated OMW was within the range suitable for most agricultural crops. The electrical conductivity (7.6 dS/m) was higher than the tolerance of pepper crop. Thus electrical conductivity of treated OMW was improved by diluting it with irrigation water in the fertilization unit. The concentrations of total nitrogen, phosphorous, and potassium (0.21, 0.06, and 0.68 respectively) were quite low and supplementary fertilization by chemical fertilizer was necessary to improve the nutritional value of the treated OMW. Moreover, the results indicated that the concentration of Ca^{+2}, Mg^{+2} and Na^{+1} (400, 320, and 370 mg/L respectively) were suitable for using the treated OMW as liquid fertilizer for most crops (Table 4).

Mekki et al. (2009) found that the application of treated OMW improved the organic matter and nutrient content of the soil. Other studies found that the disposal of treated wastewater into the soil improves the chemical and physical properties of the soil allowing the plants to benefit from the nutrients which exist in the treated wastewater (Tabatabaei et al. 2012; 2020).

Table 4 Chemical properties of the olive mill wastewater treated by solar reactor method

Parameter	Unit	Results
pH		7.5
EC	dS/m	7.6
Ca^{+2}	mg/L	400
Mg^{+2}	mg/l	320
Na^{+1}	mg/L	370
TN	%	0.21
P	%	0.06
K	%	0.68

Plant growth

The treated OMW was applied to the plant as liquid fertilizer and compared to the control that was fertilized by chemical liquid fertilizer (Table 5). Yiled, fruit number and plant length were higher in SB-OMW than SR-OMW treatments.

Table 5 Analysis of the difference between treatments with a confidence interval of 95%

Treatments	Yield (gr/plant)	Fruit number per plant	Average plant length
Control	810^{a}	35^{a}	52^{a}
SB-OMW100%	655^{b}	30^{b}	47^{b}
SB-OMW50%	633^{bc}	28^{bc}	45^{b}
SR-OMW100%	594^{c}	27^{c}	43^{bc}
SR-OMW50%	516^{d}	21^{d}	41^{c}

Data of different letters in the same column are significantly different after ANOVA using Tukeys HSD test at $p < 0.05$.

The results of this study showed that in treatments fertilized with liquid chemical fertilizer (control), yield, fruit number and plant length were significantly ($p < 0.05$) higher than that of the other treatments. The lowest values of plant growth parameters were recorded in treatments fertilized with SR-OMW 50% (Table 5). It is obvious that fertilization with treated OMW (SB 50 and 100%) has significantly increased the plant length over the period of the experiment (Fig. 4). Interestingly, the treated 50 and 100% SB-OMW has also increased the yield and fruit number compared with 50% SR-OMW (Fig. 5) and (Fig. 6). The statistical analysis showed that there was significant difference ($P < 0.05$) between the control and the other treatments, while there was no significant difference in yield production between the plant fertilized with treated OMW by stabilization bond (SB-OMW50%) and that treated by solar reactor (SR-OMW100%). The results also indicated that the fruit number in the control treatments produced the highest fruit number per plant compared to the other treatments followed by plants treated with OMW obtained from stabilization bond (SB-OMW100%) as shown in (Fig. 6). Statistically there was significant difference ($P < 0.05$) in yield between the control and the other treatments. Mekki et al. (2013) found that the application of treated OMW did not indicate any negative impact on the growth performance on any of the cultivated crops under field conditions. Moreover, Mekki et al. (2006) found positive impacts of the treated OMW as fertigation supplement which allow plant ripening and kernel filling. Furthermore, the amounts of organic nitrogen and proteins in plants irrigated with treated OMW were comparable with the control species or sometimes better as for *Hordeum vulgare* and *Cicer arietinum*.

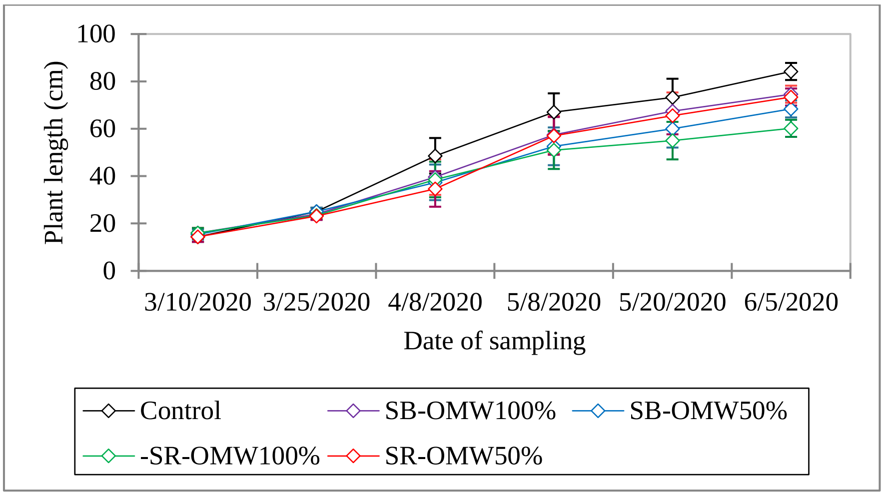

Fig. 4 The height of pepper plants fertilized by treated olive mill wastewater using solar reactor (SR-OMW) and stabilization bond (SB-OMW)

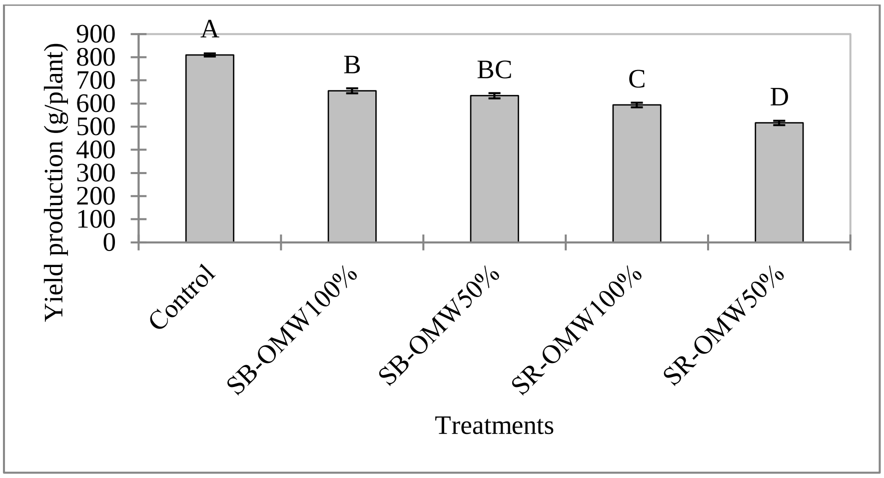

Fig. 5 Yield production of pepper plants fertilized by treated olive mill wastewater using solar reactor (SR-OMW) and stabilization bond (SB-OMW)

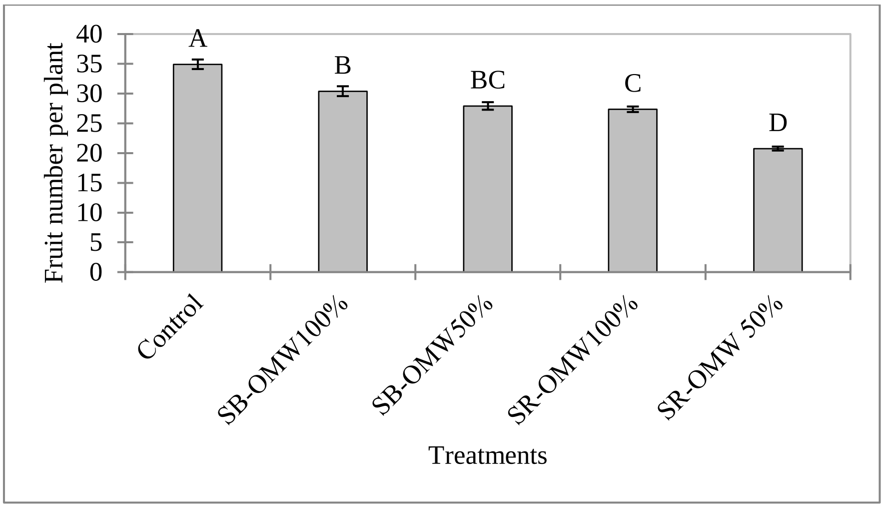

Fig. 6 Fruit number of pepper plants fertilized by treated olive mill wastewater using solar reactor (SR-OMW) and stabilization bond (SB-OMW)

Conclusion

It is concluded that the solar reactor could be a valuable tool in treatment of olive mill wastewater for agricultural purposes as well as protecting the environment mainly on small scale sites. It is also concluded that the macronutrients of the treated olive mill wastewater (N, P, K) were quite low and supplementary fertilization by chemical fertilizer is necessary to improve the nutrients value of the treated OMW. Moreover, the results indicated that the plant growth performance varied according to the type and concentration of the treated OMW.

Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest associated with this study.

References

Aggelis G, Iconomou D, Christou M, Bokas D, Kotzailias S, Christou G, Tsagou V, Papanikolaou S (2003) Phenolic removal in a model olive oil mill wastewater using Pleurotus ostreatus in bioreactor cultures and biological evaluation of the process. Water Res 37:3897-3904. https://doi.org/10.1016/S0043-1354(03)00313-0

Anastasiou C, Christou P, Michael A (2015) Approaches to olive mill wastewater treatment and disposal in Cyprus. Environ Res J 2:49-58. https://doi.org/10.3923/erj.2011.49.58

EL-Alami A, Fattah A (2020) Olive mill wastewater causing pollution in the Oum Er Rbia River and potential environmental effects and impact on the Eurasian Otter. J Anal Sci Technol 2(2):110-115. https://doi.org/10.48402/IMIST.PRSM/jasab-v2i2.24324

Gogate P, Pandit A (2004) A review of imperative technologies for wastewater treatment. I: Oxidation technologies at ambient conditions. Adv Environment Research 8:501-551. https://doi.org/10.1016/S1093-0191(03)00032-7

Iwissat S, Rahil M, Shahin N, Abuamsha R, Hilal HS, Zyoud A, Nassar I, Voogt W, Kujawa K, Salman M (2022) Fungus-based bioremediation of olive mill wastewater and potential use in horticulture. Water Environ J 1–7. https://doi.org/10.1111/wej.12771

Laconi S, Molle G, Cabiddu A, Pompei R (2007) Bioremediation of olive oil mill wastewater and production of microbial biomass. Biodegradation 18(5):559-566. https://doi.org/10.1007/s10532-006-9087-1

Lesage-Meesen L, Navarro D, Maunier S, Sigoillot J, Lorquin J, Delattre M, Simon J, Asther M, Labat M (2001) Simple phenolic content in olive oil residues as a function of extraction systems. Food Chem 75(4):501-507. https://doi.org/10.1016/S0308-8146(01)00227-8

McNamara C, Anastasiou C, Flaherty V, Mitchell R (2008) Bioremediation of olive mill wastewater. Int Biodeterior Biodegradation 61(2):127-134. https://doi.org/10.1016/j.ibiod.2007.11.003

Mekki A, Dhouib A, Aloui F, Sayadi S (2006) Olive wastewater as an ecological fertilizer. Agron Sust Dev 26(1):61–67. https://doi.org/10.1051/agro:2005061

Mekki A, Dhouib A, Sayadi S (2007) Polyphenols dynamics and phytotoxicity in a soil amended by olive mill wastewater J Environ Manage 84(2):134-140. https://doi.org/10.1016/j.jenvman.2006.05.015

Mekki A, Dhouib A, Sayadi S (2009) Evolution of several soil properties following amendment with olive mill wastewater. Progr Nat Sci 19(11):1515–1521. https://doi.org/10.1016/j.pnsc.2009.04.014

Mekki A, Dhouib A, Sayad S (2013) Review: Effects of olive mill wastewater application on soil properties and plants growth. Int J Recycl Org Waste Agric 2(15):1-7. https://doi.org/10.1186/2251-7715-2-15

Negro MJ, Manzanares P, Ruiz E, Castro E, Ballesteros M (2017) The biorefinery concept for the industrial valorization of residues from olive oil industry. In: Galanakis CM (ed) Olive Mill Waste, Academic Press, Cambridge, MA, USA, pp 57-78

Niaounakis M, Halvadakis C (2006) Olive processing waste management. Literature review and patent survey, 2nd edn. Elsevier, Amsterdam, NL

Palestinian Central Bureau of Statistics: PCBS (2017) Olive Presses Survey. Report. https://www.pcbs.gov.ps/pcbs-metadata-env4.3/index.php/catalog/318

Rengaraj S, Moon S, Sivabalan R, Arabindoo B, Murugesan V (2002) Agricultural solid waste for the removal of organics: adsorption of phenol from water and wastewater by palm seed coat activated carbon. Waste Manage 22(5):543-548. https://doi.org/10.1016/S0956-053X(01)00016-2

Rinaldi M, Rana G, Introna M (2003) Olive-mill wastewater spreading in southern Italy: Effects on a durum wheat crop. Field Crops Res 84(3):319-326. https://doi.org/10.1016/S0378-4290(03)00097-2

Saadi I, Laor Y, Raviv M, Medina S (2007) Land spreading of olive mill wastewater: Effects on soil microbial activity and potential phytotoxicity. Chemosphere 66:75-83. https://doi.org/10.1016/j.chemosphere.2006.05.019

Santi C, Cortes S, D'Acqui L, Sparvoli E, Pushparaj B (2008) Reduction of organic pollutants by using different mineral substrates as adsorbents. Bioresour Technol 99:1945-1951. https://doi.org/10.1016/j.biortech.2007.03.022

Sarria V, Parra S, Adler N, Peringer P, Benitez N, Pulgarin C (2002) Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds. Catal Today 76(2-4):301-315. https://doi.org/10.1016/S0920-5861(02)00228-6

Scott J, Ollis D (1995) Integration of chemical and biological oxidation process for water treatment: Review and recommendations, Environment Progr 14:88-103. https://doi.org/10.1002/ep.670140212

Sierra J, Martn E, Montserrat G, Cruaras R, Garau M (2001) Characterisation and evolution of a soil affected by olive oil mill wastewater disposal. Sci Total Environ 279(1-2):207-214. https://doi.org/10.1016/s0048-9697(01)00783-5

Souilem S, El-Abbassi A, Kiai H, Hafidi A, Sayadi S, Galanakis C (2017) Olive oil production sector. In: Galanakis CM (ed) Environmental effects and sustainability challenges. Olive Mill Waste, Academic Press, Cambridge, MA, USA, pp 1-28

Tabatabaei SH, Najafi P, Mirzaei SMJ, Nazem Z, Heidarpour M, Hajrasoliha S, Afyuni M, Harchegani HB, Landi E, Akasheh L, Zamanian M, Barani M, Amini H (2012) Compost' leachate recycling through land treatment and application of natural Zeolite. Int J Recycl Org Waste Agric 1(1):1-7. https://doi.org/10.1186/2251-7715-1-2

Tabatabaei SH, Nourmahnad N, Kermani SG, Tabatabaei SA, Najafi P, Heidarpour M (2020) Urban wastewater reuse in agriculture for irrigation in arid and semi-arid regions-A review. Int J Recycl Org Waste Agric 9(2):193-220. https://doi.org/1030486/ijrowa.2020.671672

Zyoud A, Nassar IM, Salman M, Iwissat S, Zyoud S, Helal MHS, Kim TW, Rahil M, Abuamsha R, Shahin N, Voogt W, Kujawa K, Hilal HS (2021) Nano‑ZnO film photo catalysts in bench‑scale continuous‑flow mineralization of olive mill waste contaminants in water. Int J Environ Sci Technol 19(5):4379-4392. https://doi.org/10.1007/s13762-021-03291-5