Techno-economic analysis of olive wastewater treatment with a closed water approach by integrated membrane processes and advanced oxidation processes

Valentina Innocenzi, Giuseppe Mazziotti di Celso and Marina Prisciandaro

ABSTRACT

In this paper, a reliable treatment process for olive mill wastewaters (OMWW) is proposed. In order to develop a more sustainable process with polyphenols recovery and water reuse, two treatment schemes have been simulated by using a process simulator (SuperPro Designer®), depending on wastewater characteristics; the first applied for 'biological' effluents by using membrane technology (microfiltration MF, ultrafiltration UF, nanofiltration NF and reverse osmosis RO), the second for wastewaters containing pesticides, in which RO is replaced with an advanced oxidation process for pesticide degradation. The results of the process analysis showed that the final permeate is a treated water suitable for both disposal in aquatic receptors and for civil or agriculture reuse. Moreover, the results of a techno-economic analysis of the proposed processes is presented, carried out by means of a life cycle cost analysis, considering the mass and energy balances obtained from process analysis. The analysis showed that the first scenario is more economically feasible. In detail, the treatment cost (€/m^3 of OMWW) was 253 and 292 €/m^3 for the first and second case study, respectively. However, the second process scheme result is inappropriate if the wastewater to be treated does not come from biological olive processing.

Key words | closed water cycle approach process analysis, membrane separation, olive mill wastewater, phenols recovery, simulation

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HIGHLIGHTS

- Process analysis was performed for the olive mill wastewater treatment with closed water cycle approach.
- Several scenarios were presented which take into account the type of olive mill wastewaters.
- Final permeate is a treated water suitable for disposal in aquatic receptors or for re-use in different purposes.
- Reverse osmosis could improve the quality of the permeate and the fresh water could be re-used for other purposes.

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INTRODUCTION

Olive oil, unlike other vegetable oils, contains polyphenols such as hydroxytyrosol, tyrosol, and oleuropein, at a concentration varying in the range 1–10 g L^{-1} (Davies *et al.* 2004).

Mainly for this reason, extra virgin olive oil is considered a unique food for human health, but even if the olive fruit is rich in phenolic compounds, only 2% of the total phenolic content of the olive fruit is present in the olive oil (Ciriminna *et al.* 2015). The oil is in fact certainly the product with the lowest content of bio-components that instead end up in large quantities in production wastes such as oil pomace and vegetation waters (olive mill waste waters – herein after OMWW), thus causing serious environmental problems. In olive oil mills, the treatment of plant waste, in particular vegetation water, is very complex and difficult to solve due to the strong organic load of the waste produced in large quantities in the short time of the oil season. Furthermore, the characteristics of vegetation waters vary according to its degree of ripeness, the storage time of the olives and the processing cycle from which they are derived. OMWW normally have characteristics that severely limit the possibilities of treatment with traditional biological or chemical-physical plants. Moreover, olive oil industries in their current status, typically small mills, cannot afford high treatment costs that in some cases could be relevant on financial statements (Pulido 2016).

Numerous stand-alone and integrated processes for the treatment of OMWW have already been proposed and developed but they have not yet led to completely satisfactory results (Pulido 2016).

Among the various treatment methods proposed, besides the classical methods for OMWW treatments (natural evaporation and thermal concentration; physic-chemical treatments including coagulation–flocculation), other processes and bioprocesses are available and are now widely spreading, e.g. by using microalgae (Hodaifa *et al.* 2020). Different photoreaction methods (UV, UV/H_2O_2 and UV/H_2O_2/TiO_2) are also proposed for the treatment of OMWW (Hodaifa *et al.* 2019), all with reasonable removal yields. Recently, ultrasound oxidation (sonolysis) combined with other advanced oxidation processes has also been successfully tested to treat OMWW (Capocelli *et al.* 2013; Al-Bsoul *et al.* 2020). Other frequently used separation processes are membrane processes, mainly ultrafiltration (El-Abbassi *et al.* 2011), often coupled with centrifugation (Turano *et al.* 2002). As a matter of fact, membrane processes are preferred when the process is aimed at the recovery of the active compounds contained in OMWW, and not only at the depuration of wastewaters (Mazziotti di Celso & Prisciandaro 2013). As already said, since during the olive oil extraction process (in the oil mill) only a small amount of polyphenols (2.5%) of the total present in the olives is transferred to the oil, while approximately 50% is retained in the vegetation waters, it should be desirable to recover these compounds (Sygouni *et al.* 2019); otherwise 50% of active ingredients, i.e. polyphenols with a very high antioxidant value, such as hydroxytyrosol and oleuropein, are disposed of with the vegetation waters (Ciriminna *et al.* 2015). Moreover, it should be preferable to reuse the huge amounts of processed water with the aim of developing a closed water cycle as well (Prisciandaro *et al.* 2016; Capocelli *et al.* 2019).

In the literature, a patented recovery process of the different fractions of polyphenols from the vegetation waters has been presented (Pizzichini & Russo 2004): this process involves the use of membranes with different molecular weight cut-offs (MWCO), e.g. microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) for the separation of the different components of the polyphenols, up to reverse osmosis (RO) which allows ultra-pure water to be obtained for plant uses.

Starting from this proposed process, in this paper two possible treatments for the effluents coming from the olive products industry are proposed and simulated by using SuperPro Designer®, aimed at polyphenols recovery. The first process scheme consists of a complete fractionation of olive mill wastewaters (OMWW) using membrane technology. The vegetation waters produced in this process are pre-treated to remove the suspended solids and then treated with membrane processes using a technology similar to the one patented by Pizzichini & Russo (2004). The permeate obtained from reverse osmosis is ultrapure water that can be used for process purposes. The second process scheme differs from the first one because the initial OMWW contains a certain amount of pesticide (Diuron). In this case the process configuration integrates membranes and an oxidation treatment to concentrate polyphenols and degrade pesticides. A techno-economic analysis of the proposed processes is presented, carried out by means of a life cycle cost analysis, considering the mass and energy balances obtained from process analysis. Process and LCC analysis allow the study of the technical and economic feasibility of the two treatments and provides useful information for possible investment by a company in the olive processing sector that wants to develop a depuration treatment of their wastewaters on site, thus avoiding their disposal. On-site treatment would allow companies to optimize the production in terms of water reuse according to a zero liquid discharge approach and valorise the residual stream containing polyphenols adopting advanced purification processes.

The aim of this paper is thus to verify the technical and economic feasibility of the two proposed scenarios by comparing the treatment cost expressed as euros per cubic meter of treated OMWW.

MATERIALS AND METHODS

Process model description

The technical and economic analysis of integrated membrane processes for the treatment of olive mill wastewater containing polyphenols was estimated by using a specific software, Intelligen's SuperPro Designer® v9.5 (SPD). The analysis was performed to recover polyphenols for possible reuse and to design a treatment zero liquid discharge. The input data are the volume, compositions and other physical characteristics of the initial wastewater stream. Mass and energy balances and equipment size are obtained as results of the process simulation and these are used to estimate the utility consumptions and equipment cost and finally for the estimation of the economic feasibility analysis of the simulated processes.

Based on the literature analysis, several scenarios were considered, in particular two processes were simulated: the first (Figure 1(a)) includes a series of membrane treatments to remove pollutants and separate polyphenols and the second (Figure 1(b)) instead integrates membranes and an oxidation treatment to concentrate polyphenols and degrade pesticides.

A simplified flow diagram of the processes is shown in Figure 1.

For OMWW, composition varies greatly by type of cultivation, location, ripeness of olives, and the extraction process. The nominal characterisation of residual effluent used in this work for the estimation of the techno-analysis feasibility is given in Table 1 (Russo 2007; Ciriminna *et al.* 2015).

The OMWW contains a series of pollutants, mainly polyphenols, that should be removed from the effluent for its possible reuse as process water for internal uses of the industrial site. In the first case, the initial wastewater comes from the processing of organic production of olives, and therefore it is pesticide free. In this scenario a possible treatment composed of a series of membranes processes is proposed. In detail, the operations for filtration and removal of pollutants are MF, UF and NF followed by RO. The output stream from this last operation is a concentrate rich in polyphenols that is sent to an evaporation section for further removal of the water content. Treated water from reverse osmosis is partly used for the cleaning of micro and ultrafiltration membranes subject to fouling. The washing operation includes first cleaning by using a dilute sodium hydroxide solution, followed by washing water with the permeate from reverse osmosis. For economic analysis the residual cleaning solutions, in a conservative way, have been considered as wastewater to disposal.

The second block scheme treats an initial solution that contains polyphenols and pesticides (Diuron has been considered as a reference compound). In this scenario the reverse osmosis has been replaced with an advanced oxidation process (AOP) like Fenton reaction, in order to degrade pesticides from the permeate of nanofiltration. Pesticides can be removed from reverse osmosis but the concentrate that also contains polyphenols must be treated as a waste and cannot be further valued and sold. For that, it has been decided to replace reverse osmosis with AOP in order to degrade pesticides. The solid residue from the Fenton process is considered as a waste, instead the treated water is disposed in a sewage system as described in the following sections. The concentrates from MF, UF and NF that do not contain pesticides are sent to an evaporation section to recover the final product and water. Washing operations for the second scenario includes cleaning with diluted sodium hydroxide solution followed by a passage of fresh water from the supply system.

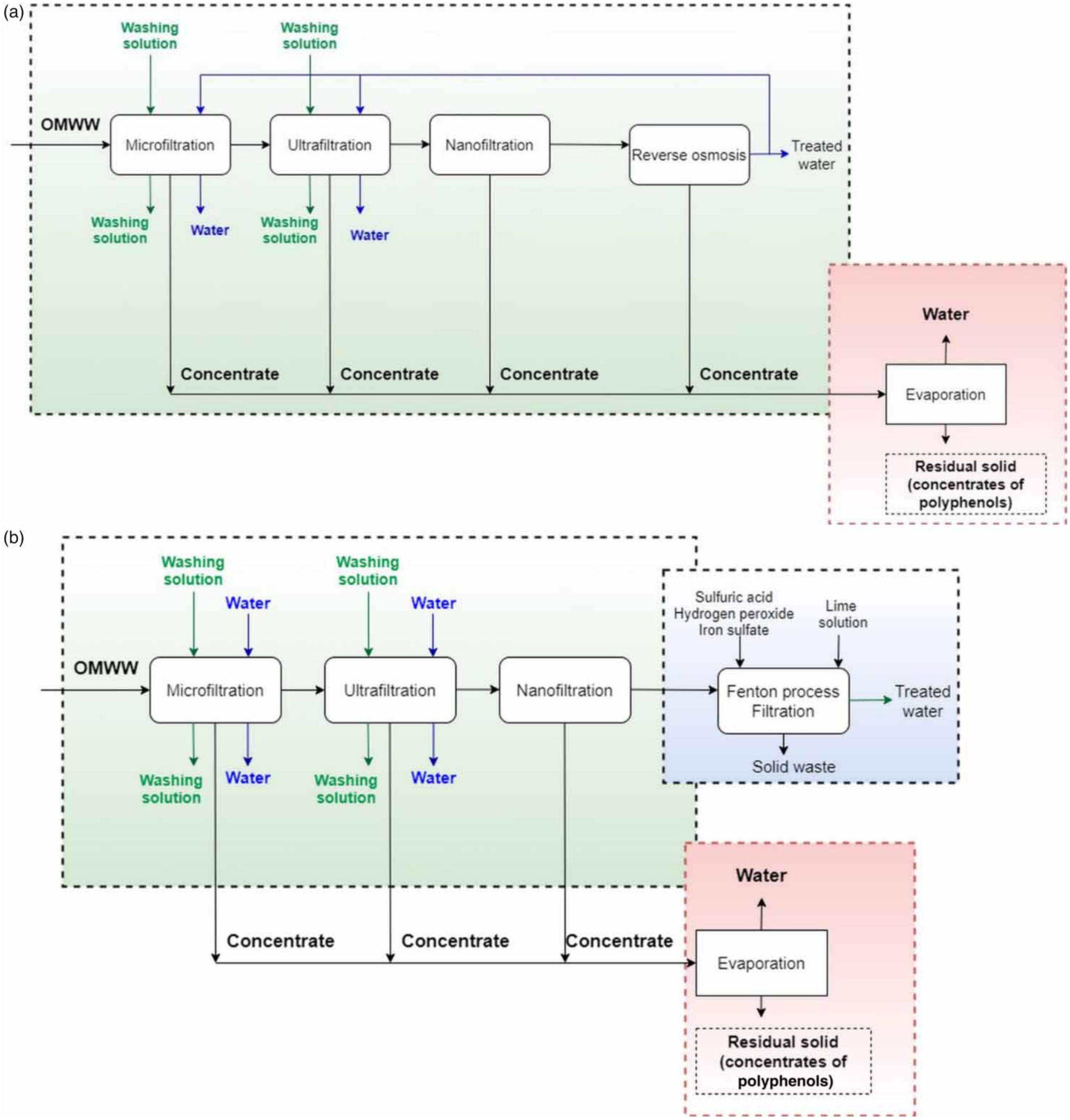

Figure 1 | Block scheme of the proposed process schemes for the treatment of OMWW.

The selected operative conditions for removal and recovery of polyphenols from OMWW as well as the choice of the sequence of treatments in the proposed process schemes derive from the optimal results reported in the scientific literature by several authors. As an example, a literature analysis showed that the retention of polyphenolic compounds is related to their different degree of hydrophilicity and hydrophobicity (Cassano *et al.* 2017). More hydrophobic components are easily removed from the membranes of MF and UF, in some cases independently

Table 1 | Composition of OMWW used for the process analysis with SPD

Substance	Chemical formula	Mass composition (%)
Caffeic acid (CAA)	$C_9H_8O_4$	0.145
Cinnamic acid (CIA)	$C_9H_8O_2$	0.109
Coumaric acid (COUA)	$C_9H_8O_3$	0.121
Ferulic acid (FA)	$C_{10}H_{10}O_4$	0.097
Hydroxytyrosol (HYD)	$C_8H_{10}O_3$	0.327
Tyrosol (TYR)	$C_8H_{10}O_2$	0.218
Vanillin acid (VA)	$C_8H_8O_4$	0.133
Minerals (MIN)	–	1.244
Glucose (GLU)	$C_6H_{12}O_6$	1.036
Oleic acid (OA)	$C_{18}H_{34}O_2$	1.244
Solids (SS)	–	5.182
Water	H_2O	90.142

of the MWCO, transmembrane pressure (TMP) and feed flowrate, leading to the formation of an adsorbed layer responsible for membrane fouling. The exposure to phenolic compounds reduced the contact angle of membranes, making them more hydrophilic, indicating a significant fraction of hydrophilic component from phenolic compounds on the membrane surface. Adsorption of phenolic compounds increased by lowering the pH of the solution: at lower pH protonation occurs reducing the electrostatic repulsion between phenolic compounds and membrane surface. In this specific case, the initial solution pH was between 5 and 5.5 and was not modified during the overall process (Garcia-Castello *et al.* 2010).

Moreover, membrane fouling caused by aggregation of the polyphenols and other substances contained in the initial wastewater is definitely one of the disadvantages of membrane processes. Several pre-treatments are applied for reducing this phenomenon such as advanced oxidation processes. Most of the substances, including polyphenols, are degraded by using these methods and then the membrane system receives cleaned water, therefore the fouling phenomenon is partly avoided or delayed (Orchando Pulido 2016). In this situation, polyphenols cannot be recovered. As an alternative in this manuscript a physical pre-treatment of centrifugation that is able to almost completely remove the suspended solids has been proposed, reducing the formation of fouling on MF and UF filtration. The centrifugation and washing of membranes does not solve the problem of irreversible fouling, it means that the membranes should be periodically replaced with new membranes. The membrane purchase cost has been included in other costs, in particular in the contingency, estimated to be 10% of the total physical plant cost (Peter *et al.* 2004).

As regards the final products from evaporations, in the present work a sensitivity analysis was performed taking into account that the solid residues can be sold and assuming a selling price between 0 and 10 €/kg of the final product.

For the process analysis, the capacity of the plant has been set at 1,000 L/h, small plant capacity (Galanakis 2017), and it has been assumed that the plant works in continuous mode. In the following, the two alternatives processes simulated by means of SuperPro Designer are described.

First scenario, case study 1

In the first studied scenario, the OMWW comes from biological processing of olives, so it is pesticide-free; wastewater is sent to pre-treatment (centrifugation) to remove the residual solids; after that the liquid is heated to 30 °C (Pizzichini & Russo 2004) and sent to a series of membranes: microfiltration to mainly separate oleic acid and in part, the polyphenols; the permeate of MF is sent to ultrafiltration to separate polyphenols and glucose; the permeate of UF goes into another membrane process, nanofiltration (NF), that removes the residual polyphenols, producing a permeate composed of water, minerals and traces of other compounds. The production of pure water is guaranteed by the last step of filtration, reverse osmosis which remove all traces of impurities. The concentrates coming from MF, UF, NF and RO are rich in polyphenols and could be sent to a final operation to remove the water and obtain a final product ready for sale.

Second scenario, case study 2

The second scenario differs from the first one because the initial OMWW contains a certain amount of pesticide, Diuron is considered as reference. The treatment line has, as for the first process, centrifugation, heating, microfiltration, ultrafiltration, and nanofiltration. After that the permeate of NF is sent to an oxidation advanced process, Fenton, to degrade pesticides and polyphenols.

The operative conditions are extrapolated from scientific literature (Barbusiński & Filipek 2001), in particular this section is constituted by a chemical reactor in which sulfuric acid, hydrogen peroxide and iron sulfate are fed in R101 to degrade the organic pollutants by Fenton reactions (Equations (1)–(3)):

$$H_2SO_4 \rightarrow 2H^+ + SO_4 \quad (1)$$

$$Fe(SO_4) \rightarrow Fe^{2+} + SO_4^{2-} \quad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \quad (3)$$

R101 is equipped with a UV lamp (150 W), used as a UV source of 254 nm to improve the efficiency of degradation of the substances (De Heredia *et al.* 2001; Kavitha & Palanivelu 2004). Sulfuric acid was added to reduce the pH of initial solution to a value near to 3.

Equation (4) describes the degradation reaction for pesticides and polyphenols. In the simulation the exact stoichiometric reactions have been added for each substance:

$$\text{Pesticides/ phenols} + OH^\bullet \rightarrow \text{Degradation products} \quad (4)$$

The yields for the degradation reactions were 97 and 100% for polyphenols and pesticides, respectively (Kavitha & Palanivelu 2004). The products of the reactions are water and carbonic dioxide for polyphenols, instead chlorides and ammonium ions are produced by the degradation of pesticides.

The Fenton reaction time was set at 1 h and after that lime solution was added in order to increase the pH and precipitate the residual impurities, in particular iron hydroxide and calcium sulfates. The set total reaction time in R-101 was 2 hours. After that a filtration step was considered to separate the solid and the treated water.

The concentrates coming from MF, UF, NF are rich in polyphenols and could be sent to a final operation to remove the water and obtain a final product ready for sale.

Process analysis

First scenario, case study 1

For the simulation, a capacity of 1,000 L/h for the OMWW treatment plant was assumed. Figure 2 shows the flowsheet of the process.

The first scenario includes the following main equipment: centrifugation, CF-101; heat exchanger, HX-101; membranes section with microfiltration, MF-101, ultrafiltration, UF-101, nanofiltration, NF-101 and reverse osmosis, OR-101; evaporator, EV-101 The line also includes the pumping section and a 'clean in place' (CIP) system for MF and UF membranes with another heat exchanger, HX-102.

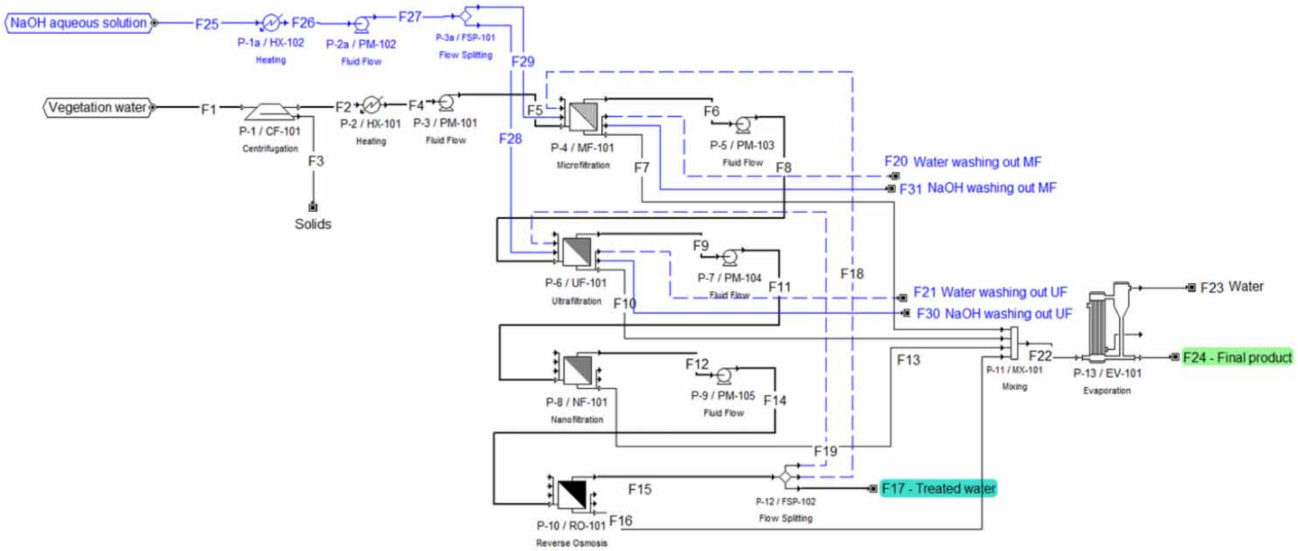

Figure 2 | Flowsheet for the first scenario, case study 1.

The equipment works in a continuous mode and the inlet flow is a residual solution coming from olive production as described in Table 1. The initial temperature of OMWW is set to 25 °C. This solution is centrifugated to remove residual solids, around 5% w/w, present in the wastewater, after that it is heated up to 30 °C and is fed to the membrane section. The operative data for the membrane section was extrapolated by scientific literature (Paraskeva *et al.* 2007; Russo 2007). Russo (2007) reports the experimental results obtained for the removal of polyphenols and other compounds from OMWW by using a series of membrane processes. In particular for MF, the use of ceramic membrane (0.45 μm) was proposed working under the following conditions: concentration factor, expressed as ratio between the volume of the feed and retentate, equal to 3; rejection yields of 40% for sugars, 20% for minerals and 15% for polyphenols. Filtration time is set to 1 h according to data reported by Russo (2007). The second process is the UF, for which the use of ceramic membrane (1 kDa) was proposed that works under the following conditions: concentration factor equal to 2.5; rejection yields of 30% for sugars, 21% for minerals and around 31% for polyphenols. Time of filtration is set to 1 h. The conditions for NF are found in the research paper presented by Paraskeva *et al.* (2007). The membrane is polymeric (200 MWCO), the permeate from UF is fed at 20 bar into the NF section. During this operation the majority of organic compounds remain in the concentrate streams. The permeate stream is colourless, free of salts and with very low concentrations of toxic components (phenolics). The operative data are: concentration factor equal to 3, rejection yields of 99.9% for sugars, 80% for minerals and 98% for polyphenols. Time of filtration is set to 1 h. The last membrane process is reverse osmosis. The use of a polymeric membrane was considered as proposed by Hydronautics (Russo 2007), which has a salt rejection of 99.5%. RO shows a rejection of 99.9% with respect to sugars and polyphenols and between 83 and 99% with respect to the ionic species. The latter fraction may therefore be safely disposed of to aquatic receptors or may be used for irrigation.

Table 2 reports the concentration of compounds in processing lines.

The permeate output from RO is water with traces of minerals and glucose. This stream can be recycled for the washing operation of membranes and partly used as process water or for irrigation. The concentrates are mixed and sent to an evaporator (P-13, EV101). Ninety-three per cent of water is evaporated by using steam at 152 °C for heat transfer. Mass balance around the equipment shows that 860 kg of steam is necessary to concentrate 792 kg/batch of retentates in 1 hour. The output of EV101 are 693.67 kg/h of water and 98.7 kg/h of concentrates having the following composition (% wt): 1.466% caffeic acid, 1.100% cinnamic acid, 1.222% coumaric acid, 0.978% ferulic acid, 10.44%

Table 2 | Composition of the flows output from membrane filtration system (Perm. is the permeate, Ret. is the retentate)

Substance (% wt)	**MF – Perm. F6**	**MF – Ret. F7**	**UF – Perm. F9**	**UF- Ret. F10**	**NF – Perm. F12**	**NF – Ret. F13**	**RO – Perm. F15**	**RO – Ret. F16**
Caffeic acid (CAA)	0.140	0.179	0.109	0.187	0.004	0.3207	0.0000	0.0102
Cinnamic acid (CIA)	0.105	0.135	0.082	0.139	0.003	0.2403	0.0000	0.0075
Coumaric acid (COUA)	0.117	0.149	0.091	0.156	0.003	0.2682	0.0000	0.0076
Ferulic acid (FA)	0.094	0.120	0.073	0.124	0.003	0.2130	0.0000	0.0075
Hydroxytyrosol (HYD)	0.316	0.405	0.244	0.423	0.0099	0.7127	0.0000	0.024
Tyrosol (TYR)	0.211	0.269	0.163	0.282	0.0062	0.4757	0.0000	0.015
Vanillin acid (VA)	0.129	0.165	0.100	0.171	0.0040	0.2935	0.0000	0.010
Minerals (MIN)	1.156	1.623	0.992	1.401	0.2803	2.416	0.0004	0.700
Glucose (GLU)	0.8100	1.660	0.639	1.066	0.0099	1.717	0.0002	0.2491
Oleic acid (OA)	0.880	2.175	0.687	1.169	0.0257	2.011	0.0000	0.064
Water	96.04	93.11	96.82	94.88	99.56	91.33	99.99	98.90
Flowrate (kg/h)	628.95	314.37	377.35	251.59	251.55	125.80	150.91	100.64

glucose, 3.300% of hydroxytyrosol, 12.53% minerals, 12.53% oleic acid, 2.200% tyrosol, 1.344% vanillic acid, 52.88% water. This concentrate can be used as fertilizer or in the production of biogas in anaerobic reactors (Garcia-Castello *et al.* 2010).

The process also includes the cleaning in place (CIP) of the equipment of MF and UF, which are the most susceptible to fouling. The CIP is simulated with two liquid currents: the first is a sodium hydroxide solution (20 g/L of NaOH), and the second one is water recycled by reverse osmosis. The washing operation is performed every 6 hours of treatment using an equal quantity of NaOH, followed by water washing, for MF and UF: 300 L/h NaOH solution and 120 L/h of treated water. Total time for CIP was set to 30 min.

Second scenario, case study 2

As previously mentioned, in this second scenario it was decided to simulate the treatment of OMWW containing pesticides like Diuron. Figure 3 shows the flowsheet of the process.

The main equipment are centrifugation, CF-101; heat exchanger, HX-101; membranes section including microfiltration, MF-101, ultrafiltration, UF-101 and nanofiltration, NF-101; Fenton reactor, R101; Filter press, FP101; evaporator, EV-101. The line also includes the pumping section and a CIP system for MF and UF membranes with another heat exchanger, HX-102.

The equipment works in continuous mode and the inlet flow is a residual solution coming from the processing of olives, as described in Table 1, but differently from Scenario 1, in Scenario 2 the solution also contains 0.017% of pesticides. The process includes the same operations considered for Scenario 1: micro, ultra and nanofiltration. The retentates from MF, UF and NF are sent to evaporation (EV-101).

Table 3 reports the concentration of compounds in the processing lines of the membrane system.

The concentrates are mixed and sent to evaporator (P-13, EV101). Ninety-three per cent of the water is evaporated by using steam at 152 °C for heat transfer. Mass balance around the equipment shows that 503.68 kg of steam is necessary to concentrate a 641.54 kg/batch of retentates in 1 hour. The output of EV101 is 554.39 kg/h of water and 87.15 kg/h of concentrates having the following composition (% wt): 1.643% caffeic acid, 1.233% cinnamic acid,

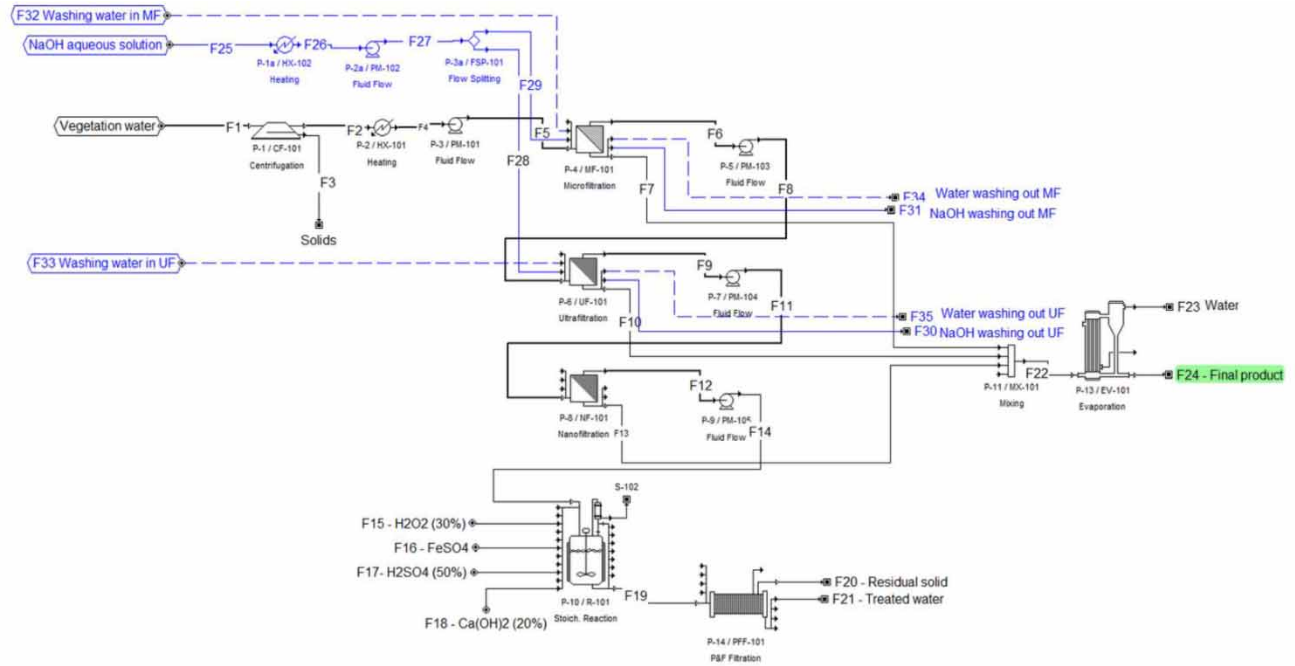

Figure 3 | Flowsheet for the second scenario, case study 2.

Table 3 | Composition of the flows output from membrane filtration system (Perm. is the permeate, Ret. is the retentate)

Substance (%wt)	MF – Perm. F6	MF – Ret. F7	UF – Perm. F9	UF – Ret. F10	NF – Perm. F12	NF – Ret. F13
Caffeic acid (CAA)	0.140	0.179	0.109	0.187	0.004	0.320
Cinnamic acid (CIA)	0.105	0.135	0.082	0.139	0.003	0.240
Coumaric acid (COUA)	0.117	0.149	0.091	0.156	0.003	0.268
Ferulic acid (FA)	0.094	0.120	0.073	0.124	0.003	0.213
Hydroxytyrosol (HYD)	0.316	0.405	0.244	0.423	0.0096	0.712
Tyrosol (TYR)	0.211	0.269	0.163	0.282	0.0062	0.475
Vanillin acid (VA)	0.129	0.165	0.100	0.171	0.004	0.293
Minerals (MIN)	1.156	1.623	0.992	1.401	0.2803	2.416
Glucose (GLU)	0.8100	1.660	0.639	1.066	0.0001	1.916
Oleic acid (OA)	0.880	2.174	0.687	1.169	0.0257	2.011
Pesticides	0.018	0.017	0.018	0.017	0.018	0.017
Water	96.04	93.10	96.80	94.86	99.64	91.12
Flowrate (kg/h)	628.95	314.37	377.37	251.61	251.53	125.84

1.371% coumaric acid, 1.095% ferulic acid, 11.83% glucose, 3.698% of hydroxytyrosol, 13.06% minerals, 14.08% oleic acid, 2.466% tyrosol, 1.312% vanillic acid, 47.88% water. The concentrate can be used as fertilizer or in the production of biogas in anaerobic reactors.

The permeate output from NF is an aqueous solution with traces of minerals, glucose, polyphenols and pesticides. This current is sent to the Fenton reactor to degrade pesticides and polyphenols by adding 25 kg of H_2O_2 (30%)/m^3 of wastewater and 10 kg of iron sulfate/m^3 of wastewater. After Fenton reaction, the suspension from R-101 is sent to the filtration system (FP-101) to separate the solid and the liquid. The residual solid (F-20) has the following composition: 45.44% of calcium sulfate, 24.57% of iron hydroxide, 29.26% of water with traces of other impurities (i.e. minerals). The composition of the treated water is reported in Table 4. In the present simulation this water was considered as wastewater to dispose of in a sewage system with a specific disposal cost as described in the following section.

The process also includes the cleaning in place (CIP) of the equipment of MF and UF which is more susceptible to fouling.

The CIP is simulated with two liquid currents: the first is a sodium hydroxide solution (20 g/L of NaOH), and the second one is water recycled by reverse osmosis. The washing operation is performed using an equal quantity of NaOH, followed by water washing, for MF and UF: 300 L/batch NaOH solution and 120 L/batch of treated water. Total time for CIP was set to 30 min.

Life cycle cost assessment

Goal and scope of the study

According to ISO 14040 (2006), the first phase of life cycle cost analysis (LCC) is to define the goal and scope of the study including the description of the product or process system, the function of the operations, the functional unit, the system boundary, data requirements, assumptions and limitations. In the present work, LCC study for the first and second scenarios for the treatment of OMWW was performed. Figure 1 shows the system boundary. The functional unit chosen for the analysis is 1,000 L/h of OMWW. The main item costs considered for the analysis were: equipment, raw material purchase, energy, labour and transport and disposal of solid waste.

LCCs are those incurred over the life span of a process system, including costs required to construct, equip, and operate the system. For each treatment process a general, annual cost estimation was developed consisting of the recurring costs (RC), also known as operation and maintenance costs, and the non-recurring costs (NRC), otherwise

Table 4 | Composition of the water from filter press FP-101

Substance (mg/L)	Treated water F21
Caffeic acid (CAA)	1.05
Cinnamic acid (CIA)	0.77
Coumaric acid (COUA)	0.77
Ferulic acid (FA)	0.77
Hydroxytyrosol (HYD)	2.45
Tyrosol (TYR)	1.58
Vanillin acid (VA)	1.04
Minerals (MIN)	2,396.29
Glucose (GLU)	0.027
Oleic acid (OA)	6.59
Pesticides	0.158
Calcium sulfate	1,827.88
Iron hydroxide	340.22
Water, %	97.24
Flowrate (kg/h)	289.61

known as capital costs, converted to an annual cost basis (Dhillon 2009).

The general equation used for the analysis model is:

$$\text{Annual LCC} = \text{RC} + \text{NRC} \tag{5}$$

RC includes annual labour costs, operational energy costs and maintenance (repair) cost and purchase cost for the chemicals and disposal costs for the produced waste (OPerating EXpense, OPEX). Non-recurring cost (NRC) is the capital investment including the equipment cost, piping, engineering, that are amortized in X years. CAPital Expenditure (CAPEX) was estimated from the cost of purchasing the equipment (PEC – purchase equipment cost), on the basis of which total direct and indirect costs have been assessed (FCI-fixed Capital Investment) contributing to the determination of the TCI. Equipment costs were obtained from vendors; if quotes were not available for the required plant capacity, the following equation was used:

$$C_n = C_0 \left(\frac{S_n}{S_0}\right)^x \tag{6}$$

where C_n = cost of new equipment, C_0 = cost of existing equipment with pricing available; S_n = size of new equipment, S_0 = size of existing equipment and X is the exponent depending on type of equipment (Peter *et al.* 2004). The reference year for the estimation was 2002 and the values were discounted by using the CEPCI – Chemical Engineering Plant Cost Index (Calculation Methodology for Cost Goals). Total fixed investment was calculated by adding equipment erection, piping, instrumentation, buildings, storages, design and engineering, contractors' fee and contingency of 10% of PCE. Additionally, a working capital of 15% of total project capital costs was added to the project capital costs, and then the total was amortized to obtain annual capital costs. Straight line depreciation over 10 years is considered with an index of 7.7.

Financial indicators as payback period (PBP) and Return on Investment (ROI) were calculated. The PBT is the time required for a project to return the initial investment. It is computed by calculating the cumulative return for each year and comparing it to the investment; the time at which this sum exceeds the investment is the payback time.

ROI (Chen 2020) is a performance measure used to evaluate the efficiency of an investment or compare the efficiency of a number of different investments. ROI tries to directly measure the amount of return on a particular investment, relative to the investment's cost. To calculate ROI, the benefit (or return) of an investment is divided by the cost of the investment. The result is expressed as a percentage or a ratio. 'Current Value of Investment' refers to the proceeds obtained from the sale of the investment of interest. Because ROI is measured as a percentage, it can be easily compared with returns from other investments, allowing one to measure a variety of types of investments against one another.

RESULTS AND DISCUSSION

Life cycle cost results

Based on the process flow diagrams shown in Figures 2 and 3, capital and production costs were calculated. Table S1 (Supplementary material) shows the main processing units required for each process.

Table 5 shows the capital costs for the proposed processes including purchase, installation, electrical service, instruments, buildings site development, ancillary buildings,

Table 5 | Capital costs for the proposed wastewater treatment plants (k€)

	Case study 1	Case study 2
Fixed Capital Investment Cost (FCI)	1,237.93	1,260.10
Working capital	185.68	189.02
Total Capital Investment Cost (TCI)	1,423.61	1,449.14

design and engineering, contactors' fee and contingency (Peter *et al.* 2004).

The FCI of Case Study 2 is higher than the FCI of Case Study 1 because it also includes the equipment cost of reactor R101 and filter press FP101 for the Fenton process. The purchase cost for centrifugation CF-101 has the greatest impact on FCI (around 45%) followed by the purchase cost of evaporator EV-101 (around 25%). The variable operating costs (RC) for the olive mill wastewater treatments are shown in Table 6. The corresponding RC are detailed in Tables S2 and S3 (Supplementary material). The maintenance cost has been considered at 3% of FCI.

Table 6 | Annual variable operating parameters (k€/y)

	Case study 1	Case study 2
Raw materials (k€/y)		
Initial wastewater	0.00	0.00
Sodium hydroxide solution (20%)	7.16	7.16
Washing water	0.00	0.67
Hydrogen peroxide (30%)	0.00	99.00
Iron sulfate solid	0.00	31.68
Sulfuric acid (96%)	0.00	4.51
Calcium hydroxide	0.00	7.13
Total	7.16	150.15
Utilities (k€/y)		
Electricity	32.08	227.88
Cooling water (20–35 °C)	177.41	140.3
Steam (152 °C)	69.53	56.07
Total	279.01	424.25
Others (k€/y)		
Waste management (transport and landfill)	48.95	72.55
Maintenance and repairs	37.01	37.08
Personal cost	792	792
Total	878.08	902.35

Labour costs were calculated considering three labour shifts of 8 h, with two operators per shift. The basic cost for a worker is 50 €/h. Moreover, operating supervision has been added, estimated to be 5% of the labour cost.

For Case study 1 the purchase cost for sodium hydroxide was the only cost related to the raw material (7.16 k€/y), and for Case study 2 the purchase cost for hydrogen peroxide and iron sulfate used for the advanced oxidation process had the greatest impact on the total raw material (150 k€/y) with an incidence of 66 and 21%, respectively, followed by the purchase cost for sodium hydroxide, calcium hydroxide, sulfuric acid and finally by fresh water for washing of MF and UF membranes. For the utilities of Case study 1, the main cost was related to cooling water (64% on total utilities cost) followed by steam (25% on total utilities cost) necessary for the evaporation and cooling of water from the evaporator, and electricity. For Case study 2, around 54% of the utilities cost was due to electricity consumption during AOP, cooling water and steam accounts for 33 and 13% on total utilities cost, respectively. Figure S1 (Supplementary material) provides the details of the utilities costs with reference to the chosen functional unit (€/m^3 of OMWW). Case study 2 had higher costs of electricity due to the presence of a UV lamp for the Fenton reaction in R101. The consumption of cooling water and steam was reduced as it is smaller from the inlet flow to the evaporator. Maintenance and repairs and personal cost have the same relevance in the 'Other costs', but the waste management cost is higher in the second case because from AOP a residual solid to disposal has been produced. This analysis shows that in Case study 2, Fenton process for the degradation of pesticides has a major cost impact on the variable operating parameters. The life cycle costs for each process were calculated according to Equation (5) and are summarised in Figure 4.

The treatment cost (€/m^3 of OMWW) is divided into capital cost including (besides insurance and taxes, estimated to be 2% of FCI) chemical for treatment, labour, maintenance and repairs, utilities (cooling water, steam, electricity) and waste management. As seen from Figure 4, other items have been added: operating supplies (15% of maintenance), laboratory charges (10% of labour cost), plant overhead cost (30% of the total labour cost) and general expenses including administrative cost (25% of plant

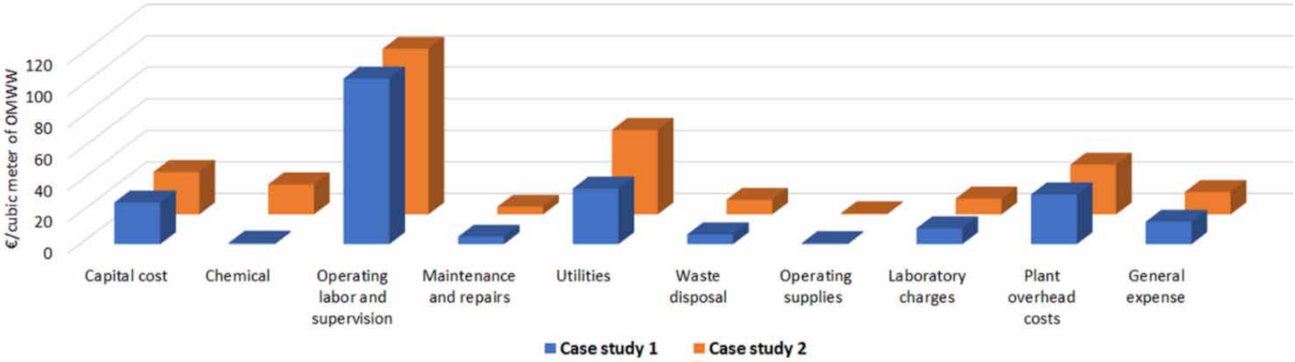

Figure 4 | Treatment cost for (€/m^3 of OMWW) for selected process schemes. Annual plant capacity = 7,920 m^3 of OMWW.

overhead cost) and research and development cost (2.5% of annual net treatment cost, NPC). Personal cost was determined to be the major component of the total annualized cost followed by utilities cost, followed by the utilities. In view of the above, the data shown in Figure 4 confirm that Case study 2 has higher variable operating costs than Case study 1, due to AOP. Figure 5 shows the details of the OPEX (€/m^3 of OMWW) for each proposed scenario. It is possible to observe once again that the labour cost had the greatest impact on operating cost, followed by utilities.

Economic feasibility

In this section the economic feasibility of the proposed processes is reported. For each scenario the annual treatment cost was evaluated as described above and the revenue from the selling of polyphenols and revenues related to the 'non-disposal' of the effluents in a specific external site (set to 120 €/m^3, real quotation). The price of polyphenols is unknown because it depends on the quality of the obtained product, therefore an economic analysis was made considering a variable selling price of between 1 and 10 €/kg. The results of this analysis are shown in Figure 6.

The breakeven point was around 1.5 and 2 €/kg for Case studies 1 and 2, respectively. The first process results were more economically feasible, mainly because in the second case the operative costs due to electricity consumption are higher as demonstrated above. To perform a comparison between the two solutions, a selling price of 2 €/kg for polyphenols was considered. The considered economic parameters, VAN, PBP and ROI, of Case study 1 are better than those of the second case. For the first scenario, the NPV_{10} over 10 years is equal to 6,000 k € and positive cash flows began after two years, hence payback time is between the second and third years. The total annual cost is 2,006 k€/y including OPEX, depreciation and contingency. For the second scenario, the NPV_{10} over 10 years is equal to 3,000 k€ and the positive cash flows

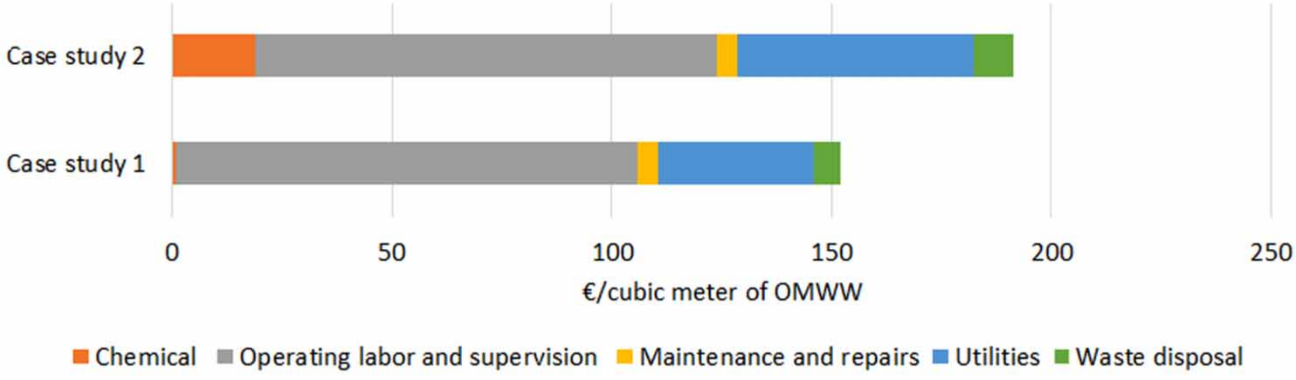

Figure 5 | OPEX (€/m^3 of OMWW).

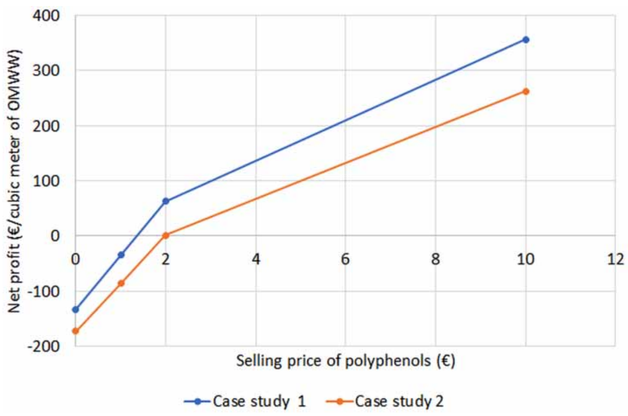

Figure 6 | Net profit as a function of selling price for polyphenols.

begin after four years, hence payback time is between the fourth and fifth years. The total annual cost is 2,323 k€/y including OPEX, depreciation and contingency.

Table 7 shows a summary of the economic evaluation.

CONCLUSIONS

In this work, two case studies for the treatment of OMWW were investigated. The best plant configuration for the OMWW treatment depends on the characteristic of the wastewater and for effluent coming from the processing of the biological production of olives, a series of membranes processes can be installed to remove pollutants and concentrate the polyphenols for possible reuse (Case study 1). On the contrary, if wastewater also contains pesticides a specific removal process is necessary, otherwise these substances are concentrated in the final product, thus resulting in a mixture of unsellable polyphenols. In this scenario reverse osmosis was replaced with an advanced oxidation process (AOP) Fenton reaction, in order to degrade pesticides; on the other hand, AOP has a significant operative cost with a substantial impact on the economic balance (Case study 2). The proposed process scheme allowed the recovery of polyphenols and water in accordance with a zero liquid discharge approach.

Table 7 | Financial parameters calculated for the proposed processes

	Case study A1	Case study B1
Net annualized cost (k€/y)	2,006	2,323
Revenue (k€/y)	2,500	2,328
Net profit (10 years, (k€)	6,000	3,000
PBP	>2 years	>4 years
ROI (%)	72	37

Economic feasibility of Case studies 1 and 2 was investigated by LCC analysis considering the mass and energy balances obtained from process analysis. The total treatment cost (€/m^3 of OMWW) was 253 €/m^3 of OMWW and 292 €/m^3 of OMWW for the first and second case study, respectively. Personal cost was determined to be the major component of the total annualized cost followed by utilities cost. For the second process, the raw materials and the utilities costs, mainly due to the electricity consumption related to the chemical removal of pollutants, had a higher incidence on the operative costs. Considering a variable price for the polyphenols, the breakeven point to have a positive profit is less than 1.5 €/kg and is near to 2 €/kg for the plant solution 1 and 2, respectively. The first scenario is more economically feasible but it is an inappropriate process scheme if the wastewater to be treated does not come from biological olive processing. It should be pointed out that the presence of reverse osmosis could further improve the permeate quality thus allowing water reuse for other purposes where high purity water is needed, e.g. for boilers.

The results of the present work provide useful information for possible investment by a company in the olive processing sector that wishes to develop a depuration treatment of their wastewaters on site, thus avoiding their disposal. From an economic point of view, any effort to optimise the operative conditions or to replace the Fenton process with an alternative AOP was equally effectively towards pesticides and could be beneficial for a company that treats OMWW from non-organic production. Nevertheless, in both cases (Case studies 1 and 2), internal treatment would allow companies to optimize production in terms of water reuse according to a zero liquid discharge approach with valorisation of the residual stream containing polyphenols.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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