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CROSS-BORDER COOPERATION IN THE MEDITERRANEAN

Mediterranean Cooperation in the Treatment and Valorisation of Olive Mill Wastewater (OMW)

MEDOLICO

Deliverable 4

Activity 6: Pilot demonstrations

- **Activity 6.4 - Pilot testing, 2nd milling campaign**

LNEG

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MEDOLICO
MEDITERRANEAN COOPERATION IN THE TREATMENT AND VALORISATION OF OLIVE MILL WASTEWATER

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Abbreviations

AOPs	*Advanced Oxidation Processes*
BOD_5	*Biochemical Oxygen Demand*
COD	*Chemical Oxygen Demand*
CPC	*Compound Parabolic Collector*
DOC	*Dissolved Organic Carbon*
EC	*Electrical Conductivity*
FLC 23	*FLOCAN 23 polyelectrolyte*
FTIR	*Fourier Transform Infra-Red*
G	*Germination*
GC-MS	*Gas Chromatograph Mass Spectroscopy*
GI	*Germination Index*
HRT	*Hydraulic Retention Time*
Jp	*Permeate Flux (L m-2h-1)*
JACTO.MBR	*Jet-loop type reactor with UF membrane*
JR	*Jacto Reactor*
MARS	*Membrane Aromatic Recovery System*
MF	*Microfiltration*
UF/NF	*Ultrafiltration followed by Nanofiltration*
MF/RO	*Microfiltration followed by Reverse Osmosis*
MS	*Mass Spectrum*
NF	*Nanofiltration*
OLR	*Organic Loading Rate*
OMW	*Olive Mill Wastewater*
OMTC	*Overall Mass Transfer Coefficient*
PI	*Phytotoxicity Index*
R (%)	*Retention, calculated as:* $R = \frac{(C_F - C_P)}{C_F}$ *where C_F is a feed concentration and C_P is a permeate concentration*
RO	*Reverse Osmosis*
IºRO	*First RO pass*
IIºRO	*Second RO pass*
SFO	*Solar Fenton Oxidation*
SVI	*Shoot Vigor Index*
TFCM	*Thin Film Composite Membrane*

TOMW	*Treated Olive Mill Wastewater*
TP	*Total Phenolic Compounds*
TS	*Total Solids*
TSS	*Total Suspended Solids*
UF	*Ultrafiltration*
VCF	*Volume Concentration Factor*
VCR	*Volume Concentration Rate, calculated as:* $VCR = \frac{V\ feed}{V\ concentrate}$
VSS	*Volatile Suspended Solids*
WWTPs	*Wastewater Treatment Plants*

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Executive Summary

Based on results from the previous set of activities (Deliverables 2 and 3), Deliverable 4 describes the experimental work developed during the second part of Activity 6, in order to evaluate the optimization of the performance for the different olive mill wastewater (OMW) treatment processes tested at pilot scale carried out during the 2nd milling campaign of MEDOLICO project (November 2013 - February 2014). The treatment processes that were evaluated during the 2nd milling campaign were:

- Combined aerobic biological treatment with ultrafiltration membrane (UF): LNEG, Portugal / JUST, Jordan;
- Integrated membrane equipment microfiltration (MF) / reverse osmosis (RO) and UF / nanofiltration (NF): UNIGE, Italy / BGU, Israel;
- Combined solar Fenton oxidation after coagulation/flocculation: Nireas-IWRC, UCY, Cyprus.

JUST was also responsible for the evaluation of actual use of recovered treated wastewater for irrigation, through a greenhouse phytotoxicity study.

Activity 6.4 describes the optimization of the above mentioned technologies performed at pilot scale. A comparison between the two milling campaigns was reported for each OMW treatment technology, while the main findings are also presented.

LNEG assessed the technical feasibility of the aerobic biological treatment of OMW at a pilot-scale JACTO reactor with UF membrane system (JACTO.MBR). The main operational parameter optimized was the hydraulic retention time (HRT), having in mind that for this type of technology it is important to achieve a maximum of feeding rate (OLR) without losses in removals efficiency. Under continuous feeding, the best efficiency of the JACTO.MBR process was in average 90% and 80% for COD and total phenolic compounds (TP) removal, respectively, achieved at tested HRT 6 d and OLR 13.9 kg COD $m^{-3}d^{-1}$. The experiments at the pilot plants installed in Jordan (100 L and 1000 L) were carried out in continuous and batch conditions and approx. 80% efficiency in COD removal was reached. The optimization process of the biological treatment demonstrated that there is no need for initial or further dilutions of OMW, which means water saving. In addition, the neutral pH obtained in the UF-permeate avoids the further addition of chemicals for pH adjustment.

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The combined coagulation/flocculation followed by solar Fenton oxidation for the integrated treatment of OMW, applied in Nireas-IWRC, UCY, seems to be a promising process for the effective purification of OMW and can be applied in countries, like Cyprus with plenty of sunshine. The coagulation/flocculation pre-treatment step resulted in an effluent stream with significantly lower solid fraction (up to 90-94%), while solar Fenton post-treatment yielded a high organic load removal, up to 94% and 100% in terms of COD and TP, respectively. The pilot testing of the 2nd milling campaign allowed the further optimization of the solar Fenton oxidation process concerning various operational conditions applied, such as the catalyst and oxidant concentrations and the irradiation time. Kinetic models and parameters (i.e. *k* values) were also proposed and determined respectively, in order to understand the reactivity of the organic matter present in OMW with hydroxyl radicals inside the reactor.

Pilot tests performed during the 2nd milling campaign at UNIGE showed that the integrated MF/RO process proposed for OMW treatment is a very effective and reliable technique. Pilot tests revealed that the MF process applied to OMW treatment allows for Volume Concentration Rate (VCR) ~5, resulting in MF permeate for further treatment in RO step and minor volume MF concentrate (by-products for valorisation or disposal). The subsequent RO step showed to be capable of removing conductivity above 97%, COD above 92% and TP above 99%, being operated up to VCR ~4.5, obtaining colourless purified water and a by-product rich in polyphenols. In addition, it was demonstrated how some process enhancement (introduction of the second RO pass: integrated MF/double RO process) can further improve the quality of purified water. Additional costs of the implementation of the second RO pass (IIºRO pass) is low, because the latter, when compared with the first RO pass (IºRO pass), treats smaller volumes of OMW giving higher permeate flux above 20 $L.m^{-2}h^{-1}$ and thus allowing for a high VCR from 6.2 to 8.9.

The evaluation of OMW by-products recovery at BGU was performed in a Membrane Aromatic Recovery System (MARS) using as a feed the NF concentrate derived from the pilot-scale experiments. The following objectives were reached: to obtain bioactive concentrates enriched in phenolic compounds from OMW using multiple filtration steps (MF, UF, and NF); to recover biophenols from this concentrate using the MARS equipped with newly developed thin film composite membranes (TFCM); and to investigate the processing conditions, in order to obtain MARS permeate with optimum component/quality characteristics.

In comparative terms for qualitative characteristics of treated OMW and regarding the best result obtained for each pilot technology tested within the project, it could be observed that for a certain condition, all tested pilot technologies showed good efficiencies for COD and TP removals higher than 90%. As demonstrated above, the best results accomplished in the framework of MEDOLICO were found for the integrated MF/double RO membrane process, obtaining a clear treated OMW with low content in organic matter and highest TP removal. The OMW integrated treatment using solar Fenton oxidation after coagulation/flocculation pre-treatment revealed likewise quite excellent results being a promising process for the effective purification of OMW, which can be applied in countries with abundantly of sunlight.

To evaluate the impact of untreated and treated OMW samples for irrigation, greenhouse phytotoxicity tests were performed by JUST, using corn as a forage crop and barley (*Hordeum vulgare* L.). The results showed that 100% OMW, 75% OMW and 50% OMW were very phytotoxic and completely prohibited seed germination. However, phytotoxicity decreased significantly using treated OMW samples from all tested technologies and raw OMW (25% diluted), which could be due to a lower content of phenols and other phytotoxic organic compounds. The most efficient treatment technology in reducing the phytotoxicity of OMW was the MF/RO process, followed by combined coagulation/flocculation followed by solar Fenton oxidation, and JACTO.MBR.

It is important to highlight that the established protocols and results obtained from the optimization procedures will be used as important data for the economic evaluation of all proposed technologies, which will be undertaken within Activity 8 of the MEDOLICO project, in order to further establish the overall economic viability of the proposed solutions to be presented in Deliverable 6.