Valorization of olive mill wastewater (OMW) in a microbial fuel cell (MFC): assessment of toxicity and bio-electrochemical characteristics

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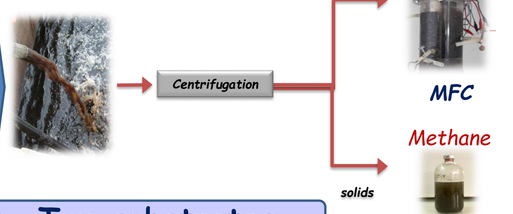
Background

Olive Mill Wastewater (OMW) is a hardly treated by-product generated during the olive oil production process. Its extremely high organic load (chemical oxygen demand (COD) of up to 150 g/L) and its low biodegradability, render its management an important environmental problem. Microbial Fuel Cells (MFCs) are bio-electrochemical systems producing bioelectricity and providing the dual benefit of energy production and simultaneous wastewater treatment. In such systems, microorganisms oxidize the organic compounds, producing carbon dioxide, protons and electrons, which are transferred to an electrode (final electron acceptor of their metabolism). The electrons are transferred to a current collector and then migrate through an external resistor to the cathode, where oxygen is reduced to water, generating electricity.

Objective

In the present study, the valorisation of OMW was studied via its bioconversion to electricity through a microbial fuel cell (MFC). OMW was initially centrifuged and separated to a liquid fraction (rich in soluble COD) and a solid residue. **The liquid fraction was used in an air- cathode single-chamber MFC** with MnO_2 as cathode catalyst and a packed bed of graphite granules as anode, aiming at the continuous treatment of OMW with simultaneous energy recovery. **The solid fraction was used** as substrate **for methane production** via anaerobic digestion (AD) through **Biochemical Methane Potential (BMP)Tests.**



Methodology

MFC- Three operational periods

1) Glucose
Effect of organic loading (0.8 and 1.2 g COD/L), Hydraulic retention time (HRT): 24 h
2) OMW
Effect of HRT (24 and 18 h) , 1.2 g COD/L
3) Glucose +phenolics
Effect of phenolics (0.13 and 0.26 g /L), HRT: 18 h

Electrochemical/Toxicity Assessment

Electrochemical experiments were conducted using a two-electrode set-up, at:
a) synthetic glucose medium at 1.2 gCOD/L (glucose)
b) OMW at 1.2 gCOD/L and HRT=24 h (OMW, 24 h)
c) OMW at 1.2 gCOD/L and HRT=18 h (OMW, 18 h)

Toxic potential was screened, at:
a) raw OMW (OMW-MFC feed)
b) MFC effluent at the HRT of 24 h (OMW-MFC24)
c) MFC effluent at the HRT of 18 h (OMW-MFC18)

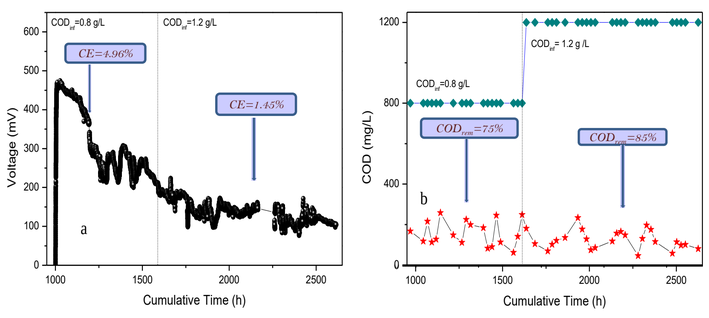
BMP tests- Two substrates

1) **Solid fraction** obtained after centrifugation of OMW, at increased initial concentrations (2, 5 and 10 g COD/L).
2) **Untreated OMW** for comparison reasons), at the same initial concentrations

Results and discussion

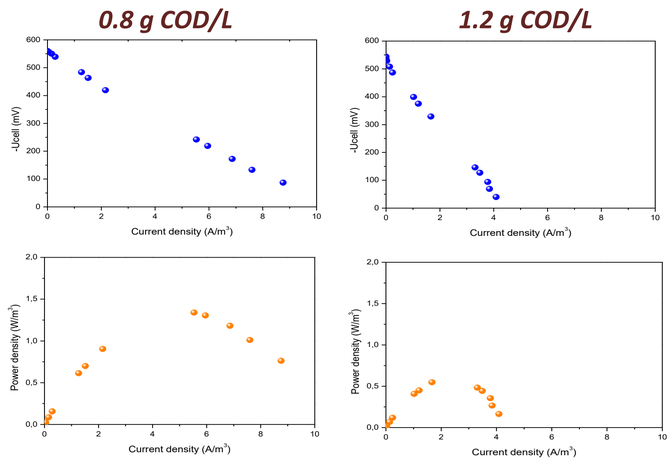
Glucose

- *Substrate: glucose-based medium (0.8 and 1.2 g COD/L)*
- *External R=100 Ω*
- *HRT= 24 h*



✓ *Increasing the influent COD concentration to 1.2 g /L, the voltage further decreased to 0.12 V*

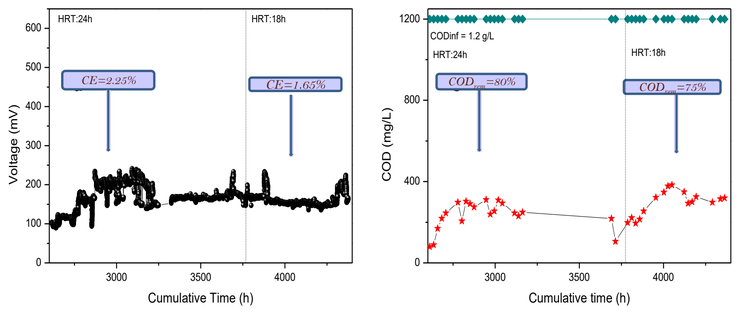
0.8 g COD/L *1.2 g COD/L*



Organic loading (gCOD/L)	P_{max} (W/ m^3)	P_{max} (MJ/ kg COD_{in})
0.8	1.34	0.15
1.2	0.55	0.04

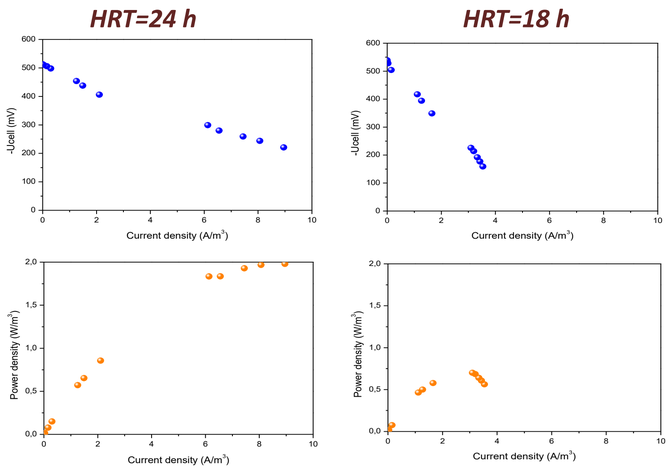
OMW

- *Substrate: OMW (1.2 g COD/L)*
- *External R=100 Ω*
- *HRT= 24, 18 h*



✓ *The voltage varied from 0.12 to 0.25 V and stabilized to a value of 0.15 and 0.18 V, at the HRTs of 24 h and 18 h, respectively.*

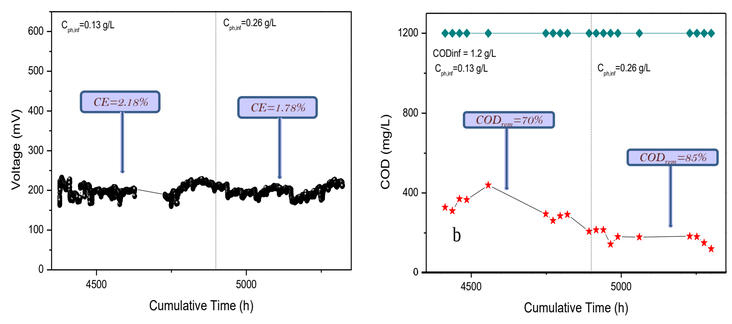
HRT=24 h *HRT=18 h*



HRT (h)	P_{max} (W/ m^3)	P_{max} (MJ/ kg COD_{in})
24	1.98	0.14
18	0.75	0.07

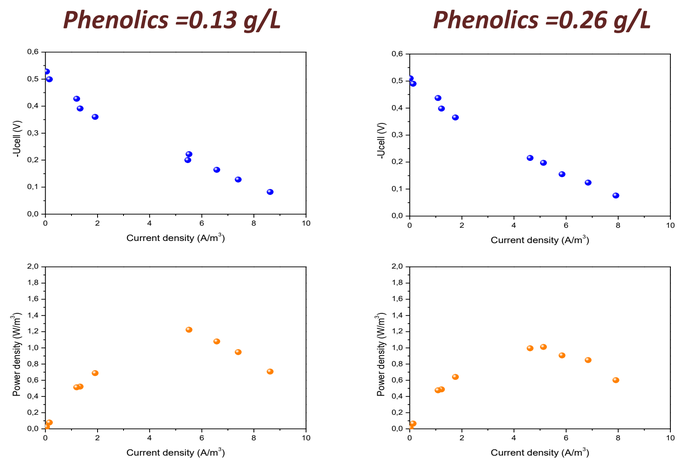
Glucose + Phenolics

- *Substrate: glucose-based medium + phenolics (1.2 g COD/L)*
- *Phenolics: 0.13 and 0.26 g/L*
- *HRT= 18 h*



✓ *High COD removal efficiency was observed, even at the higher initial phenolic concentration.*

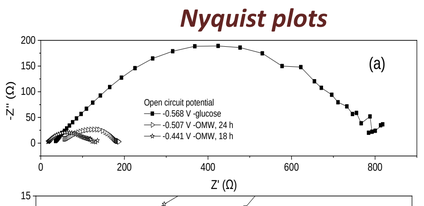
Phenolics =0.13 g/L *Phenolics =0.26 g/L*



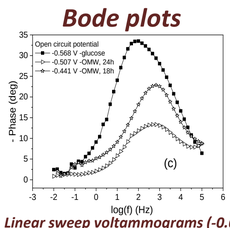
Phenolics (g/L)	P_{max} (W/ m^3)	P_{max} (MJ/ kg COD_{in})
0.13	1.02	0.12
0.26	1.01	0.10

Electrochemical characterization

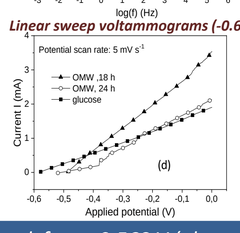
Nyquist plots



Bode plots



Linear sweep voltammograms (-0.6 – 0 V)



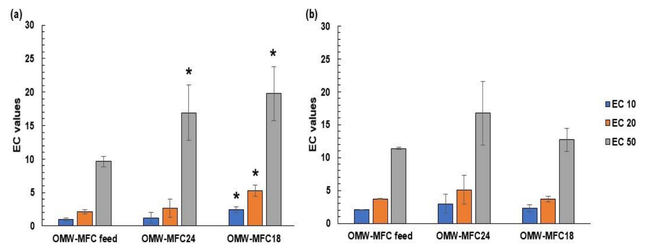
✓ *The open circuit potential (OCP) value decreased from -0.568 V (glucose) to -0.507 V (OMW, 24 h) and -0.441V (OMW, 18 h)*

✓ *The polarization resistance, R_p, gradually decreases from ca. 800 Ω (glucose) to ca.190 Ω (OMW, 24 h) and finally to ca. 135 Ω (OMW, 18 h).*

✓ *The maximum current value equal to ca. 3.5 mA was obtained for the last operational period, when MFC operated with OMW, at the HRT of 18 h.*

Toxicity assessment

Fairy shrimp Thamnocephalus platyurus *Neonates of the rotifer Brachionus plicatilis,*



✓ *Higher EC values observed in Thamnocephalus platyurus exposed to OMW-MFC18 and 24 effluent samples.*

Results from BMPs

BMP experiments were performed in
a) the solid fraction of OMW obtained from the centrifugation process (SFC)
b) the untreated OMW, at 2, 5 and 10 g COD/L

	Yield (L CH_4 /L)	Energy recovery, (MJ /L)
Untreated OMW, 2 g COD /L	52.96 ± 14.82	1.93
Untreated OMW, 5 g COD /L	39.23 ± 0.20	1.43
Untreated OMW, 10 g COD /L	28.34 ± 3.22	1.03
SFC OMW, 2 g COD /L	152.32 ± 4.79	5.44
SFC OMW, 5 g COD /L	146.06 ± 8.35	5.32
SFC OMW, 10 g COD /L	112.26 ± 4.79	4.09

Conclusions

✓ **The production of electricity and methane from OMW is a promising strategy for its valorization.**

✓ **Experiments concerning the production of electricity in a three-air cathode single chamber MFC operating with OMW at 1.2 g COD/L, at different HRTs, showed that at the lowest HRT (24 h) the best MFC performance was achieved.**

✓ **LSVs experiments showed that the maximum current value was obtained when MFC operated with OMW, at the HRT of 18 h, corroborated by the smaller polarization resistance, R_p**

✓ **Toxicity tests revealed an attenuation of the OMW toxic potential after treatment in MFC, which could be attributed to the removal of organic and phenolic compounds.**

✓ **The BMP of the solid residue obtained from the centrifugation of OMW was 152.32 ± 4.79 L CH_4 /L. Taking into account the mass balances for both fractions, the energy that could be recovered from both technologies (MFC and AD) is 0.686 MJ /L $_{OMW,}$ which is lower compared to the energy which would be recovered from the AD of OMW (1.93 MJ /L $_{OMW}$).**

We acknowledge financial support of this work by the project "Research infrastructure for Waste Valorization and Sustainable Management of Resources, INVALOR" (MIS 5002495) which is implemented under the "Action for the Strategic Development on the Research and Technological Sector", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).