Utilizing solar energy for the purification of olive mill wastewater using a pilot-scale photocatalytic reactor after coagulation/flocculation

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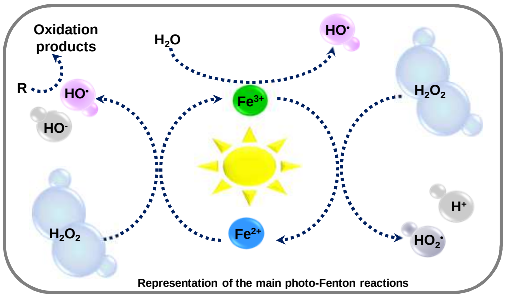
Project Partners:

Beneficiary:

Solar Fenton

The Fenton process is performed with ferrous (Fe^{2+}) salts and hydrogen peroxide (H_2O_2) under acidic conditions. Fenton oxidation is a homogeneous oxidation process and is considered to be a metal-catalyzed oxidation reaction, in which iron acts as the catalyst, while peroxide is the oxidant. The chain reactions that take place in the process produce the highly reactive and non-selective hydroxyl radicals ($HO^\bullet$), which are capable to react with a wide range of organic compounds. The combination of Fenton reagent with irradiation (up to 580 nm), has very strong synergetic effect. Irradiation leads to photoreduction of dissolved ferric ions (Fe^{3+}) to ferrous ions producing additional $HO^\bullet$, thus increasing the rate of organic degradation. In the recent years, the photo-Fenton process has gained increasing attention due to its environmentally friendly application and the prospect of operating under solar irradiation, especially in countries with plenty of sunshine, hence, lowering the operation cost considerably. In the case where solar irradiation is used, the process is known as ***solar Fenton***. The literature findings reveal that Fenton oxidation process can be applied successfully for the treatment of olive mill wastewater (OMW). However, a pre-treatment step (e.g. coagulation/flocculation, membrane filtration and separation processes, etc.) is needed, in order to reduce the solid fraction of OMW to improve the efficiency of the subsequent treatment by solar Fenton.

Pre-treatment step: Coagulation/flocculation is a chemical process that is frequently used for the pre-treatment of OMW. ***Coagulation*** treatment assists insoluble particles and/or dissolved organic matter to interact and gather together, firstly into small groups, then larger aggregates, and finally visible microfloc particles, which can be easily removed from the treated wastewater. The coagulation method takes place using mostly inorganic salts such as ferric chloride, ferrous and ferric sulfate, aluminium sulfate (i.e. alum) and calcium oxide. ***Flocculation*** is a chemical procedure where a flocculant additive is transferred into the mixture, inducing the bonding of the microfloc particles together to form larger, denser flakes helping therefore their separation. Polymeric materials such as anionic, non-anionic and cationic polyelectrolytes are mainly used as flocculant agents.



Representation of the main photo-Fenton reactions

Objectives of the study

The current study explored the efficiency of solar Fenton process combined with previous coagulation/flocculation pre-treatment at a pilot-scale reactor in removing the different organic carbon fractions present in OMW (i.e. COD, DOC, total phenolic compounds (TP)). In addition, the feasibility of the oxidation process was assessed in terms of toxicity removal using a set of bio- and phyto-assays. The toxicity of the OMW samples was assessed towards *Daphnia magna* and three plant species (*Sorghum saccharatum*, *Lepidium sativum* and *Sinapis alba*) prior to and after the photocatalytic treatment. This is of special interest in the context of sustainable water reuse strategies since the proposed treatment scheme combines technologically simple and relatively inexpensive treatment processes such as iron-based coagulation and solar-driven advanced oxidation.

Table 1. Main qualitative characteristics of OMW used in this study. OMW was supplied by a three-phase mill located in Larnaca, Cyprus

Parameter	Value*	Parameter	Value*
pH (25 °C)	5.7±0.5	TSS (g L^{-1})	19.5±7.8
Conductivity (mS cm^{-1})	8.56±0.76	TP (g L^{-1})	3.1±0.2
COD (g L^{-1})	13.5±5.1	Total-P (g L^{-1})	0.30±0.06
BOD_5 (g L^{-1})	3.17±1.5	Total-N (g L^{-1})	0.15±0.04
DOC (g L^{-1})	4.0±0.8	*Mean value of three measurements	

Main technical features

Coagulation/flocculation

The OMW pre-treatment prior to the solar Fenton process was performed in a tank (**Figure 1**) specifically designed for the coagulation/flocculation procedure. The total capacity of the tank is approximately 90 L. The OMW pre-treatment consisted at first of coagulation with $FeSO_4.7H_2O$, followed by flocculation using the anionic polyelectrolyte FLOCAN 23 (FLC 23).

Solar Fenton

The photocatalytic experiments were carried out in a compound parabolic collector (CPC) pilot plant installed at the University of Cyprus (**Figure 2**). The pilot plant comprises of six glass tubes mounted on a fixed platform tilted at the local latitude (35º) and it was operated in batch mode. The reflecting surface is constructed of resistant and highly reflecting polished aluminium. OMW flows directly from one tube to the other tank (meander flow) and finally to a reservoir tank. The overall volume capacity of the reactor V_T is 100 L and the irradiated volume V_i is 22.4 L. The UV solar irradiation was continuously recorded.

Normalized illumination time ($t_{30W,n}$)

The comparison of the data deriving from different days at different times of the day and under different solar illumination conditions was performed after applying $t_{30W,n}$.

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30}\frac{V_i}{V_T}; \qquad \Delta t_n = t_n - t_{n-1}$$

t_n: experimental time for each sample; ***UV***: average solar ultraviolet radiation measured between t_{n-1} and t_n; UV=30 W m^{-2} (solar UV power on a perfectly sunny day around noon)

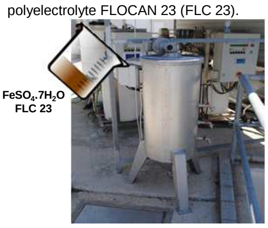


Figure 1. A pilot-scale coagulation/flocculation tank

Figure 2. Compound parabolic collector (CPC) solar reactor

Solar Fenton oxidation

Effect of Fe^{2+} and H_2O_2 concentration

A series of experiments was conducted with several combinations of catalyst (0.02-0.1 g L^{-1}) and oxidant (0.5-2.0 g L^{-1}) at pH=2.8-2.9 and irradiation time of 240 min (t_{exp}). The solar Fenton experiments were carried out using raw OMW that had been diluted 30 times with tap water (i.e. $[COD]_0$=350 mg L^{-1}). **Figure 5a** depicts the effect of Fe^{2+} initial concentration on the COD removal as a function of $t_{30W,n}$. The maximum COD removal (87.3%) was observed with Fe^{2+} concentration of 0.08 g L^{-1} at 240 min of irradiation ($t_{30W,n}$=67 min). The results indicated also that COD removal increased by increasing the concentration of peroxide from 0.5 to 1.0 g L^{-1} due to the additionally produced $HO^\bullet$. However, the use of excessive concentration of peroxide ($[H_2O_2]$=1.5-2.0 g L^{-1}), led to a slight decrease in %COD removal, possibly due to the recombination of $HO^\bullet$.

Main outputs

Pre-treatment of OMW by coagulation/flocculation

The treatment of OMW with 6.67 g L^{-1} of $FeSO_4.7H_2O$ and 0.287 g L^{-1} of FLC 23 led to approximately 44% of COD removal, whereas DOC and TSS were removed by 16% and 94%, respectively (**Figure 3**).

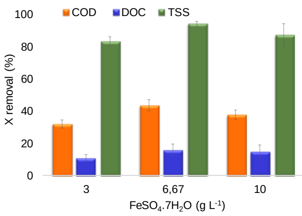


Figure 3. Organic content removal profiles during the coagulation/flocculation pre-treatment of OMW

Figure 4 shows the COD removal under different experimental conditions:

- Photolysis (solar irradiation)
- Photobleaching (solar irradiation+H_2O_2)
- Dark Fenton (Fe^{2+}+H_2O_2)
- Solar Fenton (solar irradiation+Fe^{2+}+H_2O_2)

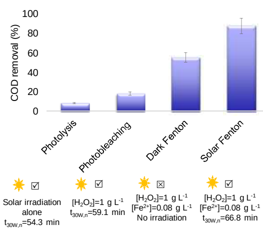


Figure 4. COD removal of OMW solution under different experimental conditions

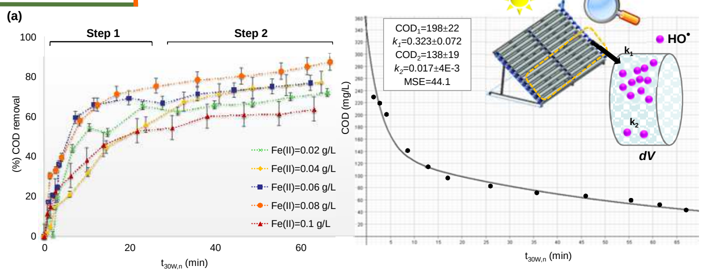


Figure 5. (a) Effect of initial Fe^{2+} concentration on the COD removal and (b) Fitting of the experimental data to the kinetic model

The fit of COD values versus time during the solar Fenton treatment at the optimum conditions (**Figure 5b**), was performed using a two-step first-order kinetic model:

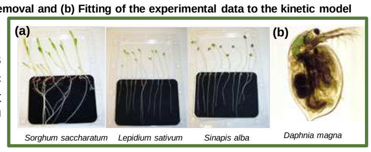
$$COD = COD_1 e^{-k_1 t} + COD_2 e^{-k_2 t}$$

Where, COD_1 and COD_2 are the initial COD of the two independent first-order reactions and k_1 and k_2 are the apparent reaction rate constants, respectively.

The two-step kinetic equation indicates the occurrence of two sequential oxidation steps during the solar Fenton process where, on **step 1**, the COD is converted quickly to intermediates, which undergo further slower degradation during **step 2** into final oxidation products.

Ecotoxicity assessment

Toxicity measurements were carried out, in samples taken at various times during the photocatalytic treatment, with: (a) the Phytotestkit microbiotest (MicroBioTests Inc.), and (b) the Daphtoxkit F™ toxicity test.

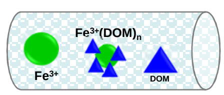


Effect of pH

Table 3. Comparison of solar Fenton experiments performed under different pH

pH	pH=2.8-2.9	pH=5.0
Parameter	(%)Removal	(%)Removal
COD	87.3%	80.6 %
DOC	41.7%	36.2%
TSS	73.4%	71.5%
TP	99.8%	99.0%

- pH=2.8-2.9: $[COD]_{removal}$=87.3%
- pH=5.0: $[COD]_{removal}$=80.6%
- $[TP]_{removal}$>99% under both pH values



The dissolved organic matter (DOM) in OMW, can contribute to the formation of soluble complexes with Fe^{3+}, therefore preventing the iron precipitation at the inherent pH.

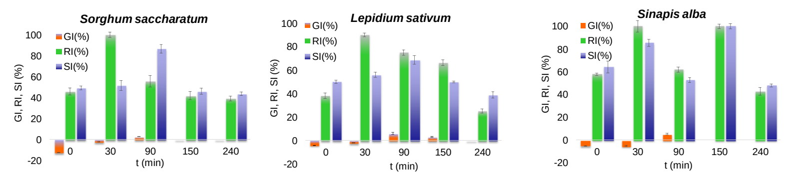


Figure 6. Seed germination inhibition (GI), root growth inhibition (RI) and shoot growth inhibition (SI) during solar Fenton process

The toxicity profile did not follow the trend of the COD removal for the three plant species examined (**Figure 6**) and *D. magna* (**Figure 7**), indicating that the toxicity may be a result of the rapid formation of toxic intermediates during the oxidation treatment. The percentage of GI and RI was not eliminated completely; however, the toxicity of the treated samples after 240 min of solar Fenton was lower than that of the raw OMW. A significant decrease of toxicity towards *D. magna* to values lower than 20% was observed at the end of solar Fenton.

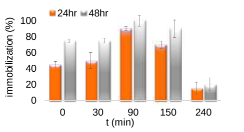


Figure 7. Evolution of toxicity to *D. magna*

CONCLUSIONS

- Solar Fenton oxidation combined with previous coagulation/flocculation pre-treatment resulted in considerable organic load removal.
- Solar Fenton was found efficient in removing a high percentage of COD at the inherent pH of the OMW.
- The polyphenolic fraction, which is responsible for the biorecalcitrant and/or toxic properties of OMW, was eliminated by the solar Fenton oxidation process.
- The OMW treated samples display a varying toxicity profile for each type of microorganism and plant examined in this study, which can be attributed to the oxidation products formed during the solar Fenton process applied. The toxicity assessment revealed that solar Fenton process is able to minimise the effluent ecological impact with regard to toxicity.

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