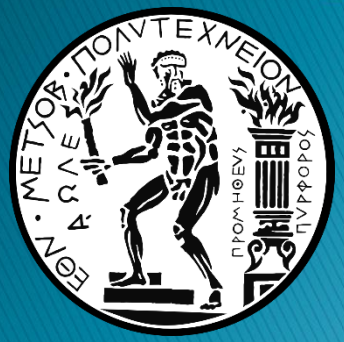
"Anaerobic Digestion of olive mill wastewater after detoxification using Fenton reagents"

A. Vlyssides*, G. Lamprou, A. Vlysidis, C. Tsiodra, G. Seintis and K. Bampalioukas



Laboratory of Organic Chemical Technology
School of Chemical Engineering,
National Technical University of Athens

Olive oil production facility

- More than 2.5 million metric ton/year is produced in Mediterranean countries
- OMWW → Very high organic load
- COD ranges from 50 to 150 mg/L
- Two orders of magnitude higher than municipal wastewater.
- Technical and economic barrier for efficient treatment and disposal due to: complex composition of OMWW, seasonal nature and wide geographical dispersion.

Combination of AOP and biological treatment

- A suitable solution for the removal of toxic compounds from OMWW.
- AOPs a based in the use of the highly and non specific-reactive hydroxyl radicals, which makes them useful for a wide range of organic compounds.
  - Benefits: Short time, optimization in chemical and optimization in energy consumption.
  - At the end of chemical oxidation follows a biological treatment for the complete removal of organic content.
- Fenton appears as a very promising technology.

Fenton oxidation and Anaerobic treatment

- Aim of the study is to investigate the potential of OMWW detoxification and susceptibility to anaerobic treatment by the application of Fenton oxidation.
- Focus on the effect of 4 operational parameters:
  - Coagulation
  - Concentration of ferrous sulphate heptahydrated ($FeSO4 \cdot 7H2O$)
  - Concentration of Hydrogen peroxide ($H2O2$)
  - Oil

Materials and methods

- Chemicals
  - $FeSO_4 \cdot 7H_2O$ (Fulka),
  - H_2O_2 (Merck, Perhydrol, 30% w/w)
- Wastewater from a typical 3phase olive mill.
  - COD 36,20±3,1 g L^{-1},
  - TOC 18,14±4,2 g L^{-1},
  - TKN 613,6±5,2 g L^{-1},
  - TPC 2,86±0,39 g L^{-1} expressed as gallic acid,
  - Oil 22,95±1,9 g L^{-1}
  - pH 4,5±0,2.

Materials and methods

- Inoculum
  - Seed sludge for the anaerobic degradation process was sludge cultivated on wastewater from a potato processing factory. The sludge was seeded from a UASB bioreactor (Upflow Anaerobic Sludge Blanket), which operates under a loading of 0,05 g COD g VSS^{-1} d^{-1}.
- Procedure
  - The OMWW was initially subjected to Fenton oxidation treatment. The oxidation was carried out batchwise at 20°C in an agitated (100 rpm) glass reactor of 500mL capacity for 30 minutes. Firstly, the Fenton oxidation reagent was added. As ferrous salt, $FeSO_4 \cdot 7H_2O$ was used and the hydrogen peroxide was of 30% concentration.

Anaerobic digestion procedure

In a 500mL beaker, 100 mL of the pre-treated wastewater (or the raw OMWW) were added as well as 100 mL of inoculant. The mixture was vigorously stirred (180rpm), in order to achieve a satisfactory oxygen transfer.

Every 1 hour, a sample was taken and analysed for TOC and VSS. For each experiment, the performance data mentioned above were collected until steady-state conditions were obtained.

Factorial design

- The aim of the experimental procedure was to determine the influence of 4 basic process parameters on the effectiveness of the oxidation treatment in terms of % TOC, TKN, TPC and fats removal and on the effectiveness of the biological treatment in terms of the biokinetic constant maximum substrate uptake rate k_{max}.

Estimation of biokinetic constants

- Biological degradation of a wastewater's organic substrate in an aerobic activated sludge biological system, can be expressed by the generally accepted model of Lawrence –McCarty that is another version of the Monod model

$$\frac{dS}{dt} = \frac{k_{max} \cdot S}{K_s + S} \cdot X \quad \text{and} \quad \frac{dX}{dt} = Y \cdot \frac{dS}{dt} - b \cdot X$$

- S = biodegradable substrate concentration, $mg \cdot L^{-1}$
- X= activated sludge concentration, $mg \cdot L^{-1}$
- k_{max}= maximum substrate uptake rate, d^{-1}
- b = biomass inactivation rate, d^{-1}
- Y = yield coefficient
- K_s = substrate inhibition coefficient, $mg \cdot L^{-1}$

Estimation of biokinetic constants

- As the wastewater gets more biodegradable, the parameter k_{max} increases.
- Data were used as input in suitable software for the solution of the differential equation system.

Results

- TOC removal :
  - The most significant linear parameters were the coagulation, the ferrous sulphate heptahydrated concentration, the hydrogen peroxide concentration and the presence of oils.
- TKN removal
  - It was proved that the most significant linear parameter was by far the coagulation followed by the presence of oils and the ferrous sulphate heptahydrated concentration.

Results

- TPC removal
  - The coagulation parameter has the highest linear coefficient, reflecting its crucial role in phenolic compounds removal. Apart from coagulation, effective breakdown of the phenolic compounds can be achieved by radical produced by Fenton reagents.
- Fats removal
  - Apart from coagulation, all other controlling parameters were not statistically significant.
- Maximum substrate uptake rate

Results

- Maximum substrate uptake rate
  - The higher maximum substrate uptake rate k_{max} that was observed was 8,6d^{-1} at the experimental point

Conclusion

- Mineralization efficiency measured as total organic carbon removal reached 43,42%. On the other hand, in some cases the %TPC and %fats removal efficiencies were much higher, reaching 82,04 and 97,1%, respectively. Thus, the Fenton oxidation step seems to meet its main goal: to break down complex chemical components. The optimum conditions achieved for the oxidation of olive mill wastewater in terms of most parameters were found to be: (with coagulation, 1g/L $FeSO_4.7H_2O$, 20mL/L H_2O_2, with oil) and TOC reduction was 31,8%, TKN 78.4%, TPC 82% and oil removal 88%.

Conclusion

- Fenton oxidation pretreatment proved to be an effective method for the detoxification of the OMWW since it resulted to higher maximum substrate uptake rates k_{max} rendering OMWW susceptible to anaerobic biological treatment. The feasibility of the pretreatment method by its incorporation in an integrated plant could be the aim of a future work. Technical and economical aspects should be evaluated.

Thank you!