OLIVE MILL WASTE WATER (OMWW) TREATMENT BY DIAFILTRATION

Paschalis E. Gkoutsidis, Konstantinos B. Petrotos, Maria I. Kokkora, Athanasia D. Tziortziou, Konstantinos Christodouloulis and Panagiotis Goulas
Laboratory of Food & Environmental Process Engineering,
Department of Biosystems Engineering,
School of Agricultural Technology, Technological Educational Institute of Larisa, 41110 Larisa-Greece.

Contact: Dr Konstantinos B. Petrotos, Biosystems Engineering Dept.-, TEI Campus, 41110 Larisa, Greece
Tel :+302410684524 e-mail: petrotos@teilar.gr

EXECUTIVE SUMMARY

Olive mills are usually small scale enterprises that can not afford the costs of a proper wastewater treatment, unless the treatment is a very simple and cheap procedure. Most treatment technologies however require high investment costs and high level of technological know-how. Thus the design of centralized treatment plants is considered more suitable to treat OMWW produced by several mills. This creates a burden to operational costs, as high transportation costs due to high geographical scattering must be taken into account. In some cases, local conditions may call for separate treatment plants. Several attempts have been recorded concerning the utilization of advanced membrane technology in the case of the olive mills waste water treatment, mainly by involving ultrafiltration membrane technology without any commercial follow out due to serious membrane fouling problems and only partial removal of COD load of the wastewater (only 80% of the total pollution potential was managed to be removed) (**Turano et al, 2002; Borsani et al, 1996**). However, provided the fouling problem has been overcome, ultrafiltration could be a useful operational step in an integrated scheme of total discharge treatment of the OMWW to produce high value products and agro-materials consuming virtually 100% of the initial wastewater flow.

In the context of the present work, it was studied for the first time and in detail a dilution facilitated and due to this fact low membrane fouling UF process which is based on the principle that by diluting the original OMWW its fouling tendency is getting reduced so that UF treatment can be effective and operational. This process is known as Diafiltration.

An experimental apparatus was constructed in order to study the feasibility of the application of diafiltration to process Olive Mill Waste Water (OMWW). This apparatus consisted of a tubular membrane accommodation module, a controlled temperature raw material stock tank and a positive displacement pump connected all together by reinforced plastic pipes.
Three tubular Ultrafiltration membranes with MWCO 8000 Daltons, 25000 Daltons and 100000 Daltons respectively were used. The performance in terms of UF permeation flux of each one of the three membranes was tested by using four OMWW/water dilutions 1:1, 1:3, 1:5 and 1:10 at three temperatures settings (30˚C, 40˚C, 60˚C) and for each respective temperatures setting at six trans-membrane pressure values adjusted within the range from 1 to 6 bars. In correspondence to the obtained experimental evidence, the overall OMWW diafiltration flux, especially by using the membranes with MWCO 25000 Daltons and 100000 Daltons, was found to be of high magnitude. This fact creates an optimism for the commercial follow-up of the process itself by using it as the main component of a promising hybridic scheme for total handling the OMWW pollution problem in a environmentally friendly and sustainable way, according to adopted by EU environmental principle of zero discharge.
The above mentioned scheme is described, and presented in the context of the present work and its central idea is to use, in a first step, diluted OMWW ultrafiltration which converts the original slurry OMWW into clear low viscosity liquid at a high rate, then in a second step the polyphenols get recovered in powder form from the clear ultra-filtrate by selective adsorption/desorption of them on macroporous resins combined with non explosive spray drying while organic fertilizers are produce by innovative high pressure concentration of the de-phenolized clear ultra-filtrate either alone or in mixture with the UF retentate. In this way, the total flow of the Olive mill waste water is converted into valuable products and this in turn contributes to significant reduction of carbon emissions to the atmosphere.

INTRODUCTION

The extraction and use of olive oil in the Mediterranean area since more than 5000 years ago is linked to the Mediterranean culture and history. Olive oil is almost totally produced in the Mediterranean region. More than three quarters of the annual production in the world produced by European Union countries located around the Mediterranean Sea **(Table 1.)**

Table 1.: Olive oil production by European Union countries around Mediterranean Sea in year 2003

	Greece	Italy	Spain	EU	World
Olive Oil Production (Metric Ton)	553 169	663 252	1 492 800	2 741 106	3 428 410
Olive Oil Production (percentage)	16 %	19 %	44 %	80 %	100 %

***Source*: FAOSTAT Database, FAO 2006**.

The Olive mill waste water (OMWW), which is a mixture of vegetation water and soft tissues of the olive fruit and the water used in the various stages of the oil extraction process, is considered to be a significant pollution problem in all the Mediterranean countries.

The difficulty in the OMWW management is caused by the huge volume of OMWW, as the annual world OMWW production is estimated from 7 to over 30 million m^3 produced in short time as well as by its basic characteristics which prove the "strong" nature of OMWW as an industrial waste and they are the following :

- Strong offensive smell
- Extremely high degree of organic pollution (COD values up to 220g/lt) and a COD / BOD_5 ratio between 2.5 and 5 (hardly degradable)
- pH between 3 and 5.9
- High content of polyphenols (up to 80g/lt) which are not easily biodegradable and toxic to most microorganisms
- High content of solid matter (total solids up to 20 g / lt)

In terms of pollution effect, $1m^3$ of OMWW is equivalent to $100\text{-}200m^3$ of domestic sewage. Its uncontrolled disposal in water reservoirs leads to severe problems for the whole ecosystem and especially for the natural water bodies (ground water reservoirs, surface aquatic reservoirs, seashores and sea). The most visible effect is discoloration, a result of oxidation and subsequent polymerization of tannins. OMWW also has a considerable content of reduced sugars, high phosphorus content and phenolic load that has a toxic action to some organisms. Some microorganisms that metabolize sugars develop more rapidly on the expense of other living organisms. The high phosphorus content accelerates the growth of algae resulting in eutrophication. Some aquatic organisms (i.e. the river fish *Gambusia affinis* and some crustaceans) become severely intoxicated even at exposures corresponding to 1 lt of unprocessed OMWW into 100 000 lt of circulating water. **(Fiorentino et al., 2004)**

OMWW dispersion on ground and its subsequent metabolization (by microorganisms, insects, earthworms etc) to humic extracts or acids could also lead to soil enrichment with nutrients (i.e. organic matter, nitrogen, phosphorus and potassium) and a low cost source of water. However, OMWW high concentration of potassium affects the cation exchange capacity of the soil, leading to change of environmental conditions for soil microorganisms and consequently to changes in the fertility of the soil. Soil porosity could also be affected. Other possible negative effects include the immobilization of available nitrogen and decreased available magnesium, perhaps because of the antagonistic effect on potassium. Finally, no land disposal of OMWW should be done, without taking under consideration its severe phytotoxic and antimicrobial properties that may damage the existing crops. **(Cox *et al*., 1997; Paredes et al., 1999; Sierra *et al*., 2001)**

The phytotoxic and antimicrobial properties of OMWW have been mainly attributed to its phenolic content and some organic acids, such as acetic and formic acid, that are accumulated as microbial metabolites during storage. Its direct application on plants inhibits the germination of different seeds and early plant growth of different vegetable species

and may cause leaf and fruit abscission as well. Different kind of crops show different reactions to OMWW spreading and some of them may tolerate a certain amount of OMWW during early growing stages. **(Rinaldi *et al.*, 2003)**
As far as its antimicrobial activity is concerned, catechol, 4-methyl-catechol and hydroxytyrosol are its most active compounds against a number of bacteria and fungi. Several authors have reported OMWW activity against soil Gram (+) spore bacteria like *Bacillus megaterium ATCC 33085, Geotrichum, Rhizopus, Rhizoctonia, Bactrocera oleae, Pseudomonas syringe.* **(Oikonomou *et al.*, 1994)**
These biotoxic properties of phenols in OMWW constitute a significant inhibitor of the biological processes that take place in common wastewater treatment plants. Such plants do not present the desired performance with treatment of OMWW. Thus, the treatment of straight OMWW together with domestic sewage is not economically feasible, because of serious overload of the sewage treatment plant. So, research is oriented towards more complex treatment methods that usually demand higher capital or operational costs.

The problems mentioned above make the technological design of an OMWW treatment plant difficult. Factors that make the economic design of such a plant difficult is the intense and seasonal production of the waste (maximum four months each winter), the great variability both of synthesis and quantity, the high regional scattering of olive mills and the small size of the majority of them in the olive oil producing regions. Because of its highly variable input and seasonal production, storage facilities for the excess quantities of waste produced during winter months should be considered during design of a treatment plant. Similar design problems would arise in holiday resorts, where the population can also increase by an order of magnitude.Finally, serious nuisance due to the unpleasant odors and insects from OMWW may cause a serious difficulty at finding a suitable location of a treatment plant. All the above introduce economical, technical and organizational constraints that vary greatly from place to place, making the adoption of an environmentally compatible approach on a wide scale very difficult.

An interesting approach of the OMWW problem is the involvement of Diafiltration membrane process. This crossflow membrane process is capable of separating the phytotoxic polyphenolic materials from OMWW and to get them diluted in a low viscosity and concentration water solution. Simultaneously, a viscous non-phytotoxic liquid residual that can be used as a biofertilizer due to its useful plant nutrients content, is obtained. The very expensive polyphenolic material can be, in turn, absorbed in solid matrix by passing its solution through it to be isolated in clean condition leading to a high profit because of its high value (it is used in medical and pharmaceutical industry). The application of this idea demands, as a prerequisite, the application of diafiltration to OMWW to be technically and financially feasible.

According to the above, the main object of the present work was to investigate the applicability and performance of the low membrane fouling Diafiltration process of OMWW in terms of average permeation flux. It is also aiming at finding out experimentally and suggesting the optimum operational conditions for the diafiltration process in order to ensure an economical operation when applied for OMWW treatment.

MATERIALS & METHODS

The OMWW raw material was obtained from three different olive mills producing olive oil located in the rural areas around of the city of Larisa-Central Greece. The crude OMWW was prefiltered through a 50 μ mesh screen and kept in a cool storage facility at 0 - 4 ˚C. 5 Kg of this filtrate was used for each experiment.

The DF experimental rig (**Picture 1.)** consisted of the following elements :

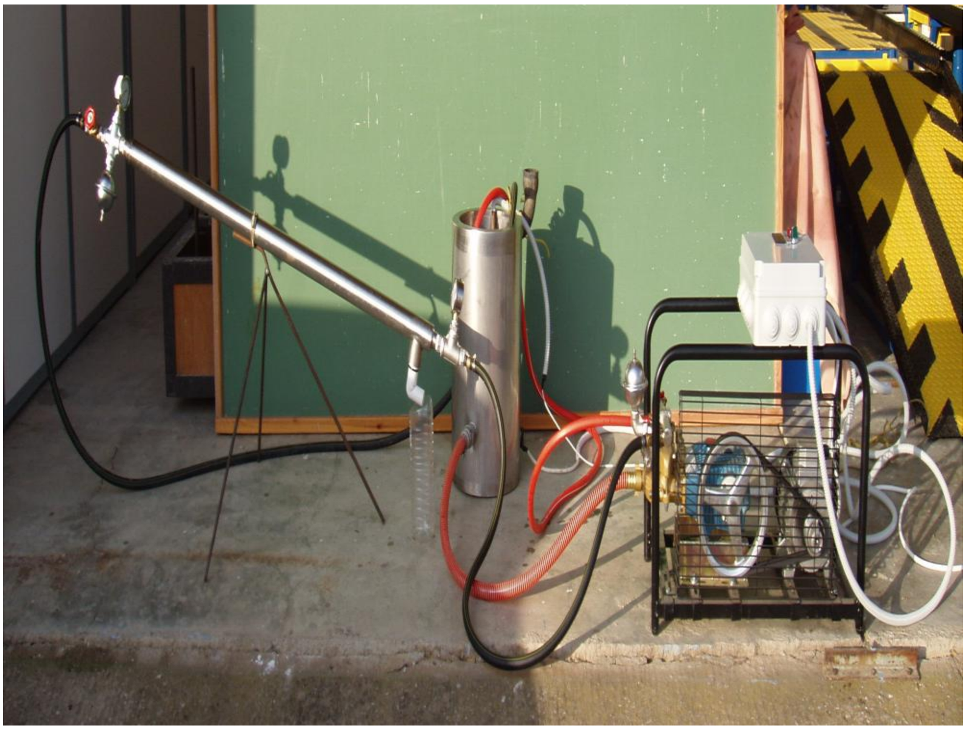
- A St 304 stainless steel tubular membrane module, with length 1200 mm and internal diameter 50 mm constructed to accommodate 2 UF membrane tubes. This was constructed by Micropoulos Co.-Oreokastro Thessaloniki-Greece, under the close supervision of the research team.
- A piston positive displacement pump. This was supplied by N. Koulousios Pumping systems Co- Larisa and it was the HP33 model of MARCO PUMPS Co. The volumetric capacity of the pump was 30 m^3 / hr and its maximum achievable pressure 50 bar. It was equipped with a pressure relief valve to by-pass the liquid in the case of a blockage and thus to protect the rig from any circumstantially developed over - pressure.
- A 6 litter jacketed stainless steel (St 304) stock tank equipped with a temperature control system consisted of a Pt100 sensor and accompanied by a digital display. This was constructed by KATERIS INOX DESIGN

Co.- Tirnavos – Larisa - Greece. The heating was obtained by an electrical resistance which was immersed in water hold in the external jacket of the stock tank.

- Two (2) Analog Pressure gauges range 0-10 bar, installed at the entrance and the exit of membrane module respectively.
- Pressure control valve installed at the output of membrane module.
- ½" OD Plastic reinforced pipes to interconnect the rig elements.
- The three types of UF membrane tubes, which were used, supplied by PCI Membrane Systems UK. The membranes were the commercially available types:

- PU 608 (MWCO = 8 000 Daltons) asymmetric type, made from poly-sulphone material
- AN 620 (MWCO = 25 000 Daltons) asymmetric type, made from poly-sulphone material
- FP 100 (MWCO = 100 000 Daltons) asymmetric type, made from poly-sulphone material

All the above mentioned membranes where easily accessible commercial products included in the commercial products catalog of the company. The membranes supplied in dozens of 1200 mm tubes in plastic containers along with their rubber gaskets (two for each membrane tube).



Picture 1.: The overview of the experimental rig **(Gkoutsidis, 2006)**.

After the procedure of installment a new membrane tube in the module a cleaning was performed with hot water (60˚C) at maximum pump speed and zero pressure (completely open back pressure valve). This cleaning was performed by re-circulating de-ionized water through the tube bore in order to clean the membrane surface from preservative. The cleaning regime lasted 30 min.

The performance of each membrane was tested first by water and then by OMWW dilutions.

The experimental procedure included the following steps:

- A quantity of 6 kg de-ionized water or diluted OMWW material at one dilution in the range 1:2, 1:3, 1:5, 1:10 was put in the stock tank.
- Initially, the temperature was selected to be as low as 30 ˚C and the UF flux was measured at six transmembrane pressures in the range 1 - 6 bars. The pressure was controlled by changing the setting of the back pressure valve. The same procedure was repeated at 40 ˚C and 60 ˚C to obtain the membrane performance at higher temperatures in terms of permeate flux.

- The flux value was calculated for each experimental point (combination of temperature and trans-membrane pressure) by collecting the permeate for 5 min, weighing and expressing its weight in kg and dividing it by 5 min = 5/12 hr and A = 0,048 m^2 (membrane surface) in order to have it expressed in kg/m^2 hr. After its weighing the permeate was returned in the stock tank.
- An average flux value for each dilution and membrane at 60 ˚C and 4 bar was calculated. This was carried out by an independent experiment for each one of three membranes and each dilution by controlling the DF transmembrane pressure at 4 bar and the operation temperature at 60 ˚C and collecting and weighing the whole permeate from the beginning of the experiment till the final remaining weight in the stock tank becomes equal of the initially undiluted material. The average flux value was then obtained by dividing by the membrane area in m^2 and time in hours elapsed since the experiment started.
- Before each measurement cycle a time of about 30 min was left to pass since the first contact of the OMWW material with the membrane. This was done in order to get measurements after the first fouling layer was installed on the membrane (asymptotic flux area) and not at the beginning were a rapid flux reduction, due to the initial built up of the fouling layer, is normal to be observed.

RESULTS & DISCUSSION

The level of the raw material dilution had a prominent effect on the magnitude of the trans-membrane flux (**Figure 1.).** It is obvious from Figure 1. that, a sharp exponential increase of the average UF flux is observed by increasing the OMWW dilution. Moreover, at all tested dilutions the membrane performance was found to of high values (almost 150 Kg/m^2 hr at trans-membrane pressure 4 bar, 60 ◦C) and thus enough to support a potential commercial use of the diafiltration process as an OMWW treatment method.

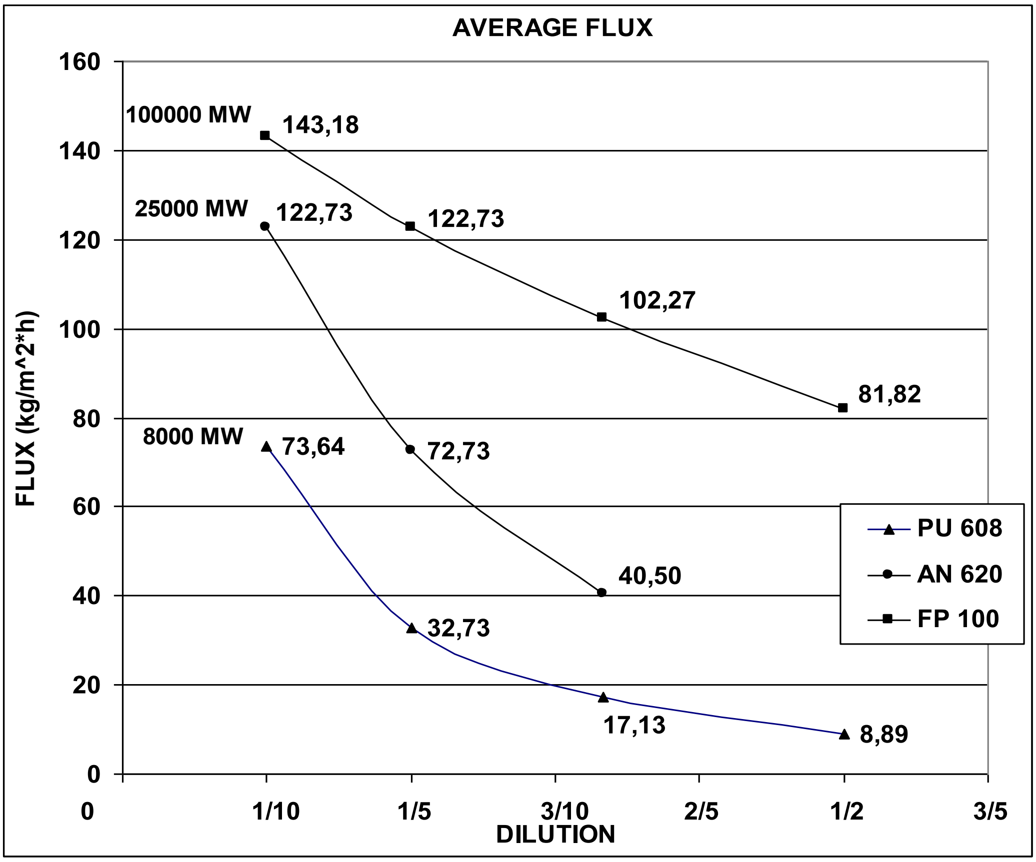


Figure 1.: Average Diafiltration flux at optimum conditions (temperature 60°C And trans-membrane pressure 4 bar) vs. OMWW dilution.

Furthermore, the temperature of the ultrafiltered material found to have a remarkable effect on the performance of the membrane. As it is indicated by **Figure 2**., by rising the temperature of the ultrafiltered OMWW material from an initial value of 30 ˚C to a final value of 60 ˚C, approximately 50% increase of membrane performance was observed. This finding is in line with the well known, since long time, ultrafiltration theory which demands an Arrhenius dependence of UF flux on temperature and explains this in terms of mass transfer. This observation have a particular importance as the OMWW material is not a sensitive material like food and accordingly it can be handled at high temperatures to facilitate and improve the diafiltration/UF process performance.

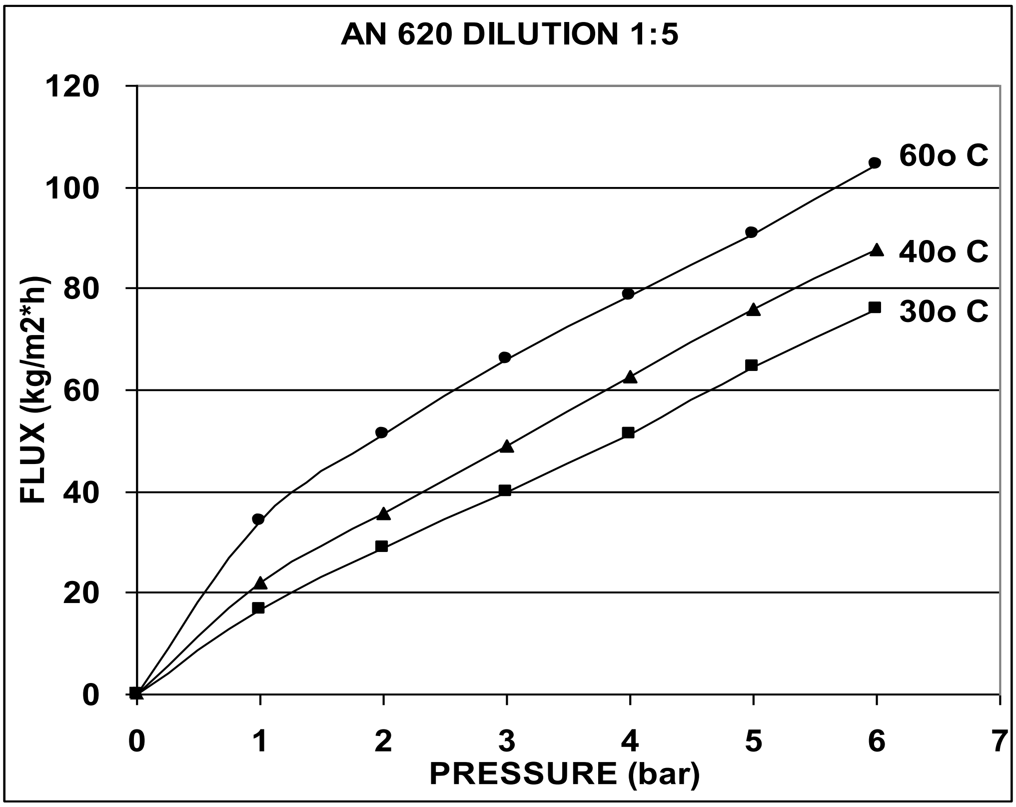


Figure 2.: OMWW Diafiltration flux vs operating temperature.

The membrane MWCO had, in general, a significant effect on the Diafiltration trans-membrane flux. As the MWCO was increased (**Figure 3.)** the corresponding flux values to different membranes at same trans-membrane pressure , same temperature and OMWW dilution was found to increase markedly. The magnitude of the flux increase at the middle of the tested trans-membrane pressure range 0 - 6 bar, was such big that the flux value at MWCO = 100000 Daltons was approximately double of the corresponding value at MWCO = 8000 Daltons with, however, only a slight difference being notable between the flux obtained by the membrane with MWCO = 8000 Daltons and by the one with MWCO = 25000 Daltons. Concerning the effect of the trans-membrane pressure on the diafiltration flux (**Figure 3**.), the well known “broken” UF curves with an initial linear section followed consequently by a virtually flat flux vs trans-membrane pressure profile were obtained by graphical representation of FLUX versus DP (trans-membrane pressure).

The commercial and practical interest of the diafiltration process is apparent as, by using this technique, isolation of the polyphenols can be achieved in a low viscosity liquid which comes as the DF filtrate (diafiltrate). While on the other side the high viscosity DF retentate will contain less than 1/10 of the contained polyphenols in the processed raw material. The low viscosity retentate will easily pass through columns filled with resins suitable to remove and recover the polyphenols without facing the problem of column blockage and fouling by fibrous and viscous material or by high pressure drop due to high viscosity. The output material from the resin column, free of polyphenols, can be concentrated

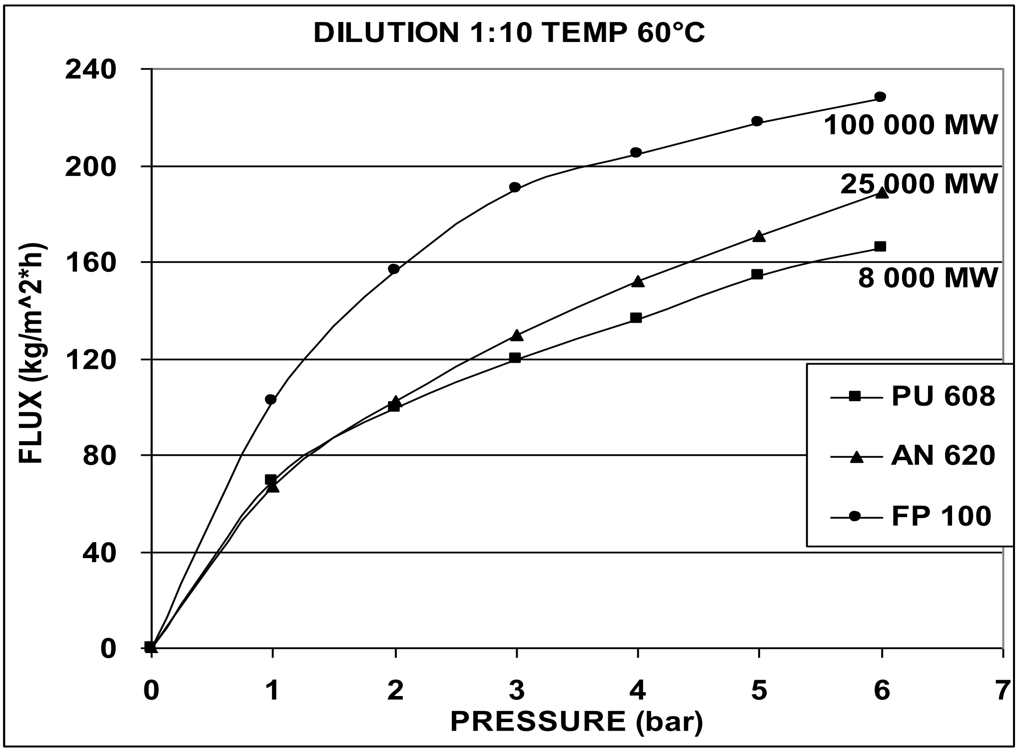


Figure 3.: OMWW Diafiltration flux at 1/10 dilution and 60◦C vs applied transmembrane pressure for different membranes.

by high pressure RO and used alone or in mixture with the DF retentate as fertilizer for crops. On the other hand, the eluted polyphenolic solution from the resins column can be used to obtain spray dried high added value polyphenol powder which can serve as raw material for pesticides and insecticides or alternatively as antioxidant for the food or even as a raw material used by Pharmaceutical Industry to prepare pills that prevent Heart Disease. An additional advantage of this method (Diafiltration) compared with the plain cross-flow ultrafiltration is that in DF the used membrane does not come in contact with highly concentrated and thus having high pollution tendency solution, as does in the case of UF. This protects the used UF membranes from a premature destruction due to precipitation of organic material that irreversibly blocks the pores and significantly extends the self-life of the membranes in the case of DF, lowering accordingly the operational cost.

CONCLUSIONS

From the measured OMWW diafiltration fluxes it is concluded that this process can be applied in commercial scale as the average values of flux were very high and in the range of 30 - 143 Kg/hr. The optimum operative conditions were trans-membrane pressure of about 4 bar and temperature approximately 60˚C. Higher trans-membrane pressure values do not cause significant flux increase while higher UF temperatures will certainly cause problems to the membrane (e.g. compaction). The diafiltration performance was higher at higher temperatures, higher dilutions and higher membrane MWCO. The well known UF flux model was found to fit perfectly the trans-membrane flux vs trans-membrane pressure data which were experimentally obtained and it was observed an exponential dependence of the DF flux on the OMWW dilution for all the tested membranes. The incorporation of the diafiltration process in a combined OMWW processing scheme including, its initial clarification by diafiltration, absorption of polyphenols on special resins, and desorption / elution of them to finally produce polyphenol powder by spray drying, along with agro products production seems to be manageable. This scheme aims at completely extinguishing OMWW by converting 100% of it in useful materials of commercial added value and resulted the target and the ultimate goal of the present investigation. The above mentioned idea has already been covered by a patent issued by the Greek Organization of Industrial Property.

ACKNOWLEDGMENT

This work was carried out in partial fulfilment of a MSc Thesis (Dissertation) in the Master 's Degree Course "Production of Quality Plant and Animal Products in Mediterranean Environment" 1st cycle 2006-2007, which was co-organized by the Technological Educational Institute of Larissa, Greece (Dept of Animal Production and Dept. of Bio-systems Engineering) and the School of Agronomy at the University of Bari, Italy. The authors wish to express their gratitude to the organizing committee for their kind financial and moral support.

REFERENCES

Borsani, R. and Ferrando, B., (1996): Ultrafiltration plant for olive vegetation waters by polymeric membrane batteries. Desalination **108**, p.281-286.

Cox, L., Celis, R., Hermosin, M.C., Becker, A., Cornejo, J. (1997): Porosity and herbicide leaching in soils amended with olive-mill waste water, Agric. Ecosyst. Environ., **65** (2**),** p.151-162

FAOSTAT database (2006), in http://apps.fao.org/default.htm.

Oikonomou, D., Koutsaftaki, L., Stefanoudaki, E., Metzidakis, G., Androulakis,I., Iniotakis,N. :(1994): Olive-mill waste water treatment with a membrane process, (In Greek), Proc. of Int.Symposium, Geot.l Ch. of Greece, Sitia, Crete, Greece, p. 156-167

Paredes, C., Bernal, M.P., Roig, A., Cegarra, J., Sánchez-Monedero, M. A. (1996): Influence of the bulking agent on the degradation of olive-mill wastewater sludge during composting, Int. Biodeterioration & Biodegradation, **38** (34), p.205-210

Paredes, C., Cegarra, J., Roig, A., Sanchez-Monedero, M.A., Bernal, M.P. (1999): Characterization of olive mill wastewater (alpechin) and its sludge for agricultural purposes, Bioresource Technology, **67,** p.111-115

Paredes, C., Bernal, M.P., Roig, A., Cegarra, J. (2001): Effects of olive mill wastewater addition in composting of agroindustrial and urban wastes, Biodegradation, **12**, p.225-234

Rinaldi, M., Rana, G., Introna,M. (2003**)**: Olive-mill wastewater spreading in southern Italy: effects on a durum wheat crop, Field Crops Research, **84** (3), p. 319-326

Sierra, J., Martν, E., Montserrat, G., Cruaρas, R., Garau, M. A. (2001): Characterisation and evolution of a soil affected by olive oil mill wastewater disposal, The Science of The Total Environment, **279** (1-3),p. 207-214

Turano, E., Curcio, S., Paola, G., M., Calabrò, V., and Iorio, G., (2002): An integrated centrifugation–ultrafiltration system in the treatment of olive mill wastewater. Journal of Membrane Science, Volume 209, Issue 2, 519-531