Executive summary:

Olives undergo a series of treatments and operations in order to reach the point at which oil is extracted from them. One of the last steps in olive oil production is the purification and final separation of the olive oil from the residual pulp and an aqueous suspension, called olive mill wastewater (OMWW). The water present in the OMWW is partially added during the process, in major extent in the three phase process. This waste water stream is a strong pollutant because of its high organic load and phytototoxic, due to the presence of antibacterial phenolic substances, resistant to biological degradation. The discharge of OMWW is not allowed trough the municipal sewage system and/or natural effluents. Unfortunately, the available technologies for the wastewater treatment are too complicated to be operated in a mill factory environment and very expensive for to the olive oil business. Aim of the PHOTOMEM project is therefore to define and implement a process for the treatment of wastewater derived from agro-food processing, in particular olive mill wastewater (OMWW) waste water.

The proposed treatment for the treatment of agro-food process residual water is performed in three basic steps:
1. Pre-treatment: the organic matter content as well as the suspend solids must be eliminated from the wastewater stream by coarse gridding
2. Photocatalytic treatment process with titanium dioxide particles and UV irradiation
3. Membrane processes: from ultrafiltration, trough nanofiltration and down to reverse osmosis, a series of membranes in batch mode are capable to separate pollutants from the wastewater at high recovery ratio.

PHOTOMEM aims to achieve a reliable, fast and economic olive mill wastewater (OMWW) treatment, defining and implementing a process based on 3 sequent steps:
- Flocculation of OMWW to remove the suspended solid and reduce up to 1/3 the initial COD content,
- Photocatalytic COD reduction process by using magnetic titanium dioxide nanoparticles and UV irradiation, reducing the COD content from 80 g/l down to 25 g/l
- Membrane filtration (ultrafiltration, nanofiltration and reverse osmosis) to reduce the COD from 25 g/l down less 0,5 g/l, the upper limit for the discharge in the municipal sewer.

The PHOTOMEM scientific and technological objectives are:
- Development of a photocatalytic treatment for high COD OMWW stream, by using ferromagnetic nanotitania, UV radiation, recovery system with magnetic filters to achieve a recovery of the particles close to 100%
- Optimization of a production process for ferromagnetic photocatalytic nanoparticles, superficially covered with titanium dioxide through sol-gel coating.
- Design and engineering of the overall water treatment process (flocculation, photocatalysis and membrane processes)
- Implementation of a pilot plant with capacity of 1 m3/day of OMWW treatment and testing to validate the performances of the process and obtain data for the evaluation of scale-up.

Project Context and Objectives:

Mediterranean countries are strongly affected by the serious environmental problem related to the disposal of the olive oil mills wastewater, since they produce 95% of the worldwide olive-oil. In these countries about 11 million tons of olives are produced per year from which around 1.7 million tons of olive oil are extracted. The seasonal polluting load of olive-oil production in these countries is equivalent to the one of 22 million people, since the in average COD value of OM http://www is about 80 g l-1 and its volume is about 0.8 ton per ton of olive. Moreover, this huge amount of polluted wastewater is produced only during 2-3 months per year (average duration of the olive oil campaign), making the storage difficult and entailing the need of an immediate treatment to eliminate its environmental hazard.

As already mentioned, the discharge of OM http://www is not allowed trough the municipal sewage system and/or natural effluents. At the same time, however, no efficient and low-cost treatment exists for the treatment of such effluents to be performed in an industrial environment such as the mill factory one.

For this reason, the current disposal systems adopted, which in most of the cases infringe the European and national regulations, are:
- Evaporation: the OMWW and the alpechin are stored in huge tanks or in evaporation ponds and the water is evaporated by sun throughout the year. The main problem are: the storage needs huge tanks, the evaporation leads to bad smelling air and must be performed far away from towns; also, a pollutant rich solid residue is generated and must be disposed.
- Disposal on terrains: the legislation allows disposing OMWW on compatible and suitable terrains (which are relatively rare and need to be toughly monitored) and within certain limits (50-80 m3/ha/y). The available terrains are not sufficient when compared to the quantities produced yearly by an average olive mill factory (20-50 m3/d). The problems caused by this procedure are pollution of the groundwater layers and of the terrains. For this reason, the procedure is considered illegal according to the EU Directive 91/271/EEC on urban waste-water treatment.

Olive oil producers then need a reliable and affordable technology solution to treat the waste water, since the presently applied methods are not acceptable from the environmental point of view, and conventional treatment not suitable from the economic aspect. Such residuals show in fact a very high amount of organic matter content (up to 200000 mg/l COD for OMWW), and a high level of toxicity, with a strong presence of polyphenols, which are very difficult to remove because of their hydrophilic characteristics.

The main objective of the PHOTOMEM project can be therefore summarized as follows:
A reliable, fast and economic OMWW treatment, based on the following steps:
- Flocculation of OMWW,
- Photocatalytic COD reduction process by using magnetic titanium dioxide nanoparticles and UV irradiation, reducing the COD content from 80 g/l down to 25 g/l
- Membrane filtration (ultrafiltration, nanofiltration and reverse osmosis) to reduce the COD from 25 g/l down less 0,5 g/l, the upper limit for the discharge in the municipal sewer.

Previous studies have been made on all the 3 steps mentioned above. The purification by membranes is very promising, capable to reduce the organic content down to 99% with a recovery of 95% of the feed stream in each batch. The expected result is therefore to recover at least 85% of the wastewater as purified water (with a COD value less than 500 mg/l). The main issues of membrane processing are:
- the fouling of the membranes and
- the disposal of the concentrate streams.

The first one can be solved by suitable pre-treatment processes, and the most used are coagulation and biodegradation. The problems here are the high costs of chemicals (in the first case) and the low constancy of performances of the biological process due to the presence of for the biomass toxic polyphenols in the stream (in the second case). Both processes need at least 3 days to be completed (flocculation and sedimentation in the first case, biodigestion in the second case).

A good alternative seems to be photocatalysis with titanium dioxide particles and UV irradiation. The colliding combination of suitable UV radiation, a titania particle, a pollutant molecule and an oxygen molecule give rise to oxidation of the organic matter. Studies have revealed that COD reductions up to 80% are possible by this method if performed correctly. Moreover, this pre-treatment reduces sensibly membrane fouling problems and is performed very quick in semi-batch systems, within hours. This allows to design very compact photo-systems, very important to treat the huge quantities of wastewater produced by the olive oil factory. In addition to this, photocatalysis is a easy to operate process, with very low operational costs (represented mainly by the agitation system and the UV light source).

The best performances of the photocatalysis are given by using nanoparticles of titania, probably due to the great increase of active surface area and photoactivity. The main issue here is the reuse of nanotitania particles in successive batches. The relatively cheap commercial titania powders such as Degussa P25 have the problem to lose at each batch 60% of the beginning performance. This is not the case by using suitable anatase nanoparticles, produced by chemical precipitation processes (which should lead to smooth surface particles with no or sensibly reduced presence of stagnation pits compared to the flame dry production process used by Degussa).

Experiments carried out in Japan have demonstrated that the use of nanoparticles of hematite superficially covered by means of titanium dioxide, allows a good degradation of organic compounds in wastewaters and a recovery by magnetic filters of the magnetic core particles close to 100%.

Advantages with respect to presently applied pre-treatments are the following:
- It requires no aluminium sulphate - a very expensive reagent - used in the flocculation stage to remove the suspended solid and 1/3 of COD, this allowing for great costs savings,
- It performs a reduction of COD up to 70% in short time (few hours),
- It drastically lowers the investment and operating cost of membranes (about 1/4),
- It strongly inhibits fouling problems,
- It leads to the design of very compact water treatment plants,
- It makes process operation easier and less expensive (50% cost saving),

Thus the PHOTOMEM S&T objectives are:
- Development of a photocatalytic treatment for high COD OMWW stream, by using ferromagnetic nanotitania, UV radiation, recovery system with magnetic filters to achieve a recovery of the particles close to 100%
- Optimization of a production process for ferromagnetic photocatalytic nanoparticles, superficially covered with titanium dioxide through sol-gel coating.
- Design and engineering of the overall water treatment process (flocculation, photocatalysis and membrane processes)
- Implementation of a pilot plant with capacity of 1 m3/day of OMWW treatment and testing to validate the performances of the process and obtain data for the evaluation of scale-up.

The PHOTOMEM technology stands as a clear step forward with respect to the available S&T solutions. Just to mention the main advancements respect to state-of-the-art techniques:

Advantages of the PHOTOMEM photocatalytic pre-treatment respect to chemical or biological pre-treatments:
- No use of chemicals and additives and related operational costs: photocatalytic particles are almost 100% recovered and can be re-used many times without efficiency loss.
- Treatment time: 4-6 hours instead of the 1 to 3 days needed with chemical or biological pre-treatments.
- Compactness of plant: same capacity in 20% of size
- Energy consumption: modest energy consumption for the agitation system and the UV light source (reduced investment costs and operational costs).
- Partial oxidation of polyphenols, which may be recovered and sold. In fact, the oxidation is less severe, around 40 %, with respect to complete oxidation by using other pretreatments like as the biological ones.

Advantages of the PHOTOMEM membrane treatment respect to state of the art techniques, thanks to a fouling reduction of 5 to 15 times, granted by the photocatalytic pretreatment:
- Compactness: 20% less membrane area to treat the same stream flow rate.
- 10% higher selectivity: due to possible operating pressure increases.
- increased membrane module longevity: substitution every 3-4 years instead of months.

Advantages of the PHOTOMEM ferromagnetic photocatalytic titania nanoparticles with respect to state of the art techniques
- Oxidation of organic compounds with photocatalytic nanoparticles is much more effective: COD reduction 2 times higher.
- Oxidation is performed much faster: same COD reduction in 35% of time.
- No need of cleaning of photocatalytic surface (reduced or no use of nitric acid, with consequent reduced maintenance cost and time): the recovered ferromagnetic nanoparticles are almost clean since coagulated organic matter is not attracted by magnetic fields and no other ferromagnetic substances are present in the WW.

The activities carried out in PHOTOMEM project was devoted to the achievement of the following strategic goals, from a technical point of view:
1. The identification of the project layout and specifications in terms of industrial applications of OMWW treatment, expected performances, costs, etc.

2. The definition of the photocatalytic nanoparticles production process, development of the nanoparticles coating and optimisation of the process itself
3. The development of both photocatalytic and polyphenols recovery processes
4. A preliminary design of the WW treatment process to be implemented and tested in the second year of the project;

These activities were followed, in the second period of the project, by the research activities aiming at:
5. The finalization of an optimized photocatalytic nanoparticles production process, with the analysis of its scale up and feasibility at an industrial scale;
6. The validation of the photocatalytic activity of the nanoparticles and the definition of a specific process for the polyphenols recovery;
7. The achievement of a final design of the WW treatment process for the PHOTOMEM treatment plant, which also takes into account a pre and a post-treatment to reach the final target on COD removal;
8. The design and implementation of the PHOTOMEM pilot plant, assembling the different steps of the process previously outlined, and including a control system driving the process;
9. The realization of beta tests on the plant and of an intensive field tests session on WW allowing the assessment of the PHOTOMEM process performances in terms of treatment efficiency and organic content removal, as indicated in the national and European regulation framework.

Specific activities were carried out in order to obtain the above mentioned goals:

First Reporting Period
- The identification of the characteristics of PHOTOMEM target wastewaters, in terms of the organic matter contents, for the definition of the WW treatment to be applied,
- The definition of the optimal lab procedure for the production of magnetic nanocores and for their coating with silica and titania, based on the comparison between different processes,
- A preliminary evaluation of the photocatalytic process efficiency and the identification of the optimal catalyst for PHOTOMEM reactor,
- The determination of the process for polyphenols recovery and relative adsorption tests, and assembly of all these stages for building up the final WW treatment process.

Second Reporting Period
- The definition of the optimal lab procedure for the production of magnetic nanocores and for their coating with silica and titania, based on the comparison between different processes,
- The subsequent optimization of the production process so as to be able to produce high quantities of nanoparticles for the PHOTOMEM process,
- The determination of the process for polyphenols recovery and relative adsorption tests, and the sizing of an adsorption column to be used after the nanofiltration stage for recovering polyphenols from the treated wastewater,
- The selection of an optimized shape for the photoreactor allowing the scale up to industrially treated volumes of OMWW, obtained by testing different reactor configurations on lab scale prototypes and assessing their performances,

- The final 3D CAD design of the chosen photoreactor including the magnetic trap for the recovery of the nanoparticles used during the photocatalytic step,
- The implementation of the pilot plant, including automation and control
- The realization of beta tests and of a session of tests on fresh OMWW collected in November for the final assessment of the organics removal performed via the PHOTOMEM process.

The main technical outputs of the project were:

- The definition of the PHOTOMEM requirements
- The system specifications and layout
- A detailed report on the produced ferromagnetic nanoparticles characteristics and on their properties
- First results on adsorption and polyphenols recovery tests
- The WW treatment process design
- The realisation of a website dedicated to the project
- A detailed report on the produced ferromagnetic nanoparticles characteristics and on the production process performed by ARMINES in collaboration with MT, with an evaluation of the production costs for the future exploitation of the technology,
- the selection of the air lift configuration for the photoreactor, and its concept and executive design based on hydraulic and photocatalytic tests carried out at lab scale
- the Process and Instrumentation Scheme for the PHOTOMEM plant
- a pilot plant for the treatment of 1 m3/day of OMWW was implemented and tested
- The sizing of the adsorption column by which the recovery of polyphenols was possible in the PHOTOMEM process,
- The results of the tests on the pilot plant, allowing an estimation of the market potential of the PHOTOMEM technology,

On the dissemination and exploitation side, the main goals achieved in the reference period were:

- The estimation of nanoparticles production costs at an industrial scale,
- The implementation of specific dissemination activities having the purpose of spreading the results of the project to an audience as wide as possible,
- The assessment of the impact that the PHOTOMEM technology might have on the market once exploited by the SMEs and the realization of an exploitation strategy for the process and the plant commercialization.

- The update of the project website

The project activities can be thought as structured in 2 main phases:
- Phase 1: the setup of the system specifications and architecture and the preliminary tests on the photocatalytic process, the trials on the nanoparticles production for the identification of the best recipe, and the studies on the polyphenols recovery process (RP1);
- Phase 2: the outline of the process final design, the implementation of the different steps of the process on the PHOTOMEM pilot plant, and the field tests on OMWW with subsequent assessment of the technology performances (partially performed in RP1 and continued in RP2).

The specific objectives of each of the ongoing Work Packages in the whole project, according to the Description of Work, were:

WP1 – Specifications and Layout
- Definition of the expected requirements for the WW treatment for the industrial application, expected performances, costs, etc.
- Definition of the technical specifications and draft of the process layout
- Definition of the expected performance of the photocatalytic nanoparticles production process and cost

Expected deliverables:
- D1: PHOTOMEM Requirements (Responsible partner: BIOAZUL - Report – M1)
- D2: PHOTOMEM Specifications and Layout (Responsible Partner: UNIRO - Report – M3)

WP2 – Photocatalytic Nanoparticles Production Process.

This WP was devoted to perform the coating the ferromagnetic nanoparticles with sol gel silica and nanotitania, to carry out the optimisation of nanoparticles production in relation to photocatalytic performance, magnetic recovery, cost, etc., and to finally define an industrially scalable production process for the nanoparticles. Expected deliverables:
- D4: Ferromagnetic photocatalytic nanoparticles characteristics (Responsible partner: ARMINES – Report – M9)
- D8: Operative conditions for optimal production of ferromagnetic photocatalytic nanoparticles (Responsible partner: ARMINES – Report - M12)
- D16: Layout and analysis of scalable production process for ferromagnetic photocatalytic nanoparticles (Responsible partner: ARMINES - Report - M18)

WP3 – Development of photocatalytic process and reactor.

WP3 was intended to perform the definition and implementation of a lab setup of photoreactor for the photocatalytic reaction, to make tests on nanoparticles in the reactor and evaluate the COD content removal efficiency and recovery capacity, and, finally, to define the photoreactor design for the PHOTOMEM pilot plant. Expected deliverables:
- D5: Preliminary results of photocatalytic tests (Responsible partner: TUC – Report – M9)
- D9: Results of photocatalytic tests (Responsible partner: TUC - Report – M12)
- D10: Photoreactor concept design (Responsible partner: TUC – Report – M12)

WP4 - Development of the polyphenols recovery.

This WP was aimed at performing an experimental investigation on the polyphenols adsorption-desorption process, at investigating the feasibility of the polyphenols recovery and at designing the adsorption recovery unit. Expected deliverables:
- D6: Preliminary results of the adsorption tests (Responsible partner: UNIRO – Report – M9)
- D11: Results of the adsorption tests (Responsible partner: UNIRO – Report – M12)
- D13: Polyphenols recovery unit design (Responsible partner: UNIRO – Report – M15)

WP5- WW treatment process design.

This WP had its main goals in the design of a pilot scale photoreactor with a recovery system for nanocatalyst, and in the design of a complete WW treatment pilot plant, integrating the photoreactor with membrane filtration steps. Expected deliverables:

- D7: WW treatment process design (Responsible partner: UNIRO – Report – M9)
- D14: Photoreactor final design (Responsible partner: TUC - Report – M15)
- D15: P&I design (Responsible partner: LABOR – Report – M15)

WP6 – PHOTOMEM pilot plant implementation and beta tests.
The main objectives of this WP were the implementation of a WW treatment plant and the performance of beta tests on the plant allowing the assessment of the technology performances in terms of COD removal and fouling issues. Expected deliverables:
- D18: PHOTOMEM Pilot plant (Responsible partner: LABOR - Prototype – M21)

WP7 – Field tests and results assessment.
The activities planned for this WP intended to reach the following objectives:
i) to realize a field tests campaign with real OMWW, and
ii) to assess results and evaluate the technical and economical impact of the PHOTOMEM technology.

Expected deliverables:
- D19: Field tests results (Responsible partner: ECS - Report – M24)

WP8 – Dissemination, exploitation and training
The main objective of this WP was to facilitate the take-up of results by the small and medium-sized entreprises (SME)s, in particular by defining a dissemination, knowledge management and IPR protection strategy, as well as a route for the exploitation of PHOTOMEM results and for the transfer of the generated know-how to the small and medium-sized entreprises (SME)s.

Expected deliverables:
- D3: Website (Responsible partner: ECS – Other – M3)
- D12: Interim plan for use and dissemination of foreground (Responsible partner: ECS – Report - M16)
- D17: PHOTOMEM brochure (Responsible partner: ECS – Other – M18)
- D20: Final plan for use and dissemination of foreground (Responsible partner: ECS –Report M24)

WP9 - Project Management: the management tasks throughout the whole project were devoted to the implementation, the monitoring and maintenance of the Consortium agreement, performing an overall, ethical, financial and administrative management aiming at the full achievement of the scientific and technological objectives of the project (No deliverables expected for WP9). Details about the specific activities carried out under this WP will be reported in the dedicated section later on in this report.

Project Results:

GENERAL REMARKS

As planned in the description of work, the first year of PHOTOMEM project was aimed at achieving a major part of the results expected for WP1, WP2, WP3, with some preliminary results coming from the tests on adsorption and photocatalysis planned in WP4 and WP5. WP8 (Dissemination) and WP9 (Management) started in the first months of the project and have been object of activity for the whole period. The first year of the project had its central goals in:

- The definition of the PHOTOMEM requirements, specifications and layout,
- The identification of the photocatalytic nanoparticles characteristics and their production process outline
- The achievement of some preliminary results, to be confirmed and validated in the second year of the project, on the photocatalytic and adsorption tests,
- The design of PHOTOMEM WW treatment process

The first objective was pursued through a constant interaction with the beneficiary small and medium-sized entreprises (SME)s, in particular BIOAZUL, that supported the identification of the European context and situation concerning the olive mills waste water treatment and legislations; this provided information on the end-users needs and expectations for respecting these directives and complying with their national regulations.

Laying its basis on the use of photocatalysis for the WW purification, the novel approach proposed in PHOTOMEM then required a deeper scientific comprehension of the photocatalytic features of the magnetic titania nanoparticles that could be used for this purpose. Therefore, these particles' features and production steps were analysed and reported in WP2. The photocatalytic tests showed the efficiency of the synthesized TiO_2, while adsorption tests at lab-scale were performed for obtaining preliminary result on the polyphenols contents and recovery.

The stages constituting the overall PHOTOMEM WW treatment process have been studied in detail, each specific step being described according to the optimal techniques tested in this first year. The second period was aimed at achieving great part of the results expected from the whole project, starting from the production process for the photocatalytic ferromagnetic nanoparticles in WP2, to the definition of the entire treatment process on the basis of preliminary photocatalytic tests in WP3 and WP5, and then to the identification of the polyphenols recovery process by adsorption (WP4) which is part of the PHOTOMEM technological treatment of olive oil wastewater, implemented in the pilot plant to be developed in WP6 and tested in WP7.

WP8 (Dissemination) and WP9 (Management) started in the first months and have been object of activity for the whole project duration. As evident from the milestones table reported later on in this report, the most of the core objectives for the PHOTOMEM project have been planned to be achieved in this second period, as a consequence of the preliminary tests on the photocatalytic activity of the nanoparticles, and on their performances at lab scale, and as a verification of the overall process validity against the initially setup requirements and specifications.

We here briefly report the main achievements of the project, following the path outlined in the milestones table, also indicating the contributions of the partners in each step:

Milestone 1: The first milestone has been achieved in this second period of the project and strongly supported by the RTD performers UNIRO and TUC, who performed intensive tests on photocatalysis at a lab-scale in order to comprehend and assess the performances on OMWW of the irradiation of the wastewater; furthermore, with the purpose of verifying the feasibility to extract polyphenols from the process and possibly sell them to nutraceutical interested companies as part of the exploitation strategy for the small and medium-sized entreprises (SME)s in the Consortium, the design of an adsorption column was carried out, to be included as part of the treatment process. The wastewater used in this phase for the photocatalytic tests was collected at FRA's olive mill in Chania, Crete (Greece).

Milestone 2: The main responsible for the definition of the PHOTOMEM process and all the necessary steps, including pre-treatment and post-treatment for the achievement of the final target COD content in accordance to the European regulations, was UNIRO.

Milestone 3: The production of photocatalytic ferromagnetic nanoparticles was performed by ARMINES, and the production of the necessary quantity of nanoparticles for the tests on the pilot plant was carried out in collaboration with the small and medium-sized entreprises (SME) Marion Technologies, that produced approximately 1.5 kg for the final photoreactor (having a capacity of about 1 m3).

Milestone 4: The pilot plant implementation, including the control system for driving the process and monitoring the timing of each step, and preliminary tests on the functioning of all the stage were performed by LABOR, in collaboration with ECS, in the month of November 2012. As described in the related section, due to the delays in the selection and testing at lab scale of the photocatalytic reactor, it was not possible within the time constraints of the project to realised the full scale air lift photoreactor designed. A backup solution of the air lift reactor was implemented and tested, which allowed to check the functionality of the concept.

Milestone 5: The tests on fresh OMWW, collected in Italy by UNIRO, were performed in LABOR in collaboration with ECS, and the final performances of the new innovative technology using photocatalysis were assessed and reported in D19 (Field tests results), and in D20 (Final Plan for use and dissemination of foreground).

In parallel, the definition of an agreed exploitation strategy and the performance of specific dissemination actions for the project have been carried out by all the partners and in particular by the SMEs in the Consortium, with the support of the WP Leader in WP8, BIOAZUL.

The Consortium Management has been carried out by ECS during the whole project, and support on the management tasks in the moderation of technical discussions and the preparation of dedicated progress meetings came from the Technical Manager UNIRO and from the other performers.

In summary, we can state that:

1. Most of the strategic and operative goals of the first period of PHOTOMEM project have been achieved;
2. The technological choices and strategic decisions for the optimal execution of the project's activities and research have been always presented and agreed to the small and medium-sized entreprises (SME)s within the Consortium; their involvement in the development of the processes for the WW treatment has been precious and always encouraged;
3. Delays were assessed in the realization of the photoreactor and, as a consequence, of the completion of the pilot plant, which were recovered at the end of the project using a backup reactor with an airlift internal loop configuration, and led to a reduction in the time of the tests and assessment activities as they had been planned from the DoW; however, the Consortium agreed that, should further tests sessions prove necessary, these will be carried out even out of the project lifetime and provided to the SMEs.

RESULTS OF WP1

FRA, as the PHOTOMEM end user has contributed for the identification of the end users requirements, which are summarised below:
1. Amount of OMWW generated. 2000 m3 as an average during the whole campaign.
2. Duration of the production. 5 months as average, from November to March.
3. Current discharge route of the OWMM and associated costs. Disposal of OMWW at an evaporation pond at the surroundings of the olive mill. Annual cost of about 10,000 EUROS to rent the ground for the construction of the evaporation pond.
4. Expected requirements with regards to COD removal (expected use) and polyphenols recovery. The main constrain is to fulfil the legal requirements with regards to the effluent. Therefore, the system proposed should at least reduce the pollutants in the effluent to comply with the legislation. The polyphenols recovery is a good option to support the investment of the system through its commercialisation.
5. Capacity/size. The system should be capable of treating all the generated OMWW (average 2000 m3/y). Moreover, it should be close to the olive mill premises in order to avoid extra transportation cost.
6. Investment and O&M costs, how much could they invest. The investment cost would be at about 10,000 to 15,000 Euros per year.
7. Trained operators. The system should be easy to operate and maintain as the end user sees as a problem to have an operator only dedicated to this work.

The different stages foreseen for our project are briefly described below.

1. Pre-treatment by flocculation

The first operation of the treatment of OMWW is necessarily the elimination of the suspended solid, which consists of organic and inorganic compounds. A fraction of the dry substance is present as suspended solid, which is around 1 % of the overall mass. A preliminary separation of the suspended solid is made by a coarse grinding, then a flocculation is performed by adding a flocculant to the OMWW and applying a suitable procedure in batch mode, through two subsequent stages of agitation and solid segregation by using a cylindrical apparatus fitted with a stirrer. The key point is the type and amount of flocculant to be added, since its cost greatly affects the economics of the process.

The targets to be achieved are:
- the fraction of the mud separated in a reasonable period of time,
- the COD reduction due to separation of the suspended solid

The technique adopted right now by UNIRO to undertake flocculation was based on the use of 4-8 g/l of aluminium sulphate (AS in the following) as flocculant. The performance either with respect the mud fraction, smaller than 20 %, or the COD reduction, around 35 %, were satisfactory. The experience of UNIRO in this respect is hereafter reported. The pre-treatment of the olive vegetation water was performed in batch mode and by using a 20 litre reactor with a height/width ratio equal to 10. AS was used as coagulant, with this procedure: the coagulant mass was added to the wastewater, at a high stirring rate. After the fast mixing regime which lasted a couple of minutes, the suspension was mixed slowly for further 20 minutes and afterwards stirring was stopped. In this period of time, the aggregates can separate by gravitation, and after 72 hours the mud was extracted from the bottom of the reactor and dried out. After the mud extraction, the remaining clarified wastewater was withdrawn from the reactor, filtered by a 50 micron sieve and send to the feed tank of the pilot plant. As expected, the organic matter concentration is reduced after flocculation by the separation of the mud. The coagulant influences the final electric conductivity ('EC') value, which results to be increased. The difference of the EC value towards the initial one indicates how much of the added flocculant is still present in the MF feedstock, and is not completely eliminated from the solution by the sedimentation process and subsequent mud extraction. The final COD reduction is about 52.7%, with a recovery of 90% of the starting wastewater volume.

In spite of the satisfactory performances obtained by the use of AS, it is not advisable to consider this compound for flocculation in the project because of its relatively high cost and its presence represents a not allowed pollution i the dry substance to be sparged over the ground. For this reason at the project start UNIRO made some attempts by adopting a new flocculation promising method consisting of a heating of OMWW and acidification with nitric acid.The COD reduction was about 52.0% and recovery of 90% of the initial wastewater volume, perfectly in line with the one measured with coagulation by AS.

2. Photocatalysis Assisted by Doped TiO2

Heterogeneous photocatalysis, based on the interaction of light and nanoparticles has emerged as an innovative and promising technique for wastewater purification. Titanium dioxide (TiO2) is the catalyst most commonly used today because of its high performance, low cost, high photoactivity, low toxicity, chemical stability, insolubility and resistance to photo corrosion.

The main drawback of this technology is the high energy consumption required to activate the catalyst and provoke the reaction that neutralizes the pollutants. This is because the wavelengths that activate the catalyst (TiO2) are up to 95% within the ultraviolet spectrum, and UV lamps on the market are much less efficient and much more expensive that their visible spectrum counterparts. On the basis of the experience of UNIRO it is possible to reduce COD of OMWW from a value of 30 g/l to 18 g/l by irradiating a stirred solution, 2 l in capacity, for 4 hours. For the relative high energy consumption, required by photocatalytic process by using UV lamp, in the last years the use of doped TiO2 by nitrogen has been proposed in order to change the wavelength at which the catalyst is activated so it falls inside the visible spectrum. This fact enables the use of low cost red lamps and sunbeams, thus decreasing the energy consumption during the purification process and improving the economic feasibility of the process.

The doping method proposed by Nadica et. al. (2008) is quite simple and consistent with the wet chemical synthesis applied by both UNIROMA and ARMINES.

Different amounts (25 ml, 50 ml, and 100 ml) of ammonia (28%) were added dropwise to 25 ml of 95% titanium tetraisopropoxide at 0° C while the solution was stirred vigorously, leading to the formation of a white precipitate. The precipitate was washed with water and dried at room temperature under vacuum until constant weight. Finally, the obtained powders were heated in air up to 400 °C for several hours in an oven. The low temperature applied in this work to reduce the ammonia loss, may be increased by maintaining the working under pressure or by providing the reactor with a condenser over the off gas.

3. Membrane Processes

Different pre-treated olive mill waste water samples were used in the past for membrane process experiments. In case of coagulation, the treatment was done in batch mode by using a 20 L reactor using as flocculant aluminium sulphate ('AS'). The coagulant mass was changed and added to the wastewater, at a high stirring rate. After the fast mixing regime which lasted a couple of minutes, the suspension was mixed slowly for 20 more minutes and afterwards stirring was stopped. In this period of time, the aggregates can separate by gravity, and after 72 hours the mud was extracted from the bottom of the reactor and dried. The optimized flocculant dosage is the minimum coagulant mass added to the solution with the greatest possible dry mud production. An optimized dosage of 16 kg m-3 of AS was found.

Finally, the second pretreatment process, that is the photocatalysis ('PC'), was performed in an agitated batch reactor irradiated by an UV lamp. Photocatalysis under UV is one of the easiest and efficient operations to decompose organic matter in wastewater streams and to eliminate contaminants from drinking water. In this respect the most commonly used photocatalyst is TiO2. In previous lab work an optimized home-made nanometric titania powder was produced. The optimum dosage of nanopowder to add to the wastewater appeared to be 3 g/l. As long as the nanoparticles are completely suspended in the reactor, mixing does not affect performances. The powders were added to the reactor after 24 hours of acid dispersion with a 0,1M HNO3 solution at pH equal 1. Afterwards, the UV light source was turned on for 20 hours, performing the treatment of the wastewater.

All pre-treatment processes successfully tested down to RO gave rise to final permeate volume recoveries equal to 62% with respect to the feedstock, with a COD value equal to 456 mg l-1and 385 mg l-1 for AS and PC, respectively. The desired target requirements, that is a COD values below 500 mg l-1 (in Italy, this is the legal limit for the municipal sewer system discharge of wastewaters), was therefore reached for both the pre-treatment processes.

4. Post-treatment processes by photocatalysis

The organic matter content of the RO permeate exiting the membrane process step could be, in some cases, still too high to permit discharge in the municipal sewer system. In this case an additional post treatment step should be necessary to reduce the residue organic matter content for the water disposal. This kind of RO permeate, which may exhibit COD values smaller than 2000 mg/l and is transparent, may be treated again by photocatalysis, using nano-TiO2 as catalyst. This time, since the wastewater stream is not opaque, the irradiation with UV is easier and more efficient. Therefore, immobilized nano-TiO2 on glass spheres in a reactor may be used. Some experiments were performed at UNIRO to check the validity of this approach. The glass spheres were coated by a solution of nano-TiO2, prepared previously by sol-gel technique, and then calcinated at 450°C for 8h three times. The obtained catalyst was then put into a reactor with the shape of an inclined half pipe. Over this fixed bed it is recycled by means of a peristaltic pump a wastewater stream from the feed vessel.

5. Polyphenols Recovery

OOMW contains a polyphenolic fraction (up to 3 g/l in the fresh material) whose composition is variable. Several low-molecular-weight phenolic compounds are present such as, for instance, the phenolic derivatives of hydroxycinnamic, ferulic and caffeic acids and, in larger amounts, tyrosol (4-hydroxyphenetil alcohol) and hydroxytyrosol (3,4-dihydroxyphenetil alcohol). Hydroxytyrosol (3,4-dihydroxyphenylethanol; DOPET) is a phytochemical with antioxidant properties; it is the most powerful antioxidant contained in olive oil and, after gallic acid, one of the most powerful antioxidants. Its oxygen radical absorbance capacity is 40,000 umolTE/g, which is ten times higher than that of green tea, and two times higher than that of CoQ10. A number of research studies have clarified the positive effects of hydroxytyrosol (and olive polyphenols in general) on the cardiovascular system, their antimicrobial and antiviral activity, cancer risk, its neuroprotection, its influence on mitochondrial health and aging, its promotion of skin health, bone, joint and muscle support, and its oxidative stess reduction in passive smokers. Every cubic meter of OOMW can provide 600 g of hydroxytyrosol with a potential value of 30.000 Euro (50.000 Euro/kg).

RESULTS OF WP2

Detail of activities:

1. Development of a procedure for core magnetic particles, based on Fe(II) precipitation followed by oxidation with H2O2.
2. This procedure was then transferred to MT for scale-up.
3. Validation by X-Ray diffraction and transmission electron microscopy (TEM) was performed on the samples.
4. A procedure for silica coating based on Stober process, and validation by dissolution test, zeta potential measurement and TEM observation were carried out. Alternative process by silicate acidification and recipes were transferred to MT.
5. The procedure for titania coating based on titanium tetrabutoxide hydrolysis was used, while an alternative recipe based on mixing at controlled pH silica coated magnetite particles with amorphous titanium oxide precipitated from oxychloride was also tried. The validation stage has been performed via photocatalytic tests, XRD, TEM

First batches of magnetite particles and silica coated magnetite particles were produced at MT according to Armines' recipes, trying to use more concentrated solutions or suspensions. More agglomerated particles were produced in this way.

In this activity, contribution to the research on the nanoparticles production came from UNIRO, who produced magnetic core nanoparticles, according to the following process:

- Production of nanoparticles of magnetite (FeO.Fe2O3) from the reaction between FeCl3 and Na2SO3 and subsequent processes (precipitation of the iron hydroxide, in presence of ammonia, by evaporation and calcination);
- Production of silica nanoparticles by sol-gel method and subsequent calcination and their addition to magnetite ferromagnetic particles as coating;
- Production of titania by sol-gel method and subsequent drying and mixing of the obtained powder with the nanoparticles produced in the step 2. The obtained nanoparticles are submitted to calcination at a temperature higher than 450 °C to transform TiO2 to the anatase phase, which holds high photocatalytic properties.

The size distribution of the produced nanoparticles was measured by means the Dynamic Light Scattering (DLS) 90 Plus supplied by Brookhaven and an average size of 40 nm resulted. A lab scale spinning disc reactor has been constructed. It is completely made of PVC and consists of an external vessel hosting at the center a disc, 8,5 cm in diameter. The rotation of the disc is provided by an electric motor, whose rotational speed may be regulated between 0 and 1400 rpm. The functionality of the disc was successfully checked for both the productions of the hematite nanoparticles by operating at ambient temperature. For the next months of PHOTOMEM project, an optimisation of the process conditions has been planned, in order to obtain hematite nanoparticles by precipitation in continuous mode of the required size, i.e. 20 – 30 nanometers.

Samples were exchanged with the Technical University of Crete (TUC) and the University of Rome (UNIRO). Fe3O4@SiO2@TiO2 particles made by TBOT coating as well as amorphous TiO2 coating were sent to the project partners for the photocatalytic performance evaluation. In May 2011 ARMINES sent 2 x 5 grams of each product to the TUC. In the beginning of July 2011 ARMINES also sent approximately 5 grams of each magnetic photocatalyst to TUC and UNIRO. Their reports were produced in the first period of PHOTOMEM project. MT also sent samples of Fe3O4 and Fe3O4@SiO2, characterized by ARMINES with XRD, SEM and tested the performance of the silica coating. The XRD diffractograms show crystalline magnetite phase. Small amounts of impurities are present.

The optimized production of photocatalytic magnetic particles is described below, together with the different procedures for the synthesis and the coating.

i) Synthesis of Fe3O4 nanoparticles

A production procedure of magnetite (Fe3O4) has been optimized. This method leads to pure magnetic particles (particle size control 50 to approximately 80 nm). We consider that this protocol is satisfactory and there is no need for alternatives.

The following procedure was adopted:

- 600 mL of freshly prepared FeSO4 solution (0.1 mol/600 mL) was neutralized at room temperature in a 1L reactor with NaOH solution (0.2 mol/200 mL) injected under vigorous stirring (500 rpm) at a flow rate around 10ml/min. Injection was stopped when pH reached a value of slightly above 8. The pH was monitored by a pH-meter coupled with an auto-burette and a computer.

- Directly after the end of precipitation, 3 mL of H_2O_2 (30% solution) diluted in 100mL distilled water were injected in the reactor at 10 mL/min. pH is continuously adjusted between 8 and 8.5 by injection of NaOH (1M) by auto-burette.
- The solution was stirred during 2 hours after H_2O_2 injection end. Precipitate was washed with distilled water by centrifugations and re-dispersed in distilled water for further steps. The dispersion is not supposed to be stable and may flocculate, which is not a problem.

UNIRO produced Fe_3O_4 nanoparticles by applying a different procedure and by using a different set up, as follows:
- Two aqueous solutions, 0.4 M $FeSO_4$ solution and 0.85 M solution of NH_4OH, were preliminarily prepared to be used for the precipitation process of nanoparticles of magnetite, Fe_3O_4. The ferric solution was acidified with HCl 2M.

The set up consists of a rotating disc reactor, 8.5 cm in diameter, and the applied rotation speed was equal to 1500 rpm and the temperature was around 20 °C. The dried particles exhibited a big magnetic activity under a magnetic field.

ii) Silica coating of magnetite particles - synthesis of $Fe_3O_4@SiO_2$

The Stober (TEOS) coating procedure was chosen over the silicate coating (previously investigated) to be the most efficient method to obtain a uniform coating protecting perfectly the magnetite particle from dissolution in acidic media. Some dissolution of magnetite with time was observed in the case of particles coated by the silicate method. The quantity of silica was calculated from the value of the specific surface area of magnetite particles and the targeted thickness of the shell (for instance in the range 5-10 nm), assuming a homogenous and dense shell of amorphous silica of volumic mass 2.2 $g.cm^{-3}$. The dissolution test proves that all particles may be considered as coated and that the silica coating produced by the Stober method is homogenous and dense.

iii) Synthesis of $Fe_3O_4@SiO_2@TiO_2$ particles

Different approaches and methods were considered and investigated to select a method that would allow the most uniform and efficient anatase coating. First, the so-called TBOT hydrolysis procedure (widely studied in the literature) was evaluated and optimized for our purposes. The method has shown to lead to a quite good anatase coating on the $Fe_3O_4@SiO_2$ particles.

Another method was based on amorphous TiO_2 crystallization directly in the presence of $Fe_3O_4@SiO_2$ core particles. The rather mild conditions of the method, as well as the availability of the specific precursors at Marion Technologies could be more advantageous in comparison with the TBOT hydrolysis.

However, the coating obtained by this method was observed to be much less uniform. Large parts of the core particles were not covered with anatase. On the other hand, the agglomerates of anatase nanoparticles were observed apart from the core $Fe_3O_4@SiO_2$. Despite of the quite good photocatalytic performance in methylene blue decomposition, as prepared $Fe_3O_4@SiO_2@TiO_2$ materials could be difficult to remove magnetically from the OMWW. Therefore, we estimate that the optimized TBOT hydrolysis is the best method of coating for the PHOTOMEM project applications.

Further procedures have been investigated, such as $(EtO)_3Si(CH_2)_3NH_2$ grafting of $Fe_3O_4@SiO_2$ particles and TBOT coating procedure with HPC. The complete production method has been shared with Marion Technologies. In Task 2.3 the plan and analysis of the scale-up of ferromagnetic photocatalytic $Fe_3O_4@SiO_2@TiO_2$ particles production were object of study. The industrial production of magnetite silica and titania nanoparticles was evaluated for the final achievement of an industrial production technology to be eventually patented in the following.

All the technical aspects of the protocols were discussed to facilitate scaling up of the procedures by MT. Primarily, samples of Fe_3O_4 and $Fe_3O_4@SiO_2$ were synthesized by MT according to the protocols and the materials were sent to ARMINES for characterization. The results were then discussed by the partners to adapt the procedures at MT.

Phase purity of the MT samples was evaluated by X-ray diffraction (XRD). In order to perform tests on a lab-scale reactor and to assess the configuration of the pilot plant, ARMINES produced a requested quantity of the magnetic photocatalyst:
- Three batches of $Fe_3O_4@SiO_2@TiO_2$ particles (45 g in total) were sent to LABOR/UNIRO in April 2012.
- Samples of the three batches (3 g each) were sent also to the Technical University of Crete (TUC).

The production of the three distinctive batches according to the same procedure (final procedure communicated to MT) allowed LABOR/UNIRO and TUC to perform the photocatalytic, as well as the reproducibility tests. Finally, an improvement on the TBOT procedure was achieved in the second period of the project: ARMINES determined experimentally that in the case of TBOT coating procedure (given in D8) it could be beneficial to carry out the coating by adding the TBOT precursor in fractions, followed by simultaneous aging and final calcination. The procedure would improve uniformity of the coating and decrease the agglomeration problems while carrying out the coating at a larger scale (by MT). The TEM-elemental analyses of the samples prove that even if one cannot observe a uniform TiO_2 coating, the composition of analyzed agglomerates is homogeneous, showing presence of Fe, Si and Ti.

RESULTS OF WP3

The catalyst KM110511 yields higher MB degradation rate than the KM110512 sample, achieving almost total MB removal within 40 min of photocatalytic treatment under UV-A irradiation. The catalysts Kronos 7101, 7100, 7000 and Degussa P25 seem to be the most suitable to degrade organic pollutants such as phenolic compounds that are usually found at OMWW, in the presence of solar irradiation. The optimal catalyst concentration for the photocatalytic treatment of OMWW was estimated at about 2 g/L TiO_2. Kinetic simulation of the photocatalytic process showed that experimental data indicate a zero-order chemical reaction, in terms of COD removal. Application of photocatalytic treatment, in the presence of solar irradiation, at OMWW with high initial COD_0, of 65 g/L, is not feasible. Increasing treatment time the energy consumption is substantially increased. Hence, the increase of the photocatalytic treatment time will not constitute an energy- and thus cost-effective solution for process performance. Experiments were not performed by artificial irradiation of higher energy power than 400W, in order to apply an efficient photocatalytic process from both an environmental and economic point of view.

Increasing hydrogen peroxide addition up to 0.1 g/L had a beneficial effect on treatment performance in terms of COD reduction. Analytically, hydrogen peroxide in the form of 35% (w/w) solution supplied by Merck was used as an oxidant. H2O2 was injected batchwise in the reaction mixture. For comparison, control experiments (runs 1 and 2) were conducted to investigate the effect of H2O2 addition during the photocatalytic process. As can be seen, addition of H2O2 in the dark gave almost negligible COD reduction (5%), thus showing that OMWW is partly susceptible to bleaching. The same COD removal percentage was yielded when the solution was irradiated in the presence of H2O2 without TiO2 (run 2). Experiments were also carried out at various oxidant concentrations in the range 0.025-0.15 g/L. The extent of COD removal is significantly enhanced by adding hydrogen peroxide. For example, when 0.1 g/L H2O2 is added in the mixture solution, COD removal reaches 47%. In general, hydrogen peroxide is expected to promote degradation since it may react with conduction band electrons and the superoxide radical anion to yield hydroxyl radicals [8]. This is consistent with the fact that increasing oxidant concentration up to 0.1 g/L had a beneficial effect on treatment performance in terms of COD reduction.

Further oxidant addition in reactant mixture was not investigated in order to prevent
(a) the increase of treatment cost,
(b) the interference of H2O2 with COD measurements, and
(c) the hydrogen peroxide scavenging of the photogenerated oxidizing species (i.e., valence band holes and hydroxyl radicals), thus reducing process efficiency.

KM110511 achieved optimal photocatalytic efficiency after only 1 h of treatment when COD removal was 26%. Optimal treatment time for the efficient oxidation of an OMWW effluent with an initial COD0 of 0.6 g/L, is estimated at 1 h, in the presence of magnetic TiO2 nanoparticles. Moreover, KM110511 catalytic activity after three consecutive runs, with regard to COD removal, remained unchanged. Finally, when effluent's COD (i.e organic compounds including toxic substances, such as polyphenols) at the end of the treatment is substantially low, ecotoxicity of the OMWW sample decreases.

The detailed activities that were performed are the implementation of lab scale experiments to assess
(a) the optimal catalyst type,
(b) catalyst loading,
(c) to perform kinetic simulation,
(d) study the addition of oxidants such as H2O2,
(e) to study the radiation efficiency,
(f) to estimate acute toxicity of the effluent,
(g) catalyst recovery and reuse,
(h) determine the degradation routes and mechanisms.

Experiments were performed on both model solutions (Methylene blue and Phenol) and on actual OMW collected by FRA olive oil mill.

The scaling up of the process has to be done gradually. The photoreactor will be designed to keep it as easy as possible, without losing efficiency and should be as flexible as possible in order to permit a wide-spread study of the operating conditions. For this reason, a larger-scale photoreactor (i.e. effluent capacity of 5 L) will be designed to be as flexible as possible in order to permit a wide-spread study of the operating conditions. In particular, the photocatalytic process will be carried out simply by using a slurry of the magnetic TiO2 particles of the solid semiconductor material dispersed in the liquid phase in a reactor irradiated with UVA light.

The photoreactor will mainly consist of the following parts:
1. Catalyst treatment step: redispersion and/or acidification of the catalytic nanoparticles,
2. Reactor tank: operating at batch mode where OMWW photocatalytic degradation will take place,
3. Mechanical stirrers: to ensure good dispersion of the catalyst nanoparticles in the liquid,
4. UV lamps: the irradiation source will be situated above the surface of the reactant solution, thus allowing the illumination of the liquid,
5. Magnetic filter: this will trap and easily separate the catalyst particles from the liquid

The photoreactor will be equipped with a magnetic filter in order to recover the magnetic photocatalyst. The trapped photocatalyst will be afterwards redispersed and reused in the reactor. A catalyst treatment tank will be used to achieve high dispersion and purification of the catalytic nanoparticles.

The type of the reactor tank was studied. There are various designs of photocatalytic reactors that can be selected for the photocatalytic treatment of OMWW. Firstly, we report the lab-scale experiments conducted in an open rectangular photocatalytic reactor (20cm x 11cm x5 cm) operating at batch mode. The UVA lamp was placed on the top of the reactor and the distance between the lamp and the liquid surface was 3.7 cm, while the depth of the reactant solution was 1.3 cm. The implementation of this reactor was not enhanced due to its large land requirements. Furthermore, other reactor types were investigated and these were Gas-Liquid reactors that are called bubble column reactors and the most relevant example is given by the so-called 'Airlift Reactors', where the density gradient generates a natural whirling circulation motion. The lowest one is fed from the bottom of the reactor and is collected on the top, while the other one follows the inverse route. Task 3.1 aimed at conducting photocatalytic experiments to investigate the efficacy of several TiO2 catalysts to decrease the organic load of OMWW.

The 'best' catalyst for the PHOTOMEM process was evaluated on the base of the following parameters:
- Catalyst concentration effect on photocatalytic degradation (optimal concentration);
- Study of substrate concentration effect on photocatalytic degradation (kinetic simulation of the process);
- Effect of the solutions pH and radiation intensity;
- Investigation of the possibility to use oxidants;
- Measurements of ecotoxicity of the solution before and after treatment on the aquatic microorganisms Vibrio Fischeri and Daphnia Magna;
- Key degradation by-products using liquid chromatography;
- Degradation routes and mechanisms;
- Catalyst recovery and re-use;

The main results of the research carried out in this WP by TUC, already reported in D9, can be summarized as follows:

- The catalyst KM110511 yields higher MB degradation rate than the KM110512 sample, achieving almost total MB removal within 40 min of photocatalytic treatment under UV-A irradiation.
- The catalysts Kronos 7101, 7100, 7000 and Degussa P25 seem to be the most suitable to degrade organic pollutants such as phenolic compounds that are usually found at OMWW, in the presence of solar irradiation.
- The optimal catalyst concentration for the photocatalytic treatment of OMWW was estimated at about 2 g/L TiO2.
- Kinetic simulation of the photocatalytic process showed that experimental data indicate a pseudo-zero order chemical reaction, in terms of COD removal.
- Application of photocatalytic treatment, in the presence of solar irradiation, at OMWW with high initial COD0, of 65 g/L, is not feasible.
- Increasing treatment time the energy consumption is substantially increased. Hence, the increase of the photocatalytic treatment time will not constitute an energy- and thus cost-effective solution for process performance.
- Experiments were not performed by artificial irradiation of higher energy power than 400W, in order to apply an efficient photocatalytic process from both an environmental and economic point of view.
- Increasing hydrogen peroxide addition up to 0.1 g/L had a beneficial effect on treatment performance in terms of COD reduction.
- KM110511 achieved optimal photocatalytic efficiency after only 1 h of treatment when COD removal was 26%.
- Optimal treatment time for the efficient oxidation of an OMWW effluent with an initial COD0 of 0.6 g/L, is estimated at 1 h, in the presence of magnetic TiO2 nanoparticles.
- When the effluents COD (i.e organic compounds including toxic substances, such as polyphenols) at the end of the treatment is substantially low, eco-toxicity of the OMWW sample decreases.
- Practically, KM110511 catalytic activity after three consecutive runs, with regard to COD removal, remained unchanged.

The photoreactor concept design task – Task 3.2 - is intended to provide an estimation of the characteristics that PHOTOMEM photocatalytic reactor will have, according to the results already obtained during Task 3.1 of the project. Efforts were made to construct a unit reflecting all the necessary features of a full scale plant taking into account practical aspects related to the use of materials, components and process controls. Generally, there are certain problems that have been associated with photocatalytic treatment of real wastewaters at large-scale. Hence, scaling up of the process has to be done gradually. For this reason, other types of photoreactors have been investigated in this WP, so as to evaluate the scale up factor of these different geometries respect to the plane one. The proposed configuration is the airlift one.

The draft-tube internal-loop type has a large section on the top to enhance to the maximum the separation of the air from the liquid, to increase the recirculation loop. Generally the velocity of the liquid phase in higher in the riser zone than in the down comer zone, so the UV lamps, considering also the transparency of the glass, can be placed around the reactor enlightening the downcomer zone, thus the contact time between light and substrate is longer.

The lamps should be contained in semi-cylindrical reflecting shelves to minimize the dispersion loss of light. LABOR and UNIRO performed a lab investigation of the best reactor configuration, from the point of view of both hydrodynamics and kinetics point of view, in order to evaluate the feasibility of adopting an air lift reactor for the experimentation at pilot scale.

With the purpose of testing other configurations, LABOR and UNIRO realized two different airlift lab scale prototypes, in which photocatalysis could be performed. The two types of reactors were tested in laboratory at LABOR and UNIRO premises. The results of such tests will be reported later on in this report.

RESULTS OF WP4

In task 4.1 the experimental results about adsorption tests performed by resins on a nanofiltration concentrate of a pre-treated 3-phase OOMW were obtained. Aim is the recovery of marketable polyphenols, mostly importantly hydroxytyrosol.

The raw OMWW used during the experimental work had a concentration of 2086 mg/l of polyphenols. The concentrate of nanofiltration has a value is reduced, down to 1691 mg/l, after the pretreatment steps (that is flocculation, ultrafiltration, nanofiltration), and has no suspended solids. This concentrate was taken as feed streams for the polyphenols recovery process.

The recovery of polyphenols from the feed stream will be performed by adsorption on resins and a subsequent desorption of the captured molecules in an ethanol-water solution. Many resins are available on the market, but only a few are suitable for polyphenol recovery. Three resins, all of them of 'Amberlite' type, were chosen and will be further analyzed by experimental work.

This pretreatment step was performed by following strictly this protocol:
1. Activation of the resin if needed (by following the procedure given by the supplier)
2. In order to eliminate entrapped air in the resin pores, 10g of resin dry mass were washed with 400 ml distilled water for 30 min under moderate mixing conditions (500 rpm), and afterwards recovered back by gridding (mesh 75 microns).
3. In a 100 ml becker glass the resin was put in contact with 50 ml of feed stream (NF concentrate) under gentle stirring conditions (300 rpm).
4. After one hour, the resin is recovered back again by gridding.
5. A first washing of the resin is performed by putting it in contact with a ethanol-water solution (at 96%wt of ethanol), for 30 min under moderate stirring conditions (400 rpm).
6. After this, the resin is recovered back by gridding.
7. The resin again is processed by a second washing step, using the same conditions as point 5.
8. After this, the resin is recovered back by gridding.
9. The samples were stored in a fridge in dark conditions at 4°C.

After the pretreatment of the resins, the batch experiments were performed. The choice of the best resin was evaluated both on the basis of results obtained by Folin-Ciocalteu and HPLC measurements after batch adsorption and desorption experiments.

The results obtained in this investigation can be therefore summarized in the following points:
- It is of primary importance that the OMWW is treated just after production, in order to avoid that polyphenols may degrade and form phenol over time. The presence of phenol is undesired since it is highly

toxic (will poison the desorbed polyphenol solution) and binds strongly to the resin (lowering the adsorption sites of the resin, and as a consequence overall performance).

- The profiles of polyphenol concentration cut seems to indicate that a residence time of 110 s is not sufficient to guarantee the complete adsorption of these substances even at the initial stage of operation. Although these results may be influenced negatively by the presence of phenols, after run start the concentration shows values higher than zero, thus indicating immediate breakthrough of at least one polyphenol in the feed stream.

In order to design the adsorption column for the polyphenol recovery from the NF concentrate within the PHOTOMEM process, in a first stage experiments were performed at lab scale. Laboratory scale packed column runs were carried out to establish viable process conditions to carry out polyphenols removal from the feedstock and enable the design of a pilot plant recovery unit. The test rig included a feed tank, a constant-flow rate peristaltic pump (the tubing size was modified to adjust the feed flow rate to the desired value), and a jacketed, glass column which was packed with the target resin. Two different geometries were adopted for the column in order to investigate the effect of the linear liquid feed velocity upon removal efficiency.

The column was operated with ascending flow to minimise air entrapment which would lead to an erroneous estimate of the local linear liquid flow rate. Upon exit from the packed bed the liquid left the column and was collected in a single collection vessel for sampling. The principal dimensions of the column, that is the length L, the inner diameter Di and the particle size of the resin dp. The data was chosen on the basis of previous lab work performed on smaller columns. The adsorption resin was chosen on the basis of the tests carried out on the different resin types (macroreticular aromatic polymer, cross-linked phenolformaldehyde polycondensate, macroreticular aliphatic crosslinked polymer, polystyrene crosslinked with divinylbenzene, and polystyrene) supplied by two producers: Rohm & Haas and Purolite.

The resins were characterised for their capability of adsorbing and desorbing the compounds of interests, i.e. polyphenols. Equilibrium and kinetic runs were carried out to characterize the adsorption phase from OOMW and the desorption phase in ethanol/water mixtures.

The results of the equilibrium experiments were plotted as adsorption/desorption isotherms and gave the base for the selection of the resin to use for the column adsorption runs. Here, we only recall the adsorption/desorption isotherms for resin FPX66 by Rohm & Haas, which has been selected for use in column runs described in the following, and some adsorption isotherms for Purolite resins. The reason we do not give full account of Purolite resin, nor we adopt them for column runs despite the apparent favourable adsorption results is that those results were obtained on a synthetic system for the unavailability, at the time of the experimentation, of OOMW nano-filtration concentrates.

Kinetic runs were carried out to highlight the time profile of adsorption and desorption, and The main results of these runs are:

- The kinetic profile of tyrosol adsorption;
- Adsorption equilibrium data specific to tyrosol;
- Desorption equilibrium data for tyrosol in aqueous solutions at varying concentrations. 30 minutes of contact with EtOH/Water at 96% or 50% (v/v)

suffice to completely desorb tyrosol; leaner solutions slow tyrosol recovery down to 73% in the same time frame;
- operation under cooling (10 °C vs 25 °C) increase adsorption by ~10%;

Based on the above results, it results that adsorption should be carried out at 25 °Cm while column regeneration should be carried out with 50% (v/v) EtOH/Water solutions for cost reasons.

Overall polyphenols and hydroxytyrosol recovery fractions were calculated for all the tested resins using 96% (v/v) EtOH/Water solutions. The result of these runs is given as total polyphenol concentration (measured by the Folin-Ciocalteau method) in the outlet stream as a function of time. In principle, one would expect the breakthrough to go from essentially zero to the inlet concentration of the adsorbed species. However, it was evident that, in our case, this did not happen; rather, we obtained a prolonged plateau characterised by a concentration significantly lower than the inlet concentration.

We investigated the reason of the discrepancy and found that phenol, which is present in the feed, was absent in the outlet stream. This means that, while the column is essentially saturated with polyphenols, still some species (among which phenol) continue to be adsorbed onto the resin. While it is clear that a breakthrough for polyphenol adsorption is reached at about 33 min, we did not observe the phenol adsorption breakthrough during our run; therefore, we can say that it won't be earlier than 292 min.

Column 2, that is larger (2 x) and taller (2 x) has the same aspect ratio as Column 1 and 8 times the packed volume of Column 1. At the same flow rate as Column 1, however, it has a lower (1/4) linear liquid velocity.

Given the ratio of bed volumes, it has 8 times the adsorption capacity of Column 1 and, at the same inlet flow rate, the expected saturation time is 8 times that of column 1.

The experimental test shows that:
- the breakthrough time in Column 2 (28.5 h) is much retarded compared to the calculated time based on the results obtained in Column 1 (which is 4.4 h);
- the outlet concentration after the breakthrough is, again, lower than the inlet concentration (1200 vs 1600 ppm (poly)phenols, as determined by the Folin-Ciocalteau method).

The significant delay in the appearance of the breakthrough may be meaningful of a diffusional controlling resistance; this means that only the external layer of a resin particle can actually be saturated with polyphenols, while the whole resin pore allowance is available for phenol absorption.

Pilot plant and operation of the system

The pilot plant for the recovery of Polyphenols was then designed. A spreadsheet calculation model was set up to ease the analysis of lab-scale data and for the design of a pilot-scale column. According to the module calculations a minimal, continuous-flow design of the plant was designed. The packing height is the minimum which is necessary to ensure a reasonably regular geometry of the packing (aspect ratio 1:0.7) and the number of columns in parallel (4) ensures that the linear flow velocity is sufficiently low as to capture polyphenols and fully exploit bed capacity. The safe design adopted allows for a 2x safety margin in packing height and includes multiple nozzles at various vertical positions in order to accomodate for flow conditions in the bed which might be differ from those experienced by the lab-scale columns. A 2-cm layer of glass beads below the resin will ensure a regular distribution of the liquid feed. A fine metal mesh should be included to separate the layer of glass beads from the resin packed bed. A distribution cone may be included if necessary, and with limited variation of the column base geometry, at the base of the column.

Only one column will be used for polyphenols recovery, which means that the liquid outflowing from the dephenolisation column cannot be sent directly into the polyphenol recovery column. Rather, it should be collected into an intermediate buffer tank wherefrom a pump should feed it to the polyphenol recovery column at the appropriate flow rate that is one fourth of that to the dephenolisation column. The overall polyphenols recovery system cycles over adsorption and desorption phases. During adsorption, the columns operate in series. The outlet stream from the first column (DP-C) is sent straight to the inlet nozzle to the second (depolyphenolisation, DPP-C) column.

During the regeneration phase, the columns operate in parallel with an ethanolic was solution. The outlet stream from DP-C is rich in phenol and also contains some polyphenols. The outlet stream from DPP-C is rich in polyphenols and does not contain polyphenols; therefore, it is ready for concentrating polyphenols for commercial formulation.

Conclusions

Following the results of the runs described in the project deliverables on the process for recovering Polyphenols, the following design choices will be adopted for the PHOTOMEM plant:

- Polyphenol recovery will be carried out in batch mode. If polyphenol recovery must be made semi-continuous, multiple units of the type described will be required.
- Two packed adsorption column will be used, adopting the same resin (FPX66), the former for dephenolising the nanofiltration concentrate (Dephenolisation Column, DP-C), the latter for recovering the polyphenols contained therein (Depolyphenolisation Column, DPP-C).
- DP-C will be sized and operated in order to minimise polyphenols adsorption while still capturing all phenol.
- DPP-C will be sized and operated in order to maximise polyphenols adsorption and ensure a reasonably long operating time before regeneration. During the adsorption procedure, DPP-C will be arranged so as to be downstream of DP-C.

Column arrangement will be different during the adsorption and desorption phase:

- during the adsorption procedure, DP-C will be arranged so as to be upstream of DPP-C; this way, DPP-C will only target polyphenols recovery without bothering of unwanted compounds. The liquid out flowing from column DPP-C will be sent to wastewater treatment.
- during the desorption procedure, DP-C and DPP-C will be operated in parallel, and each will be fed an ethanol/water mixture.

The liquid out flowing from DP-C is rich in phenol and will be sent to treatment; the liquid out flowing from DPP-C is rich in polyphenols and will be sent to a polyphenol concentration unit (evaporation, or other).

Tests on the adsorption columns for the PHOTOMEM pilot plant

First of all, the general characteristics of the polyphenol recovery unit were determined and are listed below.

- Operating mode: Polyphenol recovery was implemented according to a two-column scheme including a dephenolisation column (which rapidly saturates in polyphenols and continues to adsorb phenol long after polyphenol saturation) and a polyphenol recovery column (which adsorbs polyphenols from the dephenolised product.
- Working volume: the volume of the adsorption columns will will be 0.5 L for both columns. Packing height will be 10 cm for the dephenolisation column and 20 cm for the polyhenol recovery column.
- Materials: the adsorption columns will be in contact with an aqueous solution during adsorption and with an ethanolic solution during the desorption phase; consequently the column material will require compatibility with organic solvents. For the pilot plant, both columns will be manufactured in glass.

The resins will be:
- For the dephenolisation column, the FPX66 resin by Rohm and Haas;
- For the polyphenols recovery column, the MN202 resin by Purolite

During the actual implementation of the pilot plant, a downflow approach was adopted to control the risk of upsetting the packed bed which is inherent in the upflow approach. The conceptual scheme of the downflow approach is reported in D18. Both the dephenolisation and the polyphenol recovery stages are implemented according to the same scheme. The feedstock continuously leaks into the adsorption column top, wherefrom it is either withdrawn by the aspiration of pump P-1 or sucked by pump P-2 as soon as it reaches the assigned level of the feedstock in the upper feed volume and sent by a pump back to the NFC-T tank as soon as it reaches the predefined level in said tank.

Following the results of lab-scale runs, the identified flow parameters were tested at the larger scale to test whether a column packed with the FPX66 resin was able to dephenolise the nanofiltration concentrate (NFC) feedstock. The dephenolised NFC (DPNC) was then used to test the MN202-based polyphenol recovery.

Three operational configurations of the pilot plant were used.

Correspondingly, three NFC dephenolisation runs were carried out.

The results of the runs provide us with time profiles of the adsorption and desorption phases which serve as validation/refinement of the lab-scale estimates.

The results were given in terms of 1. phenol and 2. sum of tyrosol and hydroxytyrosol (i.e., the valuable polyphenols) because a much higher accuracy is obtained on their sum because of their very close elution times. For the details of the tests carried out on the dephenolisation process, please refer to D19 – Field tests results.

Polyphenols Recovery

After purification from unwanted compounds such as phenol, polyphenols were concentrated and further purified by a polyphenols recovery column according to the selected operating parameters.

The outlet stream from the dephenolisation column was fed into the polyphenols recovery column in order to mimic the operating scheme. During the adsorption phase essentially all phenolics contained were retained (HPLC reported zero on all recorded species) and the output stream was clear.

It should be observed that, due to the limited amount of available feedstock, the testing was not extended beyond the bare necessity of showing the capability of DPC to dephenolise the NFC. However, the operating window between the time when DPC becomes saturated with polyphenols and the time when it is also saturated by phenol is quite large, as the lab-scale runs show. Correspondingly, this would permit a significant increase in polyphenols recovery and plant capacity.

RESULTS OF WP5

First of all, the general characteristics of the pilot photocatalytic unit were determined and are listed below.

Operating mode: the pilot photocatalytic reactor will operate at batch mode, while the whole process time for each photocatalytic run will be 3h (i.e. 1 h for catalyst treatment and 2 h for the photocatalytic oxidation of OMW).

Working volume: the volume of the photocatalytic reactor tank will be 350L (about 350000cc in volume).

Catalyst treatment tank: the volume of the catalyst treatment tank will be 150 L.

Materials: all the tanks will be constructed by stainless steel (SS316) as OMW is slightly acidic it requires special non-corrosive materials.

As it was observed at D9 – Results of photocatalytic tests of this project the addition of H_2O_2 up to 100 mg/L has a beneficial effect on COD removal with the e.g. 3-h conversion being 14%, 18%, 35% and 47% at 0, 25, 50 and 100 mg/L H_2O_2, respectively. Hence, some series of experiments were performed to investigate whether the addition of hydrogen peroxide can increase COD removal for OMW at various initial COD values. It is worth noticing that the addition of 0.05 g/L H_2O_2 enhances process efficiency from 20% to 38% and from 8% to 25% when the initial COD is 0.6 and 10 g/L, respectively. This is of major importance as the enhancement in COD removal remains practical the same at about 15% without being affected by the OMW's initial COD value. Therefore, the efficiency of the photocatalytic reactor could be enhanced by about 15% by the addition of 0.05g/L H_2O_2, a relatively low amount of reactant that will not significantly increase the operating cost of the overall process.

Moreover, the addition method(s) of the nanoparticles into the wastewater stream will be studied. This may lead to the necessity to perform some chemical step on the nanopowders (such as acid redispersion or stabilization) prior to the photocatalysis.

At lab-scale experiments, it was observed that magnetic TiO_2 nanoparticles require an additional step, other than the mechanical stirring, in order to achieve high dispersion of the magnetic nanoparticles in the reactant solution. Therefore, the effect of the pre-treatment catalyst step on process efficiency (i.e. COD reduction of OMW) was investigated. For this reason two different catalyst pretreatment methods were used to ensure high dispersion of the catalyst particles into OMW effluent: (1) Treatment with ultrasounds, and (2) Acidification treatment.

It must be noted that when ultrasounds is used as a catalyst pre-treatment technique then the process performance is slightly higher in terms of COD removal. However, there are some practical obstacles if applying the ultrasounds at large-scale and these are the high energy consumption of this technique when large liquid quantities are treated.

On the other hand, the acidification pre-treatment method yields some certain advantages compared to the ultrasounds, and these are listed below:
- Simple to apply at large scale
- Simple for the users to operate at large scale
- Cheap, as there is no initial fixed cost

Furthermore, the results indicate that photocatalytic efficiency performance, in terms of COD removal, remains about the same for both pre-treatment techniques. Hence, in the present project it was decided that the acidification method is more cost-effective than the ultrasounds techniques and its implementation at pilot-scale will be easier and cheaper, thus contributing to lowering the cost of the whole PHOTOMEM treatment strategy.

A main concern in the case of slurry reactors, is the fact that the performance of the reactor might be severely affected by the low irradiation efficiency attributed to the turbidity of the slurry, thus by lowering the lamp position light penetration into the whole volume of the OMWW solution will be enhanced. Therefore, experiments were carried out in order to investigate whether process efficiency is affected from the position of the lamp, when this is placed on the top of the photocatalytic reactor (i.e. the distance between the lamp and the surface of the effluent). All photocatalytic experiments were performed after the pre-acidification of the TiO2 catalysts with 0.1 M HNO3, for 1 h. It is evident that the lower the distance between the liquid surface and the lamp the higher the photocatalytic efficiency will be. Hence, in this project the lamp will be placed in the photocatalytic reactor in such a way that the whole irradiation emitted by the lamp will be exploited for photocatalytic oxidation reactions. It is widely known that when the lamp is immersed into the reactant liquid mixture then all the illumination is utilized for the oxidation reaction. Therefore, in this project the UV lamp will be immersed in the OMW effluent to implement the pilot photocatalytic reactor.

The detailed activities that were performed are the performance of lab-scale experiments to further optimize and provide feasible solutions regarding the (a) the distance between the lamp and the surface of the effluent, (b) the addition method of the magnetic nanoparticles and their pre-treatment, (c) the addition of hydrogen peroxide in the effluent to enhance the overall photocatalytic efficiency.

Photocatalytic Reactor Shape and Geometry

There are various designs of photocatalytic reactors that can be selected for the photocatalytic treatment of OMW. The lab-scale experiments were conducted in an open rectangular photocatalytic reactor (20cm × 11cm ×5 cm) operating in batch mode. The UVA lamp was placed on the top of the reactor and the distance between the lamp and the liquid surface was 3.7 cm, while the depth of the reaction solution was 1.3 cm.

The rectangular large-scale reactor with a volume of 350 L and a constant liquid depth of 10 cm was initially designed as reported in D10 and D14. To implement the pilot rectangular photocatalytic reactor an area of 35 m2 (10m×3.5m) will be necessary to construct the photocatalytic reactor. From an economical and technical point of view, this is rather a non-realistic option. This area is prohibitively large for an average olive mill to treat its wastewaters. Moreover, an open tank with a liquid depth of only 10 cm will probably lead to the natural evaporation of this liquid before its photocatalytic treatment. Hence, it was decided that this type of reactor is not suitable for the PHOTOMEM project implementation and new reactor types, such as airlift, were investigated.

To adapt a reactor having the suitable capacity to PHOTOMEM project, two main aspects must be taken into account:
- The scale-up factor: the aim of the pilot plant scale is processing about 1m3/24h of OMW split in three batch processes of 350L/3h each. Such mass flow rate requires huge dimensions of the parts and influences the choice of the construction materials, preferring stainless steel over glass, guarantying minor costs, an easy manufacturing and heavy toughness;
- The UV diffusion: the choice of steel, instead of glass, obviously implies that the most convenient placement of the UV lamps must be now considered. The main advantage related to glass, that of transparency, is in fact no more present when taking into account this configuration, and the same OMW, even if previously subject to flocculation, presents a percentage of particles matter which obstructs the diffusion of light.

So, taking in account both issues, two solutions were proposed to the partners.

Here we report a short description about a sizing hypothesis of the reactors:
- Working volume: 350L/3h;
- Hypothetical distance of penetration of the UV light: about 10cm. The cylindrical geometry sets the internal diameter of the inner cylinder at 25cm, considering two times the radius plus 5cm the diameter of the lamp (if the lamp is submerged in the reactor);
- Keeping the downcomer width of 10cm we have a total diameter of 45cm which can be rounded up to 50cm, corresponding to a base area of 1960cm2;
- The ratio working volume/base area gives the height of the reactor, H=180cm. The height can be reduced in the glass reactor configuration due to the presence of the larger zone on the top.

Following these considerations, two laboratory scale airlift reactors were developed:
A. Internal Draft Tube Airlift Reactor: working volume 5L;
B. External Tube Airlift Reactor: working volume 0,7L;

To evaluate the behaviour of both reactors some hydraulic tests were performed. The tests were aimed to optimize the air flow rate thus to have an optimal suspension and recirculation of the ferromagnetic nanoparticles of titanium dioxide, the catalyst used for the photocatalysis.

Hydraulic tests were performed on both reactors with the final aim of selecting the best one for the pilot plant. In particular the tests suggested to work at the maximum of the possible flow rate, as lower rates showed the formation of a sediment of nanoparticles.

The problem was solved for the external tube reactor but it didn't disappear for the internal draft tube even at 5LPM, because of the difference in the dimension of the diameters of the tubes, 15cm against 4cm, and of the total working volume, 5L against 0,5L. Therefore, an additional scale up would have increased the problem. In the end, the external airlift reactor showed a better recirculation of the nanoparticles so it was decided to continue working in this direction.

Photocatalytic tests on the external airlift reactor
The Photocatalysis step was conducted by UNIRO according to the following experimental conditions:
- External tube airlift reactor, working volume 0,5L,
- Irradiation: UV light 365nm 40W lamps;
- Time of irradiation: 2h dark + 2h light;
- Air flow rate: 4LPM;
- Ferromagnetic nanoparticles calcinated at 450°C for 4h;
- Liquid: pre-treated OMWWs (flocculated OMWWs);

The reactor was modified replacing the plexiglas portion of the riser with an equivalent one of glass of the same diameter in order to let the UV light reach the inside the OMWWs inside the reactor itself. The plexiglas filters the UV light so it was impossible to use the reactor as it was.
In order to improve the efficiency in light transmission (UV) a mirroring system, consisting in applying a silver foil around the reactor, was used.

Final design of the photoreactor
The tests performed at laboratory scale level suggested the best configuration regarding the shape of the photoreactor which will be used in the PHOTOMEM pilot plant. In the end the external tube airlift configuration proven to be more effective than the internal draft tube so the sizing of the reactor was adjusted to the working volume of 350L, able to cover a total of 1m3 of OMWWs treated daily. A laboratory scale reactor is easy to handle, works with low volume of liquids and doesn't need particular attention regarding its toughness. On the other hand, a pre industrial scale reactor like the one intended in the project must deal with these issues.

Even if it is mandatory to take into account the importance of the light diffusion, it is impossible to build a 350L reactor made of glass and/or quartz both for economical and for resistance reasons.

Therefore the reactor will be made of stainless steel. Even if the the scale up of the reactor can appear easy, some issues must be well evaluated:
- The lamps disposition: 30 UVA lamps (30W each) will be placed around the Plexiglas transparent cylinder in the upper region of the riser, while 3 UVA lamps (60W each) will be submerged into the riser. This is directed to maximise the UV total output voltage to ensure a good radiation during the photocatalysis.
- The plexiglas cylinder: usually the plexiglas adsorbs the UV light. On this purpose a special Plexiglas is used: PLEXIGLAS 7H whose UV absorbance in function of the wavelength can be observed. This kind of

material still is blocking UV light but only the low region of the UV spectrum, under 300nm, having a good transparency in the high region of the spectrum up to 95%.

Conclusions

The photoreactor was designed to keep it as easy as possible, without losing efficiency, and as flexible as possible in order to permit a wide-spread study of the operating conditions. The flexible design of the apparatus will allow multiple investigation and evaluation of the efficiency of the process, concluding an optimization of the best suitable operating conditions to maximize the recovery yield of the suspended ferromagnetic nano-particles by assisted sedimentation of magnetic fields and of the organic matter reduction.

Specifically, the pilot reactor will consist of the batch-type reactor, configuration as external tube airlift type, tank with both surrounding than immersed UVA lamps. Air will be continuously sparged into the reactor riser to allow its efficient mixing.

The magnetic photocatalyst will be recovered by means of a magnetic trap and afterwards re-dispersed and reused into the reactor. The magnetic trap will provide also the regeneration to achieve high dispersion and purification of the nanoparticles. Moreover, it was observed that the efficiency of the photocatalytic reactor could be enhanced by about 15% by the addition of 0.05g/L H_2O_2, a relatively low amount of reactant that will not significantly increase the operating cost of the overall process. It was found that the acidification method is more cost-effective than the ultrasound technique and its implementation at pilot-scale will be easier and cheaper, thus contributing to lowering the cost of the whole PHOTOMEM treatment strategy.

Task 5.3 of this WP produced as main output the P&I scheme of the overall PHOTOMEM process. Deliverable D15 – P&I, illustrates every single step of the process, which is composed of 6 sections:

i) Section A – Flocculation;
ii) Section B – Photocatalysis;
iii) Section C – Ultrafiltration (UF);
iv) Section D – Nanofiltration (NF);
v) Section E – Reverse Osmosis (RO);
vi) Section F – Adsorption;

For each section the relative item list required to set up the section and the consequent logic control was reported. The logic control manages also the cross-linking between sections and the cleaning procedure to regenerate the membranes global process (UF+NF+RO) and the adsorption column for the recovery of polyphenols. Finally a series of 'active control alarms' supervises the perfect functioning of the pilot plant sensors and equipments interacting with the users through a software giving warnings every time a problem or any particular situation occurs. In the following we are summarizing the process steps and their functioning. The logic control is included in D15 only.

- Section A - The first section covers a pretreatment step, the flocculation, where the OMWW is treated by means of a new optimized flocculation process method, where a preliminary separation of the suspended solids is made by first an acidification followed by a temperature ambient recirculation of the OMWW stream. The process permits to reduce the COD content up to 50% and the recovery of 90% of the initial wastewater volume after decantation of the suspended solid by means of gravity force once the recirculation is stopped. The great advantage of this type of process is the low cost if compared to the traditional methods performed usually adding chemicals like aluminum sulphate which is a very expensive and polluting reagent.

- Section B - The second section of PHOTOMEM project is photocatalysis, which proposes a novel technical solution based on degradation of organic pollutants through photocatalytic UVA irradiation using ferromagnetic particles of titanium dioxide to reduce the COD content of OMWWs. Therefore the industrial production process for ferromagnetic photocatalytic nanoparticles was optimized covering the particles with titanium dioxide through sol-gel coating.

The advantages of this catalytic step are:
- the photocatalytic oxidation with TiO2 is effective under UVA light in destroying a wide range of contaminants in aqueous phases, the COD can be removed by treating OMWWs with 1-3 g/l of TiO2 for few hours;
- TiO2 shows high resistance to corrosion, biological immunity and relatively low cost. The particles can be recovered up to 98% through the use of a magnetic filtering system;
- Oxidation of organic compounds with photocatalytic nanoparticles is much more effective than conventional ways: COD reduction is up to 2 times faster.

- Section C-D-E - The third step of the PHOTOMEM process is a membranes process which involves three similar sections: section C ultrafiltration, section D nanofiltration and section E reverse osmosis. PHOTOMEM optimized this membrane multi-stage process which is capable to separate pollutants from up 85% of the wastewater and to reduce its COD content. The other economic benefit will be the production of less than 10% of organic dry mass coming from the concentrated wastewaters suitable for compost production as terrain fertilizer.

- Cleaning of the membranes - the cleaning membrane procedure is started when a pressure active control related to the membranes process is activated. To clean the surface of the membranes the clarified waters deriving by the end of the reverse osmosis and collected in tank T09 are used. After the cleaning is done the section which caused the activation of the pressure active control alarm is resumed and the PHOTOMEM process can continue.

- Section F - The last step of the PHOTOMEM process is a packed column adsorption process having the aim to recover the polyphenols content inside the OMWWs and selling them to the nutraceutical/cosmetics markets for the reduction of the net cost of the treatment. In fact, polyphenols oxidation during the whole PHOTOMEM process is less severe, around 40%, with respect to complete oxidation by using other biological pre-treatments.

- The control system - The control system is capable to supervise each single operation of the pilot plant.

The system includes:
- Sensors, in order to read the most important process parameters real time and permit the control system to take control decisions accordingly,
- Regulation devices, such as electromagnetic on-off and regulation valves to allow flow control, electric heaters to allow temperature

control, peristaltic and centrifuge pumps for liquid transfer and pressurization,

The control unit, core of the control system which is connected to all sensor inputs, contains the control logic and is provided with a user interface to permit interaction with the maintenance supervisor, and is divided into timers, alarms and individual feedback controllers.

RESULTS OF WP6

The main output of the work carried out in this WP is the PHOTOMEM pilot plant located at LABOR facilities in V. Giacomo Peroni 386, 00131 Rome, Italy.

Following the P&I scheme of the process, the different steps of the treatment were implemented in the plant as follows:

1. Flocculation

Olive Mill Waste Waters (OMWWs) collected from oil mills are stored into T02. Then they are pumped into flocculation reactor R01, where the pH is adjusted by means of a peristaltic pump connected to a nitric acid solution, while they are circulating. Once the correct value of the pH is achieved the circulation is kept for 20 minutes, flocculation phase, then the circulation stops and a 23-hour sedimentation phase begins. The clarified waters are pumped into the photoreactor where they will be processed while the sedimentation residues are discharged manually. The concrete realization of the section A is very easy operation because it mainly consists of a series of tanks and pumps connected by means of piping. The flocculation reactor R01 was connected to the centrifuge pump P02 and then to three-way valve V02 in left position to let the recirculation in tank R01 occur. In addition, the volumetric pump P01 was connected to three-way valve V02 for the nitric acid solution addition.

On the side of the tanks low level and high level magnetic sensors are mounted, whose body is made of nylon to be resistant against chemical agents. The control of the pH value during the flocculation phase is performed by automatically reading the pH and addition of nitric acid solution through the volumetric pump P01 connected to three-way valve V02.

2. Photocatalysis

The clarified OMWWs from flocculation are stored into a intermediate storage tank T03 to allow flocculation start another run, then the first batch of waters (working volume 350L) are loaded into the photoreactor. The catalyst, the magnetic core titanium dioxide nanoparticles, is added, the air flow and the UVA lamps are switched ON and the photocatalysis starts for 4 hours.

Once ended, the photoreactor is depleted by means of a centrifuge pump which pumps the OMWWs through the magnetic trap where the nanoparticles are retained switching ON electromagnets.

Because of the delay experienced in the lab testing, selection of the optimal configuration and design of the photoreactor (as indicated in D14), the pilot plant was equipped with back up internal draft tube photoreactor.

The pilot photoreactor is made of:

- A tank of 0.5 m3 capacity, filled up to 350 liters, with a wooden board on the top to support the lamps, a marine propeller with 4 PVC draft tubes, each provided with a sparger, and a PVC piping air system;
- On the bottom side of the board 24 UVA lamps (each rate 30W) are mounted to irradiate the liquid surface with the UV needed for the photocatalysis;
- Four draft tubes placed inside the reactor, to reproduce the behaviour of four internal draft tube airlift reactors;
- The air inlet piping system providing air to the draft tube air lifts to generate the conditions of recirculation of the water and provide oxygen for the photocatalysis to happen: four branches each one ending in the bottom centre of each draft tube;
- A propeller placed in the centre of the reactor to help maintain the catalyst in suspension

3. Magnetic trap

The recovery of the nanoparticles is performed by means of a Plexiglas magnetic trap, in the shape of a vertical cylinder inside which a septum is placed to force the flowing of the waters, rich in nanoparticles content, in a U-shape route through the bottom of the cylinder. The magnetic trap is placed on the top of a chessboard, having square holes where up to 16 super magnets can be inserted.

The magnetic trap is therefore connected to the back-up photoreactor and the photocatalyzed OMWWs are flowed through it to the ultra filtration tank. At the end of the process the magnetic base in removed and the nanoparticles remaining at the bottom of the trap are collected to be regenerated and reused for the next photocatalysis.

4. Membrane process

The three membrane processes, UF-NF-RO, are working in series. They work in the same way, i.e.: photocatalysed OMWWs are circulated from UF tank T04 through the corresponding membrane module M01 where the concentrated is separated from the clarified waters to return into T04. Clarified waters fill the NF tank T05 and the next membrane step starts.

The only difference with filtration is that the concentrated waters deriving from UF are discharged while the ones from NF and/or RO can be redirected to section F adsorption for the recovery of polyphenols. Each membrane module contains 4 radial membranes and it is connected to its respective tank:
- Ultrafiltration (UF): 4 UF membranes inserted into UF/M01 module connected to UF/T04 tank;
- Nanofiltration (NF): 4 NF membranes inserted into NF/M02 module connected to UF/T05 tank;
- Reverse Osmosis (RO): 4 RO membranes inserted into UF/M03 module connected to UF/T06 tank.

5. Adsorption

The column feeding tank T07 collects the residues of the NF process. The residues are therefore irculated through the packed column R03 where polyphenols are trapped inside the resin filling the column. The adsorption phase lasts 3 hours and the waste is discharged switching the three-way valve V14 into right, R, position. After that a desorption process follows, lasting 1 hour, where an ethanol/water solution is flowed through the column to release the polyphenols which are collected switching V14 from R to L position.

The adsorption column should be the completing part of the PHOTOMEM pilot plant. The capacity of waters to be treated, deriving from the nanofiltration process is not so big to require a massive equipment.The maximum input capacity to be treated in the column adsorption deriving from a single batch photocatalysis step is 60 litres. This amount of waters can be treated by means of a lab scale column adsorption therefore the tests for the recovery of the polyphenols were performed in the laboratory facilities of the performer UNIRO.

6. The control system

The control system of the PHOTOMEM pilot plant, as illustrated in deliverable D15, is able to supervise each single section of the process. It controls:
- Sensors: in order to read the most important process parameters in real time and step-in taking decisions according to the read values;
- Actuators: such as on-off and regulation valves to allow flow control, peristaltic, volumetric and centrifuge pumps for liquid transfer and pressurization;

The control unit, core of the control system which is connected to all sensor inputs, contains the control logic and is provided with a user interface, a touch screen panel control pc to interact with the operator. A dedicated software developed in Labview is installed and all the operations of each section can be followed and controlled in real time.

Conclusive remarks

The PHOTOMEM pilot plant was enforced to function manually to let the partner Ecosystem perform the tests of processing the olive mill waste waters according the whole PHOTOMEM process.

The aim of the this tests is to validate the PHOTOMEM technology showing the efficiency of the photocatalytic treatment to reduce the COD content of the OMWWs and to show the efficiency in the recovery of the polyphenols from a permeate of the membrane treatment. The next step is related to the RTDs partners commitment towards the small and medium-sized entreprises (SME)s to fulfil the missing activities indicated in the Grant Agreement by implementing the missing parts of the plant and the complete automation of the system.

Therefore the future work will be focused essentially into:
- The realization and the set up the definitive photoreactor in the configuration of the external tube airlift reactor;
- The development of the control system and the related software controlling in automatic all the processes of each section;
- The debugging of the software itself;
- The final tests of complete functioning of the system.

The PHOTOMEM pilot plant was implemented to allow the testing of the functionalities and the evaluation of the results by processing the olive mill waste waters according the whole PHOTOMEM process. The aim of the these tests is to validate the PHOTOMEM technology showing the efficiency of the PHOTOMEM process (flocculation + photocatalysis + membrane treatment) to reduce the COD content of the OMWWs and to show the efficiency in the recovery of the polyphenols after the membrane treatment. To allow the realisation of the tests in the framework of the project timeline, due to the delays in the lab scale testing, choice, design and implementation of the photoreactor, it was decided to realise a back-up solution for what concerns the photocatalytic reactor: a manually operated air lift photoreactor was realised by using a commercial tank, instead of the specifically designed photoreactor reported in D14.

This was decided to allow the realisation of the final tests in due time and to validate the functionality of the air lift photoreactor concept and of the PHOTOMEM waste water treatment technology, even though with a different layout of the photocatalytic reactor. The installation and testing of the specifically designed PHOTOMEM photoreactor will be completed after the end of the project and results will be provided to the small and medium-sized entreprises (SME).

RESULTS OF WP7

Two operations were performed at pilot plant lab scale: the polyphenols recovery and the post-treatment, consisting in a photocatalytic reactor, assisted by immobilized nanostructured TiO2 catalyst. This latter operation was adopted to reduce the COD content under 0,5 g/l. Chemical oxygen demand (COD) measurements were made by applying the Standard Method 5520 C. pH measurements were performed by using a Mettler Toledo EL120 instrument. Electro conductivity (EC) was measured by using a Delta Ohm HD9021r2 instrument. The concentration of total polyphenols was estimated by means the Folin Ciocalteau method, whereas the content of hydroxytyrosol, phenol and total phenols were performed by HPLC analysis performed by using an instrument Agilent 1200.

Flocculation was performed by using the protocol previously developed and described in detail in 'paragraph 1 Section A Flocculation' of Deliverable D18 - PHOTOMEM Pilot Plant.

During flocculation the following steps were performed:
1. addition of nitric acid solution (36% in weight) to the feedstock in order to reach a pH value equal to 3.2 in strong mixing conditions.
2. slow mixing for a period of 20 minutes, used to favour mixing.
3. Finally, flocculation takes place within the next 23 hours, during which the suspended solids - while flocculating -aggregate and give sedimentation.

The 10% of the feedstock at the bottom of the flocculation reactor is discharged and collected as mud. The remaining 90%, as clarified wastewater is sent to the next process step: Photocatalysis. The water was left to sediment for 24 hours, obtaining a well defined separation between the mud and the clarified phase. The water, as expected, results rich in solid residues. The same process of flocculation was performed on 1m3 of raw OMWWs by means of the reactor R01 of the PHOTOMEM pilot plant.

At the end of the process two samples were taken:
- one of clarified water, from the top of the flocculation reactor;
- one of muds, from the bottom of the flocculation reactor;

Again the two samples were analyzed in lab to investigate the flocculation stage performed on a huge amount of waste waters, to compare the efficiency between a laboratory scale and a pilot plant scale.

Photocatalysis was performed by using the backup photoreactor developed and described in in detail in 'paragraph 2 Section B Photocatalysis' of Deliverable D18, by using the protocol developed and described in the same document.

The tests carried out consist in:

1. addition of 2g/l of ferro-megnetic titania nanophotocatalyst to the feedstock
2. implementation of the photocatalysis for 4 hours, under the UV light (24 lamps having a total consumption of 720W with a wavelenght of 365nm) and the air supply (air flow rate equal to 200 Nm3/h)
3. Recovery of the photocatalyst through the magnetic trap described in 'paragraph 2.2 Magnetic Trap'.
4. The 100% of the feedstock is sent to the next process step, that is ultrafiltration.

Tests for Utrafiltration, Nanofiltration and Reverse Osmosis were performed by using the plant section and the protocol described in detail in 'paragraph 3 Section C-D-E Membrane processes' of Deliverable D18.

The tests on Ultrafiltration consisted in:

- separation by using 4 Desal Osmonics spiral wounded membrane modules (type GM 4040F), featuring a total membrane area of 32 m2 with a pore size about 2nm. The operating pressure was optimized during the testing phase to 4 bar, to maximize productivity without incurring in severe fouling.

Tests on Nanofiltration were performed as follow:

- separation by using 4 Desal Osmonics spiral wounded membrane modules (type DK 4040F), featuring a total membrane area of 32 m2 with a pore size about 0.2nm. The operating pressure was optimized during the testing phase to 8 bar, to maximize productivity without incurring in severe fouling.

Tests on the Reverse Osmosis were performed as follows:

-separation by using 4 Desal Osmonics spiral wounded membrane modules (type SC 4040F), featuring a total membrane area of 32 m2. The operating pressure was optimized during the testing phase to 25 bar. Fouling is not a severe issue here, therefore the minimum operating pressure capable to guarantee maximized selectivity was chosen. The recovery of the polyphenols was performed by using the protocol previously developed and described in detail in 'paragraph 4 Section F Adsoprtion' of Deliverable D18 - PHOTOMEM Pilot Plant.

- Operating mode: Polyphenol recovery was implemented according to a two-column scheme including a dephenolisation column (which rapidly saturates in polyphenols and continues to adsorb phenol long after polyphenol saturation) and a polyphenol recovery column (which adsorbs polyphenols from the dephenolised product.

- Working volume: the volume of the adsorption columns is about 0.5 L for both columns. Packing height is 10 cm for the dephenolisation column and 20 cm for the polyhenol recovery column.

- Materials: the adsorption columns is in contact with an aqueous solution during adsorption and with an ethanol solution during the desorption phase; consequently the column material requires compatibility with organic solvents. For the pilot plant, both columns are manufactured in glass.

The resins used to pack the column are the following:

- For the dephenolisation column, the FPX66 resin by Rohm & Haas;
- For the polyphenols recovery column, the MN202 resin by Purolite.

During the actual implementation of the pilot plant, a downflow approach was adopted to control the risk of upsetting the packed bed which is inherent in the upflow approach.

The feedstock continuously leaks into the adsorption column top, wherefrom it is either withdrawn by the aspiration of pump P-1 or sucked by pump P-2 as soon as it reaches the assigned level of the feedstock in the upper feed volume and sent by a pump back to the NFC-T tank as soon as it reaches the predefined level in said tank.

Following the results of lab-scale runs aimed to identify the flow parameters at larger scale to test whether a column packed with the FPX66 resin was able to dephenolise the nanofiltration concentrate (NFC) feedstock. The dephenolised NFC (DPNC) was then used to test the MN202-based polyphenol recovery. Correspondingly, three NFC dephenolisation runs were carried out.The results of the runs provide us with time profiles of the adsorption and desorption phases which serve as validation/refinement of the lab-scale estimates. The results were given in terms of 1. phenol and 2. sum of tyrosol and hydroxytyrosol (i.e., the valuable polyphenols) because a much higher accuracy is obtained on their sum because of their very close elution times.

Post-treatment

Both the organic matter content and the pH value of the RO permeate exiting the membrane process step could be, in some cases, still not within the limits to permit discharge in the municipal sewer system. In this case an additional post treatment step should be necessary to reduce the residue organic matter content and the pH value adjustment for the water disposal.

This kind of RO permeate, which may exhibit COD values smaller than 2000 mg/l and is quite transparent, may be treated again by photocatalysis, using nano-TiO2 immobilized over glass spheres as catalyst. This time, since the wastewater stream is not opaque, the irradiation with UV is more easy and efficient. Therefore, immobilized nano-TiO2 on glass spheres in a reactor may be used.

In the particular case of the test run here reported, the COD of the RO permeate is equal to 850 mg/l, therefore a post-treatment to lower the COD value down to less than 500 mg/l was required. The adopted immobilized nanostructured catalyst consisted of glass spheres 1-2 mm in size coated by TiO2 sol gel material, previously prepared, calcinated at 450°C for 8 h three times. The obtained catalyst was then put at the bottom of the photo-reactor of rectangular section, irradiated on top by an halogen lamp of 150 W. After a 15 h of the photocatalytic operation, a COD value of 412 mg/l was obtained.

As further need to permit the discharge of the purified OMWW into a civil sewer its pH has to attain a value higher than 5.5. To get this target a pH adjustment was performed by adding 0.065 mg/l of concentrated NaOH solution (1M NaOH).

The obtained results from field test performed at pilot plant scale are hereafter summarized:

- 75.3% of the initial raw OMWW was obtained as purified wastewater solution whose composition was consistent with its discharge into a municipal sewer system. The applied process sequence consisted of: 1) acid flocculation; 2) photocatalysis by nano-TiO2 with a magnetic core; 3) ultrafiltration, nanofiltration, reverse osmosis; 4) post-treatment based on photocatalysis assisted by immobilized nano-TiO2 on glass spheres; 5) neutralization by NaOH.
- The pilot plant capacity was of 1 m3 of OMWW per day, as foreseen in the project proposal.
- The photocatalysis assisted by the developed magnetic core TiO2 catalyst was quite effective, leading to a COD reduction of 35 %.
- The magnetic trap was able to recover 96% of the magnetic photocatalyst.
- The separation by membrane processes exhibit an overall effectiveness as expected, however the separation by NF was better than predicted, whereas the RO underperformed.
- In order to get the COD target of 500 mg/l a post-treatment based on photo-catalysis assisted by immobilized nanostructured TiO2 was applied.

This operation not considered in the proposal, was developed during the project. This operation was tested at lab scale.

- A neutralization was also undertaken as the final process step to increase the wastewater pH over the value of 5.5, required for the discharge into civil sewer.
- The process recovery of polyphenols represented the hardest task to be achieved, because of the presence in the OMWW of phenols which was unpredicted at the time of the proposal submission. The presence of phenol fostered a process development based on a two stages adsorption.
- The feedstock chosen for the polyphenol recovery was the NF concentrate, because it was by product aqueous stream without solid suspension more rich in polyphenols. This stream, in the test run, had around 500 mg/l of hydroxytyrosol + tyrosol.
- Around 8 % of the available hydroxytyrosol and tyrosol in the NF stream were recovered by adsorption/desorption process. No phenol was present in the hydro alcoholic solution outlet stream from the adsorption section.

The PHOTOMEM process is effective to reduce the COD content to values in line with the limits imposed by legislation.

One of the objectives of the project is to make the initial investment of the plant and the cost of treatment acceptable, in line with the present cost of disposal for mill wastewater (which is nowadays around 30-40€/m3).

Furthermore, the recovery of Polyphenols at the end of the treatment is meant to further reduce the final net cost of the overall treatment.

In this section an estimation of the investment and operational costs associated to each step of the PHOTOMEM process is reported for a plant of 40 m3/day, so as to compare them with the initial objective and to be able to evaluate – with the support of the small and medium-sized entreprises (SME) working in the project and operating in the sector – the attractiveness and the commercial potential of this solution for the wastewater sector.

For ease of reading, we will highlight:

i) The costs of the components of the plant that will bring to a final evaluation of the initial investment associated to a 40m3/day plant using the PHOTOMEM process;
ii) The costs of operation of the same plant for an estimation of the cost per m3 of OMWW treated.

The indicators identified at the beginning of the project showed a cost of less than 300.000 EUROS for the 40m3/day plant (investment), and a cost of operation reduced respect to the current 40 EUROS/m3 estimated for the existing technologies and disposal treatments. The estimated investment for the plant for the PHOTOMEM plant with capacity of 40 m3/day is therefore 286,000 EUROS, in line with the target of the project. As already mentioned, the recovery of polyphenols has not been taken into account in this evaluation. The plant is here supposed to be operating 24 hours a day, for about 4,5 months (135 days per year), which means 3.240 hours per year. The depreciation of the plant has been therefore estimated as daily depreciation on such a basis.

Total cost per day
The estimation of the costs of operation of the plant comes as a consequence from the values reported above. The depreciation over the 15 years hypothesized for the plant itself has been calculated accordingly.

The parameters used for this estimation are the following:
1) The days of operation along one year (estimated: 135 days);
2) The hours of operation of the plant in one year (135 days x 24 hours a day = 3.240);
3) The capacity of the plant, 40 m3 treated per day;
4) The cost of chemicals;
5) The cost of electricity;
6) The personnel costs;
7) The daily depreciation cost including the maintenance cost;

The estimated cost of operation is of the order of 60 EUROS/m3, which is slightly higher than current treatments (40-50 EUROS/m3) However, the cost can be optimized with the following measures:
- recovery of polyphenols which are added value products which can have an outstanding market value (refer to the following paragraph)
- reduction of the membrane size and operating pressure, reducing the installation, maintenance and operational costs. This aspect is considered to be feasible due to the presence of the pretreatment realized by flocculation and photocatalysis. A centrifuge could be included in the plant to reduce the charge experienced by the membranes.
- reduction of the cost of the MAG TiO_2 nanocatalyist for the operation, which represents the most relevant share of the cost of operation.

This can be achieved by:
a. optimization of the production costs of the Nanoparticles
improvement of the regeneration of the nanocatalysts. The number of batches after which the nanocatalyst cannot be regenerated, now estimated to be 8, should be verified in detail with further tests. Also a stronger regeneration process could be studied and assessed. In case it would be verified the possibility to regenerate the nanocatalyst for 12 cycles (3 days) the cost of the nanocatalyst would be reduced of 33% and the total cost of the OMWW treatment would be reduced to 46 €/m3.

Conclusions

Following the results of the tests carried out on OMWW collected from an Italian olive mill near Rome, it is evident that:

- 75.3% of the initial raw OMWW was obtained as purified wastewater solution to discharge into a municipal sewer system.
- The photocatalysis assisted by the developed magnetic core TiO2 catalyst was quite effective, leading to a COD reduction of 35 %.
- The magnetic trap was able to recover 96% of the magnetic photocatalyst.
- The separation by membrane processes exhibit an overall effectiveness as expected, however the separation by NF was better than predicted, whereas the RO underperformed.
- In order to get the COD target of 500 mg/l a post-treatment based on photo-catalysis assisted by immobilized nanostructured TiO2 was applied. This operation not considered in the proposal, was developed during the project.
- The process recovery of polyphenols represented the hardest task to be achieved, because of the presence in the OMWW of phenols which was unpredicted at the time of the proposal submission. The presence of phenol fostered a process development based on a two stages adsorption.

An economic evaluation of the investment and operation costs of the PHOTOMEM plant scaled up to a common treatment capacity for a medium olive mill (40m3 of WW treated per day) was performed. As it can be seen from the results of such analysis:
a) The target of the 300.000 EUROS investment for the plant was achieved: from the costs of equipment and accessories for assembling the plant it is evident that a major part of the investment is due to the necessity to have a high number of modules for the membrane stage, which represents a core step in the purification process of the plant. High costs are also associated to the purchase of the tanks and reactors for the treatment, to the electric wiring and cabling, to the start up phase of the plant and to the use of valves and UV lamps. As a final estimation, we can say that the investment for the PHOTOMEM plant is in line with the expected, having a value of about 294.000 EUROS, considering a lifetime of 15 years.

b) The target of reducing the operation costs respect to the current estimation of 40€/m3 has been exceeded: in fact, this initial requirement has not been reduced. This refers to a mean value for the treatment of olive mill wastewaters with other techniques respect to the ones constituting the PHOTOMEM technology. This one makes great use of chemicals and of a catalyst for the photocatalytic step which, even for high production quantities, remains quite an expensive consumable. The cost of the overall treatment is therefore increased by the addition of several techniques like the membranes and the photocatalysis ones, making the final cost of operation per m3 exceed the value of already existing treatment technologies.

RESULTS OF WP8

In this WP, two important documents summarizing the intentions of the partner small and medium-sized entreprises (SME)s in the Consortium to disseminate and exploit PHOTOMEM results were produced: the first is the Interim Plan for Use and Dissemination of Foreground, and the second is the final version of this deliverable, the Final PUDF, completed with the latest considerations on the achieved results and on the basis of the performances obtained during the field tests on the plant. We hereby summarize the main results that this WP produced in the whole project duration.

Public Deliverables and Brochures

The partner small and medium-sized entreprises (SME)s specifically requested and arranged to have 3 different materials for dissemination:
- Brochure for dissemination purposes,
- Brochure with technical aspects of the project,
- The project poster

The reason for this choice is mainly due to the intention, of the project partners, to differentiate the tool to be used with the target audience; in particular:
- The brochure for dissemination is intended as an immediate and communicative material, that can be spread to any type of public, not specifically expert in technological fields or in the sector addressed by the PHOTOMEM project. This material can reach any type of public, and proves easy to read, rich in bullet points summarizing the objectives and the results expected from the research, and highlighting the improvements that this innovative treatment aims at providing to the wastewater market sector in the reference countries and in Europe.

Furthermore, to reach a wider audience and with the purpose of allowing the beneficiary small and medium-sized entreprises (SME)s to reach any of their already ongoing contacts with dedicated materials, the partners also arranged for a translation of these brochures into the Consortium languages, in particular:
- ECS translated into Italian the 2 brochures,
- MT translated them into French,
- BIOAZUL translated them into Spanish, and
- FRA translated the brochures into Greek,

- The technical brochure is intended as a more detailed description regarding the research leading to the PHOTOMEM project results, thus represents an optimal tool to be diffused among the technical staff of the existing wastewater plants, either technicians or plant responsible; this brochure shows the different steps of the process, going into detail of each of them. It therefore supports the communication with the expert audience, to whom the specifications and the layout of the overall process can be described accurately.
- A dedicated, specific dissemination material of immediate impact, especially when participating to national or international events of relevance in the industrial wastewater sector , is the project poster. In fact, it can be used for several purposes, when organizing seminars or dedicated speeches to the target audience, or when taking part to fairs or exhibitions to show the innovation behind the project.

Finally, other 2 communication vehicles were chosen by the Consortium to further spread the project results, the Wiki Page (see http://www.wiki-site.com/index.php/PHOTOMEM online) and the press release published on CORDIS WIRE at the end of the project life, and that can be found at the following link:
(see http://cordis.europa.eu/wire/index.cfm?fuseaction=article.Detail&rcn=33151&rev=0 online).

Newsletter and Contacts

In order for the project to be duly disseminated to a representative group of companies belonging to this type of audience, the project partners, and the small and medium-sized entreprises (SME)s in particular, identified, thanks to their networks and already established contacts, a list of potentially interested small and medium-sized entreprises (SME)s to be involved in the diffusion of news about PHOTOMEM. The main tool used for these contacts was the newsletter via mailing. Appendix II of the PUDF Deliverable reports the list of companies were these updates regarding the project developments were sent. This list has been updated with some other companies through the second period of the project.

As a general rule, each small and medium-sized entreprises (SME) in the Consortium sent a newsletter to the companies listed for their reference countries, so that:
- ECS promotionally emailed the Italian companies involved in the OMWW treatment or oil production in the region of Rome (Lazio),
- BIOAZUL contacted via email the Spanish companies,
- MT the French ones, and
- FRA the Greek ones.

Particular attention was given, by the Technical Manager, in the person of Prof. Angelo Chianese from UNIRO (University of Rome 'La Sapienza' - Department of Chemical Engineering) to keeping the contacts with a big player in the market of olive oil production in Italy, Oleifici Mataluni - http://www.oleificimataluni.com/oliodante/.

The Technical Manager travelled to Benevento, where the companies' plants are located, in the southern part of Italy (Campania region), to establish potentially useful contacts for the future. In fact, following a preliminary analysis of the non-confidential materials sent via email in the course of this dissemination activity, this company showed great interest in following the project and its development for possible future collaborations or for buying this technology for their plant from the owner small and medium-sized entreprises (SME)s of the project.

Events and training to the small and medium-sized entreprises (SME)
As for the participation to events in the wastewater treatment sector, relevant respect to the project scope and technological objectives, demonstration events, as initially planned in the interim PUDF were not possible, due to the assessed delays in the finalization of the pilot plant and the tests sessions necessary for the fulfillment of a proper assessment of the results.

In the work in the training and know-how transfer task, however, the possibility to arrange for a demo event was faced with the Consortium. It emerged that:
Despite the Consortium had a detailed planning for such Task in WP8, the delays assessed in the implementation of the pilot plant also delayed the possibility to demonstrate the effective functioning of the plant to external interested companies in a dedicated event.

Furthermore, November represents the core of the collection campaign for most of the olive oil mills in Italy and abroad; for this reason, it would have been extremely difficult to get the technical staff or the plants representatives involved in any event organized during this month. The Consortium then focused the attention on the member small and medium-sized entreprises (SME)' knowledge of the process, and thus organized a visit to the plant located outside LABOR facilities in occasion of the two-day final meeting held in Rome, Italy.

On this occasion, the first day of the meeting (29th November 2012) was devoted to the general aspects of the project like reporting, financial statements realization and conclusion of the ongoing RTD and DEMO activities. The second day (30th November 2012), the small and medium-sized entreprises (SME) were trained on the plant's functioning by receiving information and materials on the process and instrumentation scheme. Dr. Marco Stoller from UNIRO led the visit a showed the components and the plant to the attending SMEs.

In the framework of the project, and despite the impossibility of the Consortium to concretely show the technological results and the functioning of the pilot plant implementing the treatment process for the OMWW, some dissemination events were attended anyway by the project partner BIOAZUL, with the purpose of spreading the recent news about the state of the project, its ambitions and objectives, and to provide useful contacts for the potentially interested companies receiving the news.

Patent and publication search

Respect to the original patent and publications search performed in the Interim Plan for use and dissemination of foreground deliverable, we now selected only the most relevant ones, having a certain connection to the results developed in PHOTOMEM. This research was of support in the definition of the exploitation strategy, which was intended in the project as a way to take advantage of a new treatment technology, on which no direct application or commercialised product has already been found on the market.

Exploitation Strategy and IPR Management

The concrete output of the IPR Management tasks was the definition of an agreed strategy for the exploitation of the obtained results. The PUDF reports the degree of completion of each specific result of the project, with the missing steps for their commercialization, and the exploitation intention of the owners for the future.

In the second period of the project, when a major part of the implementation phase was carried out, internal discussions were established with the beneficiaries to refine the exploitation plan outlined when results were not available, on the basis of the performances assessed and on the status of completion of the same results.

The output of such discussions led to the identification of the following points for the exploitation plan to be adopted by the SMEs for the plant commercialization and exploitation:

1) The photocatalytic reactor developed in the project cannot be exploited as a stand-by result, especially in case of an application for a patent;
2) The production process for the ferromagnetic nanoparticles, owned by the French SME Marion Technologies should not be patented alone, as patenting a process might not be successful if not related to a specific application;
3) The PHOTOMEM plant, because of its commercial potential, will be object of exploitation by the owning partners, ECS and BIOAZUL, and thus patents will not be sought after for this result.

On the basis of these considerations, the partners decided what follows:

The only attractive solution, for the enterprises owning the project results, for the protection of the knowledge generated in the project, is to unify at least 2 results of the project to apply for a patent covering several aspects of the treatment process. In particular, the best option for the protection of the IPs coming from the PHOTOMEM research was considered to be the application for a patent including the design of the photocatalytic reactor using dispersed photocatalytic ferromagnetic titania nanoparticles for the treatment of high COD wastewater.

This strategy would therefore include:
i) The use of result no. 1 - that is, the photocatalytic ferromagnetic titania nanoparticles produced by ARMINES and MT,
ii) The use of part of result no. 2 – that is, the procedure outlined for photocatalysis, which represents one of the steps of the overall PHOTOMEM treatment, and
iii) The use of part of result no. 3 – that is, the photocatalytic reactor allowing for further reduction of COD contents in the olive wastewater with respect to the traditional techniques.

According to this choice, the intention of the beneficiaries owning this result – BIOAZUL, ECOSYSTEMS and MT - is that of performing a deep analysis of the photocatalytic treatment in terms of COD reduction, and to eventually decide to apply for a patent which considers the specific application of photocatalysis, via a photocatalytic reactor with dispersed photocatalytic nanotitania particles, to the treatment of high COD waste water.

In summary, the exploitation strategy for each of the beneficiaries can be outlined:
- ECS , MT and BIOAZUL intend to jointly:
1) Study and evaluate the possibility to patent the photocatalytic reactor with dispersed nanotitania for treatment of high COD content wastewater on the basis of the tests assessment and on the performances of photocatalysis in reducing the organic content in the olive wastewater;

MT intends to:
1) Act as exclusive producer of the ferromagnetic nanoparticles for the PHOTOMEM and other plants installed by ECS and BIOAZUL (and their licensees), provided that:
- they furnish the nanotitania for PHOTOMEM plants at a market value,
- the particles are produced in the respect of the quality standards required for the process.
2) Modify or apply the production process to any other application or for producing other materials;

FRA intends to:
1) Exercise an exclusivity option for the use of PHOTOMEM in Crete for 2 years after the end of the project;
2) Request to have the pilot plant at his facilities after the end of the project, or to have a new plant (at own costs);

ECS and BIOAZUL intend to:
1) Commercialize the PHOTOMEM plant in their countries (Spain and Italy);
2) Use the plant in other WW treatments and to license the results to third parties;
3) Jointly look for a licensee of PHOTOMEM plant in other markets.

On the base of the evaluation of how to proceed with the exploitation actions mentioned above, the PHOTOMEM beneficiaries co-owning results of the project will develop a Joint Ownership Agreement.

Potential Impact:
Each of the participating small and medium-sized entreprises (SME) in the Consortium will receive great benefits and gain competitive advantage by owning the project results as they have been agreed and shared, in relation to each partner's business line.

In fact:
- the proposer SMEs, ECS and BIOAZUL, specialized in the wastewater treatment plants design and construction will strongly benefit from the possibility to sell the PHOTOMEM wastewater treatment plant in 2 different countries (Italy and Spain).
- On the other hand, the producer of custom-made ceramic powders and nanostructured materials for industrial use (MT) intends to produce and provide the ferromagnetic photocatalytic titania nanoparticles.
- Finally, the end-user FRA (Greece) will apply the technology in its production site and will contribute to validate the purification process.

We believe the market potential for such a solution would be of the order of several tens of millions of Euro. The tangible outcomes of the PHOTOMEM project, available to small and medium-sized entreprises (SME) partners for exploitation will be:
1) Production process for ferromagnetic photocatalytic titania nanoparticles
2) Economical wastewater treatment for OMWW based on photocatalytic pretreatment, membrane filtration and polyphenols recovery
3) PHOTOMEM pilot plant of 1 m3/day capacity to validate the OMWW treatment.

The attached file to this report shows a table indicating:
- For each result, the SMEs proposers who are going to have a main role in the exploitation, and the RTD performer who are providing research services,
- Competences and role of the SMEs and RTD performers

The group of SMEs will exploit the Intellectual Property Rights gained in the project, targeting to patent the 'photocatalytic reactor with dispersed photocatalytic nanotitania for treatment of high COD waste water' developed in the project.

The system, with needed know how, will then be commercialised directly and indirectly to the olive oil production industry. For each SME the results and benefit gained from the PHOTOMEM project have been indicated (please refer to the attachment to this report). A preliminary analysis on the commercialization route after the project shows how the proposers will make profits out of the commercialization and installation of the PHOTOMEM plant in the 5 years after the end of the project itself. This analysis will be further detailed in the IPRs management sections in the progress report and the in related attachments.

Apart from direct commercialisation and installation of OMWW plants, ACS and BIOAZUL will also seek for cooperation with other installers located in other regions. In particular a Greek licensee will be sought for the application in Greece. The royalties from such commercialisation have not been considered in the business plan and would therefore be an add-on.

The PHOTOMEM technology is expected to have great impact also on another important aspect for the small and medium-sized entreprises (SME)s, the creation of employment. In fact, to duly operate a plant, maintain it and install it, technicians and engineers will be employed, with an increase in the technical staff of the small and medium-sized entreprises (SME)s.

It is estimated that, in the 5 years following the end of the project, in which the plants commercialisation will occur, MT will increase the staff number by 2, and ECS and BIOAZUL by 4 persons.

The economic impact for the end-user FRA, estimated in total savings for the olive wastewater treatment, represents about the 10% of the revenues of the company, thus confirming that this new technology will have a huge impact on this small company, increasing without any doubt its competitiveness.

List of Websites:
http://www.photomem.eu/.