

Executive summary:

The main aim of the CLEAN WATER was the development of efficient and viable water detoxification technology exploiting solar energy and recent advances in nano-engineered titania photocatalysts and membranes for the destruction of extremely hazardous compounds in water, including novel emerging pollutants (toxins, hormones) of high environmental and health impact. This innovative approach has been implemented by integrating extensive research and development (R&D) efforts of the consortium members spanning a wide range of interdisciplinary activities from the development of novel nanomaterials and membranes to reactor engineering and analytical methods for emerging water pollutants as well as pilot plant scale studies and cost analysis for water purification. The integrated efforts of the CLEAN WATER consortium have thereby resulted in a number of important science and technology (S&T) achievements that provide the basis for a sustainable and cost effective solar energy technology for water treatment:

- The synthesis of highly reactive TiO₂ photocatalysts with markedly improved photocatalytic performance for water detoxification by a wide range of organic pollutants (phenolic compounds, pesticides, herbicides and azo-dyes) as well as caffeine and diphenhydramine, an important pharmaceutical water pollutant, exceeding that of commercially available titania photocatalysts.
- The development of innovative visible light responding nanocatalysts based on anion (N, F, S, C) doped TiO₂ with tailor designed physicochemical properties and advanced nanocomposites of TiO₂ with carbon nanomaterials (carbon nanotubes and graphene oxide) with unique reactivity under visible and solar light.
- The challenging fabrication of double side photocatalytically active ultrafiltration membranes operating at high flux and low trans-membrane pressure with high photocatalytic and rejection efficiency for water pollutants combined with enhanced antifouling and hydrophilicity as well as minimal generation of toxic condensates in their retentate side.
- Application and validation of the innovative nanocatalyst for water detoxification by the extremely hazardous cyanobacterial toxins (microcystin-LR), taste and odour pollutants released by cyanobacteria (geosmin and 2-methylisoborneol) and endocrine disrupting compounds (17-estradiol, bisphenol-A and tetracycline) combined with the development of analytical methods for pollutant detection and toxicity-biodegradability analysis of the photocatalytic processes.
- The development of an innovative continuous flow photocatalytic membrane reactor integrating the photocatalytic ceramic membranes and the novel nanomaterials immobilised on alginate polymeric fibres (EP2409954- Photocatalytic Purification Device), accomplishing a major target of the CLEAN WATER project i.e. to merge advanced oxidation processes with nano/ultrafiltration membrane technology in a sustainable water purification device.
- Up-scaling of materials and processes together with the evaluation of their water detoxification efficiency in a solar pilot plant as well as cost analysis and process engineering of the developed technology.

The project implementation was based on a critical mass of highly experienced scientists to face the severe technical challenges involved in developing a water treatment technology based on nano-engineered photocatalytic materials. Such a demanding task has been accomplished by pooling the complementary skills of

established experts from six EU member countries (Greece, Spain, Portugal, France, Italy and UK) and a leading overseas expert in photocatalytic water treatment (USA), comprising four Universities, one Research Organisation, and two SMEs, reducing the ensuing high R&D risks. As a result of an extremely productive cooperation between the involved partners an especially a very fruitful interaction with our overseas partner, a net improvement of the S&T capabilities worldwide has been achieved in terms of science, analytical tools and technological products (nanostructured photocatalytic materials and water purification device) on water pollution abatement across different but related sectors comprising nanomaterials, solar energy based environmental protection, and water purification. This has been combined with extremely high research outcome and broad dissemination of the project results, including: coordination of a Special Issue in Journal of Hazardous Materials, production of 2 patents (European), publication of 48 papers in International peer review Journals and 152 presentations in conferences*. This significant outcome resulted from a coordinated and fruitful interaction between the consortium partners that has been accomplished via exchange of samples, short stays in partner's laboratories, technology transfer, training and creation of a new generation of research community (Phd students, post-docs, experienced researchers) in a multidisciplinary field. Potential end-users have already expressed (expressions of Interest from Adventech, EYDAP S.A., Center for Blue Gold Cluster-Korea, Development Agency of Karditsa S.A.) their high interest in the exploitation the project results. Finally, the implementation of the project has leveraged new developments to photocatalytic air purification, hydrogen production, solar energy conversion (solar cells), thus opening new horizons in the nanotechnology driven Environment and Energy fields.

Additional dissemination (European Parliament Magazine, ADEME brochure, EPF society, ACS meetings, IWA conferences, ...)

Project Context and Objectives:

Environmental pollution abatement and especially the growing demand for clean water pose one of the most severe challenges worldwide. Besides the scarcity of water resources, the presence of hazardous chemicals with serious adverse health effects, even at extremely low concentrations, impose serious considerations for the quality of drinking water emphasising the need for advanced treatment methods. The inability of conventional treatment processes for drinking water purification (coagulation / flocculation / sedimentation, filtration, activated carbon adsorption, and chlorination), alone or in combination, to eliminate all toxic organic and inorganic contaminants in potable water sources has sparked the development of modern water treatment processes. These processes include membranes, UV disinfection and advanced oxidation technologies (AOTs) that can be supplementary to conventional ones. Recent advances in membrane manufacturing have revolutionised the applications of membranes in water treatment. Depending on the membranes pore size and the process conditions (i.e. pressure), membrane technologies have been classified as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. While membrane technologies are currently cost-competitive to other conventional purification processes for certain applications, they suffer from two fundamental limitations. First, they provide only physical separation “sieving” of the organic and inorganic contaminants (depending on the size of the pores and the mechanism of separation) in drinking water. In fact, the concentrate stream, which can be of significant volume (i.e. 10% or more of the treated water volume), contains active microorganisms, which can impose a serious threat to the receiving stream or site of discharge. Second, membrane processes suffer from fouling (physical fouling and biofouling), which is especially problematic with polymeric membranes. Regular cleaning and gradual increase of trans-membrane pressures are normally needed for stable membrane flux, increasing the operation cost, while biofouling is irreversible to some extent and membrane permeation properties are not fully restored after cleaning.

Advanced oxidation technologies have emerged as one of the most promising chemical oxidation processes, anticipated to play a crucial role in water treatment as stand-alone processes or in combination with conventional technologies. Among the various AOTs (UV/H₂O₂/O₃, TiO₂ Fenton...), TiO₂ photocatalysis has spawned an immense amount of research on the development of photocatalytic materials as a versatile and clean technology, which could successfully address environmental pollution relying on the use of solar energy. Ample verification of the effectiveness of TiO₂ to generate highly reactive chemical species (e.g. hydroxyl radicals) upon UV illumination along with its environmentally benign properties (i.e. non-toxicity, absence of dissolution in water, photostability) and relatively low cost, rendered TiO₂ a key material for the complete destruction of recalcitrant organic pollutants in water. This interest stems from the ability of the process to oxidise virtually all organic contaminants, while at the same time producing no harmful end products when applied at optimum conditions. However, despite the marked progress in the development of TiO₂ photocatalytic materials, their practical application is challenged by two inherent limitations of titanium dioxide, namely the low quantum yield, which is primarily determined by the recombination of photo-generated charge carriers, and the narrow light-response range that is limited by the wide band gap of TiO₂ to the UVA spectral range. Both factors undermine the photocatalytic efficiency

of TiO₂ and its enormous potential as an essentially “green” technology for the destruction of noxious organic compounds in water under solar light.

The CLEAN WATER project aims at the development of innovative water detoxification technology exploiting solar energy and nanostructured titania photocatalysts in combination with membrane technology. This innovative approach builds upon recent advances in nano-engineered TiO₂ photocatalysts and membrane engineering to produce a viable water detoxification technology for the destruction of extremely hazardous toxins and pollutants in natural waters and water supplies. Recent progress in the synthesis of nanoengineered mesoporous titania towards visible light responding photocatalysts by anion doping will be exploited and further advanced by the challenging fabrication of TiO₂-nanocarbon composites and TiO₂ supported photocatalytic membranes with tailor-designed porosity and interwoven inorganic framework, through innovative chemical and engineering methods. Most importantly, the development of an innovative continuous flow photocatalytic membrane reactor operating at both the UV and visible spectral ranges is further projected to lead to a sustainable and cost effective water treatment technology that will effectively combine advanced oxidation processes with nano- / ultra-filtration membrane technology in a sustainable water purification device. CLEAN WATER is thus intended to afford multiple functions in water treatment technology (separation, disinfection, organics destruction, and anti-biofouling), together with the development of materials and processes (photo-reactor technology) that enable photocatalytic water purification under solar irradiation that are key to the reduction of energy requirements. Comparative evaluation of the UV-visible and solar light efficiency of the modified titania photocatalysts for water detoxification will be intensively investigated on various target pollutants ranging from classical water contaminants such as phenols, pesticides and azo-dyes to the extremely hazardous cyanobacterial toxins and the emerging endocrine disrupting compounds in order to evaluate/optimize the materials performance and validate their competence on water treatment. In this context, particular efforts will be devoted to the analysis and quantification of degradation products endowing the project strong societal impact by facing serious environmental problems related to the quantification and monitoring of specific pathogenic water pollutants i.e. cyanobacteria toxins and endocrine disruptors. The final goal is the scale up of materials and processes by the large scale production of the most promising photocatalytic materials and the evaluation of their water detoxification efficiency in pilot water plant as well as process engineering of the developed reactor technology.

The specific objectives of the work involved in this project are the following:

1. The preparation of nanostructured UV-Vis photocatalysts by means of innovative template- and self-assembling sol-gel chemical routes and their combination with activated carbon to develop visible-light responding nanostructured titania with tailored photocatalytic performance by anion (N, C) doping.
2. The development of composite carbon nanotubes / titania nanostructures by using different synthetic and engineering routes based on chemical vapour deposition and sol-gel methods. Technological implementation of the hybrid materials will be further pursued through the exploitation of the thickness of alumina filters or their embedment into polymer nanofibres.

3. The development of photocatalytically active nanofiltration membranes with optimal doping content, enhanced surface area, and tailored pore size and retention efficiency for target water pollutants, for visible and UV photocatalytic activity by means of both chemical vapour deposition and sol-gel dip coating techniques.
4. Evaluation of materials activity for the photodegradation of water pollutants by comparative studies of the UV-visible and solar light efficiency of the modified titania photocatalysts in water detoxification with specific target pollutants: MC-LR cyanobacterial toxins, geosmin, 2-methylisoborneol, endocrine disrupting compounds and their interference with classical water pollutants such as phenols, pesticides and azo-dyes. Analysis and quantification of the degradation products as well as elucidation of the mechanism/process of photodegradation using the innovative titania based photocatalysts will also be performed to ensure the effectiveness and the environmental impact of the engineered nanomaterials.
5. The development of a laboratory-scale continuous flow photocatalytic-disinfection-membrane reactor integrating the photocatalytically active nanofiltration membranes produced at previous stages of the project, which combine the UV-vis photocatalytic efficiency and immobilisation of the novel materials, with the benefits acquired by selective removal of the reaction by-products through the NF membranes.
6. Up-scaling of materials and processes by the large scale production of the most promising photocatalytic materials and the evaluation of their water detoxification efficiency in pilot water plant as well as process engineering of the developed reactor technology to enable transfer of knowledge to public companies having the management of water resources supply.
7. Evaluation of the efficiency of the novel photocatalytic methods at the reduction-elimination of toxicity. Toxicity and biodegradability analyses will complete the photocatalytic water detoxification processes. Risk assessment of the photocatalytic processes will be carried out in order to investigate the possibility that the processes lead to the formation of toxic intermediates or byproducts. The work will comprise the selection and optimisation of toxicity tests, the monitoring of toxicity evolution during the application of the novel photocatalysts and the investigation of the effect of the novel photocatalysts on biodegradability.

The accomplishment of the CLEAN WATER objectives relies on the implementation of three main research directions provided by eight interacting work packages (WPs):

- WP1: Doped TiO₂ nanostructured photocatalysts
- WP2: Composite carbon nanotubes/titania nanostructures
- WP3: Photocatalytic nanofiltration membranes
- WP4: Photocatalytic water detoxification I: phenols, azo-dyes, pesticides
- WP5: Photocatalytic water detoxification II: Microcystin-LR, geosmin and 2 Methylisoborneol
- WP6: Photocatalytic water detoxification III: endocrine disrupting compounds
- WP7: Development of laboratory UV-vis membrane photoreactors
- WP8: Up scaling materials and processes: Large scale evaluation-Process engineering

The CLEAN WATER project is subdivided into three subprojects. The first subproject composed by WP1, WP2 and WP3 is focused on the preparation of novel nanostructured photocatalyst materials and membranes. In addition, mechanistic and analytical methods are used to thoroughly investigate the new materials together with

investigations of the photocatalytic processes occurring on the surfaces. The results of the first subproject will have a direct input for the second and third subprojects in form of knowledge together with samples of newly developed active nanocatalysts.

The second subproject composed by WP4, WP5 and WP6, is focused on water detoxification by the novel nanostructured photocatalysts. The efficiency of the new materials and the photocatalytic process under UV-vis and solar light will be studied for water detoxification by classical water pollutants, i.e. phenols, azo-dyes, and pesticides and most importantly by the extremely hazardous cyanobacterial toxins (microcystin-LR), taste and odour pollutants released by cyanobacteria (geosmin and 2-methylisoborneol) and endocrine disrupting compounds (17-estradiol, bisphenol-A and tetracycline) for which analytical methods will be developed. Moreover, the disappearance of the water pollutant and at the same time the intermediates evolving prior to mineralisation will be monitored, as these intermediates could be even more toxic than the parent compounds.

The photocatalytic materials developed and evaluated in the first and second subprojects will provide input for the third subproject (WP7, WP8) for the development of a novel continuous flow photocatalytic membrane reactor that will incorporate the innovative photocatalytic membranes and the immobilised nanocatalysts. Successful implementation of this technological objective has been a major target of the CLEAN WATER project i.e. to merge advanced oxidation processes with nano- / ultra-filtration membrane technology in a sustainable water purification device. In addition, crucial aspects of this work involve up-scaling of the developed innovative TiO₂ photocatalysts, large scale (pilot plant) evaluation of their water detoxification performance and process engineering that will enable future application of the developed technology.

Project Results:

WP1. Doped TiO₂ nanostructured photocatalysts

The first objective of the project work concerned the development of nanostructured UV-Visible titania photocatalysts based on anion doped-TiO₂ by using innovative template- and self-assembling sol-gel chemical routes and their combination with activated carbon.

This target was successfully addressed through a systematic scheme of work implemented within WP1, where the first stage was focused on the optimisation of the synthetic conditions of bare TiO₂. The synthesis of highly reactive TiO₂ photocatalysts has been thereby accomplished by means of an efficient sol-gel method combined with the removal of larger aggregates, correct aeration and optimisation of the calcination temperature. In particular, the catalyst calcined at 1023 K and mechanically dispersed (ECT-1023t) presented markedly improved photocatalytic performance exceeding that of commercially available titania photocatalysts, especially the benchmark Evonik Aeroxide® P25 catalyst that finds widespread use in most practical photocatalytic applications. This enhanced photocatalytic reactivity stems primarily from the higher propensity of the catalyst to generate highly reactive hydroxyl (HO•) and hydroperoxyl (HOO•) radicals. The high crystallinity of the optimised material accompanied by a low concentration of defects and the favorable faceted morphology of the major anatase particles as well as the presence of anatase/rutile heterojunctions promote photo-induced charge separation with low e⁻/h⁺ recombination rates. Further development of this sol-gel route by the use of sulfuric acid resulted in the synthesis of a new, even more reactive TiO₂ photocatalyst that is being patented (EU Patent Application number: PCT/ES2012/070086 February 10th, 2012).

Innovative sol-gel synthesis based on the self-assembling template method has been applied to synthesise mesoporous anion doped TiO₂ with N-F, S and C hetero-atoms using suitable surfactants and reagents, to improve simultaneously the structural, morphological and electronic properties of TiO₂ nanomaterials and achieve anion doping of titania with high visible light photo-induced reactivity. Co-doping of TiO₂ by N and F anions was achieved by a modified sol-gel method using a nonionic fluorosurfactant, as pore template material and fluorine source combined with ethylenediamine as nitrogen source.

Varying the fluorosurfactant ratio R in the range of 1.0 to 5.0 allowed tailoring the materials physicochemical properties (surface area, porosity, crystallite size and pore size distribution) that resulted in the marked enhancement of the N-F TiO₂ photocatalytic efficiency for microcystin-LR (MC-LR) degradation under visible light, with optimum performance at R=5.0.

Carbon doped TiO₂ nanoparticles were synthesised by the self-assembly sol-gel route using oleic acid (OA) as pore directing agent and carbon source. Different molar ratios between oleic acid (OA) and titanium tetraisopropoxide (TTIP) (OA:TTIP = 1:1, 3:3, 5:1) together with low temperature calcination (350°C) were employed to optimise the physicochemical properties and the visible light photoactivity of C-TiO₂.

This surfactant assisted sol-gel technique was applied for the synthesis of S-doped TiO₂ thin films, not foreseen in the initial workplan, using the polyoxyethylene (80) sorbitan monooleate (Tween 80) surfactant and H₂SO₄ as sulfur and water formation precursor. The calcination conditions were carefully controlled in order to maximise sulfur incorporation into the TiO₂ lattice and its photocatalytic performance. The optimised anion-doped TiO₂ nanomaterials presented high surface area and porosity together with a narrow pore size distribution and small crystallite size. Such highly interconnected TiO₂ pore-networks offer abundant adsorption-desorption sites that ease pollutant diffusion during the photocatalytic reaction, while inhibiting the aggregation of TiO₂ nanoparticles and promote photogenerated charge transport and separation, all being key aspects for heterogeneous photocatalytic processes.

Incorporation of anion species in TiO₂ nanomaterials resulted in the extension of their optical absorption in the visible range with absorption thresholds of 2.85, 2.94 and 2.69 eV for the NF-, S- and C-doped TiO₂, respectively. Thorough investigations of the formation and nature of the anion species and the visible light activation of the doped TiO₂ by means of XPS and light-dependent EPR measurements indicated the formation of localised energy states above the TiO₂ valence band enabling light harvesting in the visible range. Combination of the advantageous nanomaterials' porous structure with the effective anion doping of the TiO₂ lattice and the concomitant formation of localised intra-gap states afforded the development of highly efficient nanocatalysts. These TiO₂ nanomaterials exhibited unique reactivity in the photocatalytic degradation of the extremely hazardous MC-LR toxin in water by visible light (> 420 nm), outperforming both commercial photocatalysts (Aeroxide® P25) and reference TiO₂ materials prepared in the absence of surfactants and/or anion doping reagents.^{5, 6, 7.}

Furthermore, immobilisation of the anion doped TiO₂ nanomaterials on glass substrates provided nanostructured photocatalytic thin films with enhanced mechanical stability and reusability upon consecutive photocatalytic experiments under visible light. Moreover, the NF-TiO₂ films underwent slow visible light induced hydrophilic conversion, with a reduction of the wetting angle at 80° in contrast to the UV limited optical response of their undoped analogues. The phenomenon occurred at a slower rate than the corresponding one of UV stimulated superhydrophilicity. The wetting response of the NF-TiO₂ films correlates well with the variation of their optical properties and surface morphology and most importantly with their photocatalytic activity, rendering these materials very promising for self-cleaning applications under visible light.

Composite NF-TiO₂/P25 films were further developed as a promising means to circumvent limitations in the activity of anion-doped TiO₂ photocatalysts for solar driven photocatalytic purification of water from cyanobacterial toxins. The addition of Aeroxide® P25 nanoparticles in the sol resulted in films with higher BET surface area, pore volume, porosity and total TiO₂ mass, as well as larger thickness and roughness after heat treatment. The composite N-F TiO₂/P25 films showed significant photocatalytic activity for the degradation of four microcystins (MC-LR, -RR, -LA and -YR), and cylindrospermopsin under visible and UV-vis light.

The synthesis of N-modified TiO₂ was optimised using combustion sol-gel synthesis employing urea as fuel. Both the urea content and calcination temperature were optimised, providing the optimal absorption threshold of 2.19 eV for solar light harvesting. The optimised nanocatalyst exhibited significant photocatalytic activity under pure visible (440-460 nm), UVA and solar light. This activity is attributed to the formation of core crystalline TiO₂ nanoparticles covered homogeneously with a carbonaceous shell, acting as visible light sensitiser. The photocatalytic reactivity is further promoted by the high surface area and porosity of the catalyst as well as by the retardation of recombination effects due to the small nanoparticle size and the improved charge separation at the inorganic/organic heterojunction.

On the other hand, thorough investigations of amine template-assisted sol-gel precipitation and hydrothermal treatment using hydrazine or TEA as templating agents have shown that reproducible N-doping of TiO₂ with high UV-vis photoactivity is not achieved by this means. Hydrothermal treatment was also found to increase the catalysts surface area, but deteriorate their photocatalytic activity mainly through the modification of their surface chemistry by adsorbed wastes. Systematic optimisation studies of the TiO₂-activated carbon (AC) combination in terms of reactivity, recycling and separation for different water pollutants (phenol, 4-aminophenol, 2,4 dichlorophenoxyacetic acid) have shown that the presence of AC does not improve significantly either the reactivity or decantability of the most efficient ECT-1023t catalysts, and therefore this modification was discarded for further application in the project.

WP2. Composite carbon nanotubes/titania nanostructures

Well-aligned carbon nanotubes (CNTs) were produced by means of chemical vapour deposition (CVD) using surfactant-stabilised Fe₃O₄ particles and anodised alumina disks as templates. The surface chemistry of both single, and multi-wall CNTs was finely tailored by HNO₃ hydrothermal method in order to allow efficient binding with titania nanoparticles through oxygenated surface groups. Combining the analytical power of temperature programmed desorption with water adsorption/desorption, resonance Raman spectroscopy, thermogravimetry and N₂ porosimetry we were able to control and quantify oxygen functionalities on CNTs as well as to explain the origin of the pore structure alteration with respect to the functionalisation conditions and the properties of the pristine CNTs.

The functionalised CNTs were employed to prepare a wide variety of nanostructured TiO₂/CNTs catalysts by different synthetic and engineering routes in the form of both powders and films. It was concluded that the dispersion of TiO₂ particles in the functionalised CNTs depends on their nature, while the CNTs functionalisation is a crucial factor for the preparation of efficient TiO₂/CNT composites. Additional work was devoted to the synthesis of nanocarbon-TiO₂ composites using carbon nanomaterials that have recently gained major attention in photocatalysis, namely graphene oxide (GO) and fullerenes (C₆₀), besides CNTs. Graphene oxide-TiO₂ composites (GOT) and comparatively C₆₀-TiO₂ and CNT-TiO₂ were synthesised using the liquid phase deposition method with different nanocarbon content and subsequent post-reduction upon thermal treatment in N₂ at different temperatures. By combining several analytical techniques (AFM, SEM, TEM, TGA-DTG, diffuse

reflectance UV-Vis, XPS, Raman, N₂ porosimetry) the optimal assembly and interfacial coupling of the TiO₂ nanoparticles with the GO sheets was reached at 3.3-4.0 wt.% of GO after post thermal treatment at 200°C.

An alternative synthetic route for hybrid CNT/TiO₂ nanostructures was developed by metal-organic chemical vapor deposition (MO-CVD), which provided a scalable preparation method, avoiding the use of solvents and time consuming hydrothermal procedures as well as the necessity for CNT's functionalisation.

A template assisted CVD procedure was developed, which resulted in the production of hybrid nanotubes each one comprising two firmly adhered coaxial tubes, the internal being multi-wall CNTs and the external being titania nanotubes. Different MO-CVD configurations were subsequently investigated, including template assisted CVD, MOCVD post treatment of CNTs and the technique of simultaneous CNTs growth with TiO₂ deposition, in order to optimise the development of CNT/TiO₂ hybrid nanotubular photocatalysts with controlled phase composition and structural characteristics and most importantly the possibility of up-scaled production. Technological implementation of the TiO₂ based nanomaterials was successfully realised through their embedment into Ca alginate polymer-hollow fibers manufactured by the dry/wet spinning process. The biopolymer/TiO₂ fibers in either the hydrogel non-porous form or in the highly porous aerogel form prepared by sc-CO₂ were found to effectively disperse and stabilise efficient photocatalysts such as P25 and GOT in their matrix.

WP3. Photocatalytic nanofiltration membranes

The development of double side active photocatalytic ceramic membranes (PCMs) for target water pollutants was implemented via two different CVD processes on alumina membranes. The first method proceeds via the pyrolytic decomposition of titanium tetrakisopropoxide vapour (TTIP) and TiO₂ nanoparticle formation through homogeneous gas phase reactions and aggregation of the produced intermediate species followed by further particle growth and deposition on the membrane surface under thermophoretic or diffusion driving forces. These membranes were termed as Nanoparticles Growth CVD (NG-CVD/PCM). The second approach proceeded through physisorption of TTIP vapour on the membrane surface and inside its pores at room temperature followed by thermal treatment up to 300°C in oxidative conditions that promote surface reactions (TTIP polymerisation through alkoxy groups condensation). The physisorption and oxidative treatment cycles were repeated several times and therefore this approach was termed as Layer by Layer CVD deposition and the respective membranes as LBL-CVD/PCM. Both methods were optimised with respect to the reactor temperature, the gas flow carrying the TTIP vapour, the pressure difference

Highly reactive titania/alumina membranes possessing two photocatalytically active layers were synthesised, exhibiting high water flux and anti-fouling properties. Double side active photocatalytic membranes were alternatively developed by sol-gel dip coating deposition of selected titania photocatalysts on ceramic alumina membranes. This work resulted in the production of highly efficient graphene oxide-TiO₂/ceramic ultrafiltration membranes (GOT4/PCM) and nitrogen modified

TiO₂/ceramic ultrafiltration membranes (N-TiO₂/PCM), the latter being highly active under visible light. The membranes performance to adsorb and/or repulse and photocatalytically degrade water pollutants was for the first time evaluated in a continuous flow membrane reactor operating in the cross-flow mode under UV-vis illumination, which was developed within the project framework (vide infra).

WP4. Photocatalytic water detoxification I: phenols, azo-dyes, pesticides

For the implementation of objective 4, the photodegradation efficiency of the innovative UV-Vis titania nanocatalysts, the nanocarbon-TiO₂ composites and photocatalytic membranes was extensively evaluated for water detoxification at laboratory scale using various types of probe organic molecules: phenol and derivatives such as hydroxyphenols (catechol, resorcinol and hydroquinone), aminophenols (2-aminophenol, 3-aminophenol and 4-aminophenol), cresols (o-cresol, m-cresol and p-cresol), pesticides (2,4-dichlorophenoxyacetic acid, pyrimethanil, triadimenol, propanil), azo-dyes (methyl orange, methyl red, acid red, methylene blue), as well as caffeine and diphenhydramine, not foreseen in the initial workplan. The evolution of the pollutants concentration during irradiation, including intermediates, was monitored by means of HPLC, UV-Vis spectroscopy and TOC analysis.

Thereby, it was established that the innovative photocatalyst ECT-1023t and its variant EST-1023t were highly reactive for most probe organic molecules, exceeding the performance of the benchmark Aeroxide® P25 photocatalyst. The efficiency of the ECT-1023t catalysts was further studied for the degradation of an important pharmaceutical water pollutant, diphenhydramine (DP) under different catalyst loadings (up to 2.00 g L⁻¹) and initial solution pH (3.0-11.0) in comparison to the Aeroxide® P25.4 The results showed that DP is very stable under non-catalytic conditions but complete degradation and considerable mineralisation (ca. 60-70%) under near UV to visible irradiation (~50 mW cm⁻²) can be achieved in 60 min by selecting the appropriate TiO₂ loading. ECT-1023t was verified to be a highly active for both degradation and mineralisation of the DP pharmaceutical, surpassing P25 at catalyst loads higher than 1.00 g L⁻¹.

In general, the pseudo-first order rate constants increased with the catalyst loading up to a certain value where the activity reached a plateau, evidencing a heterogeneous regime, and also with the initial solution pH, mainly attributed to the formation of the reactive hydroxyl radicals at the catalyst surface. The highest rate constant was obtained for ECT-1023t at pH 11 ($173 \times 10^{-3} \text{ min}^{-1}$ against $116 \times 10^{-3} \text{ min}^{-1}$ for P25).

Evaluation of the photocatalytic performance of several TiO₂/CNT composites verified that the oxygenated groups introduced on CNTs play an important role on composites activity. The effect of oxygenated groups on the composites efficiency was identified to be beneficial as these groups promote the dispersion of TiO₂ nanoparticles on CNTs, increase the TiO₂ surface exposed to the irradiation and enhance the CNT-TiO₂ binding. Moreover, the TiO₂ crystalline phase, particle size, textural and chemical properties are important parameters for the enhancement of the photocatalytic efficiency. In particular, the TiO₂ particles size is one of the most critical factors for the TiO₂-CNT interaction. Furthermore, immobilisation of the

TiO₂/CNT composite in the form of films showed performance enhancements through synergistic effects between the CNT and TiO₂ constituent phases, depending on the type of TiO₂ nanoparticles and different optimal CNT loadings, compared to the powder analogues.

However, the most pronounced enhancement of the TiO₂ photocatalytic activity was achieved for the reduced GO-TiO₂ composites upon optimal interfacial coupling.¹⁶ In particular, the photocatalytic performance of the graphene oxide-TiO₂ composites for the degradation of DP and methyl orange under near-UV/Vis and visible light irradiation was found to depend markedly on the GO content and post-calcination temperature. Almost complete degradation and significant mineralisation of both water pollutants was achieved within less than 60 min under UV/Vis irradiation for the composites with 3.3-4.0% wt. GO after post-annealing at 200 °C in N₂. The photocatalytic activity of the optimal GOT composites exceeded that of the benchmark P25 photocatalyst for both DP and MO pollutants, especially under visible light, where P25 is fairly inactive. This indicates that reduced GO-TiO₂ heterostructures may effectively enhance the photocatalytic activity of TiO₂ in the visible range without compromising its performance under UV light, a major drawback of most visible light active TiO₂ photocatalysts. Photogenerated holes were identified as the main reactive species in DP photocatalytic degradation process for both bare TiO₂ and GOT composites under UV/Vis irradiation, according to photocatalytic experiments in the presence of hole and radical scavengers.

However, an enhanced contribution of radical mediated oxidation was evidenced under visible light, which, together with the distinct quenching of the GO photoluminescence under visible and NIR laser excitation, indicate that reduced GO may also operate as a visible light sensitiser of TiO₂, enabling electron transfer from GO to TiO₂ under visible light. Relying on these results and the inhomogeneous variation of the size of sp² clusters, it was accordingly proposed that the GO sheets upon binding with TiO₂ can act as electron acceptor or electron donor under UV and visible light excitation, respectively. Optimisation of the GO-TiO₂ interface could be thus a very promising route to improve charge separation and, most importantly, to extend the photocatalytic activity of TiO₂ into the visible range.

The nanocarbon-TiO₂ composites prepared by the liquid phase deposition method with different CNT and C60 contents were further evaluated in the photodegradation of DP under UV/Vis and visible light in comparison with the reference TiO₂, P25 and GOT composites. Combination of the nanocarbon phase with TiO₂ resulted invariably in the increase of the catalyst efficiency for DP and MO degradation and mineralisation compared to the bare TiO₂ confirming the presence of synergistic effects between the constituent phases. Among all the prepared composites, GOT comprising 4 wt.% GO exhibited the highest photocatalytic activity under UV/Vis and visible light, exceeding that observed for the bare TiO₂ and P25 used as references. However, the optimal carbon content varied for the different nanocarbon-TiO₂ composites. Regarding CNT-TiO₂ composites, a CNT to TiO₂ weight ratio of 20% has been determined to be optimal for the degradation of several water pollutants, due to the extended pollutant adsorption, the enhanced light absorption and separation of photogenerated charge carriers. Concerning the C60-TiO₂ composites, the BET measurement showed that the contribution from different C60 contents to the specific surface areas is negligible, while the photocatalytic activity increased continuously

with the carbon content, indicating that the increase of the C60-TiO₂ photocatalytic activity is not associated with the surface area or to the adsorption capacity of the composite but rather with the interfacial charge transfer process that can inhibit electron-hole recombination. The photocatalytic activity of the tested materials under visible light for DP degradation decreased in the order: GO-TiO₂-4 > CNT-TiO₂-12 > CNT-TiO₂-4 > C60-TiO₂-4 > GO-TiO₂-12 ~ C60-TiO₂-12 > P25 > TiO₂, corroborating the role of CNT and GO to extend the photocatalytic activity of TiO₂ under visible light. On the other hand, no appreciable DP or MO degradation was observed for the composites containing C60. This complies with the rather weak enhancement of the optical absorption in the visible spectral range for the C60-TiO₂ composites, in contrast to the strong increase of visible light absorption obtained for the GOT and CNT-TiO₂ composites.

Furthermore, comparison of the photocatalytic activities of the GOT composites and those prepared with functionalised CNTs and P25 (P25-CNTf-20) in the degradation of DP and MO under UV/Vis and visible light confirmed the much superior performance of GOT for both pollutants. Further studies verified that the combination of CNTs with the highly reactive ECT-1023t as well as P25 decrease their photocatalytic activity, in contrast with the results obtained when CNTs were combined with Sigma-Aldrich (SA) 100 nm TiO₂ nanoparticles. However, the enhancement in the photocatalytic activity of SA-CNT-20 composites in powder form was not as significant as that obtained with GOT prepared at the optimal conditions under any illumination source. On the other hand, SA-CNTf-20 composites were the most efficient catalyst when applied as films, indicating that they could be very promising for applications of thin film photocatalysts.

Comparative evaluation of the photocatalytic activity of ECT-1023t, N-TiO₂ and the best GOT composite under both -UV/Vis and visible light confirmed that ECT-1023t and GOT are highly active photocatalysts for DP degradation, with comparable efficiency conversion and mineralisation, competing with P25. The composite GOT presented markedly higher activity for the conversion and mineralisation of the MO dye. Under visible light, P25 was practically inactive and GOT (for DP) and N-TiO₂ (for MO) were the most efficient photocatalysts for visible light applications. According to photocatalytic experiments with scavenging agents it was concluded that direct oxidation with photogenerated holes are more important for the modified TiO₂ materials (N-TiO₂ and GOT) than for ECT and P25, which present higher availability to generate radical species from photoinduced holes. A photoreduction mechanism on the surface of the photocatalysts was observed for MO, where the addition of an electron donor (EDTA) was greatly enhancing the rate of MO photoreduction.

The solar light photocatalytic performance of the most efficient TiO₂ based nanocatalysts prepared in the frame of the CLEAN WATER project was comparatively evaluated under identical conditions in batch reactors. Phenol, 2,4-dichlorophenoxyacetic acid (2,4 D) and basic red dye were selected as model water pollutants and Aeroxide® P25 and Kronos VLP 7000 were used as reference photocatalysts. The following nanomaterials produced in the CLEAN WATER project (all presenting higher efficiency than the commercial photocatalysts) were selected based on their activity performance for water purification and the specific type of the process- reactor:

- (1) ECT-1023t and its analogue EST-1023t were selected for experiments with the pilot plant photoreactor based on Compound Parabolic Collectors (CPCs), working in slurry conditions under actual solar light.
- (2) GOT composites with 3.3-4.0% wt were selected for photocatalytic experiments in the continuous flow membrane photoreactor (vide infra) after immobilisation in the matrix of alginate hollow fibers and upon deposition on ceramic membranes (GOT/PCM).
- (3) N modified TiO₂ was selected for its enhanced visible light activity and was used as coating on ceramic membranes (N-TiO₂/PCM) also applied for water detoxification in the continuous flow membrane photoreactor.

Overall, extensive evaluation of the selected materials prepared under optimal conditions indicate that they are highly active photocatalysts, but under different conditions. Selection of a single photocatalyst is therefore not feasible as its activity depends essentially on the process conditions (form of the catalyst, irradiation source and catalyst loading). Specifically, GOT presented markedly high photocatalytic activity when applied as powder but ECT-1023t seems to be more active in the degradation of most water pollutants at catalyst loading higher than 1.0 g L⁻¹, when applied as slurry under solar light conditions. Therefore, ECT-1023t and EST-1023t were selected as the most efficient materials for pilot plant CPC-photoreactors working with slurries under solar light, while GOT and N-TiO₂ were more suitable when immobilised and/or for visible light applications. It is also important to note that the TiO₂/CNT composite with functionalised CNTs (20% wt.) exhibit high photocatalytic efficiency in the form of films and, therefore could be very promising for application in flat-plate photoreactors (not considered in the current project).

Performance evaluation of the developed PCMs for water purification was carried out in the continuous flow membrane reactor, as described below (WP7). Thereby, the innovative concept of double side photocatalytically active ultrafiltration membranes operating at high flux and low trans-membrane pressure with high photodegradation efficiency when irradiated on both their sides was established. Moreover, the developed membranes exhibited good antifouling properties, high hydrophilicity, while inhibiting the generation of toxic condensates in their retentate side. Comparison of the rejection efficiency and permeability under dark conditions between standard nanofiltration (NF) membrane (1-2 nm pore size), the ultrafiltration (UF) alumina membranes of 5 and 10 nm that we used as supports for the PCMs, the NG-CVD PCM and finally an LBL-CVD membrane that we developed for extended period of CVD treatment to effectively control the pore size down to the nanometer level, showed that the produced PCMs, especially the NG-CVD/PCM and the LBL-CVD/PCM, can be classified as nanofiltration membranes (Figure 19).

The performance of the four different types of photocatalytic membranes, namely the NG-CVD/PCM, LBL-CVD/PCM and the GOT/PCM and N-TiO₂/PCM prepared by sol-gel dip coating deposition, for water treatment was directly compared for the photodegradation of azo dye water pollutants in the continuous flow membrane reactor under UV and visible light. The most efficient membranes under UV illumination were GOT4/PCM and LBL-CVD/PCM, which removed the higher amount of water pollutants at the lowest energy cost. On the other hand, the N-TiO₂/PCM exhibited the best performance under visible light showing a steady state pollutant rejection efficiency of 40 %. Moreover, the high visible light activity was

accompanied by photo-induced hydrophilic conversion resulting in the continuous increase of water flux during the photocatalytic filtration runs. A combined photocatalytic ultrafiltration process for organic load removal from water with only energy input the solar light has been accordingly put forward as an energy efficient alternative to the typical nanofiltration process.

In particular, the developed membranes offer significant advances in the treatment of polluted water:

- Operation in the flow through mode without significant fouling due to the continuous photodegradation of the organic solutes in the concentration polarisation layer. In this way, the need of high water flux and high cross-flow to permeate ratio is alleviated and the generation of toxic concentrated retentate effluents is avoided.
- Two photocatalytically active surfaces on one membrane element. The external surface prevents fouling during filtration, while the internal, which is the most active due to the high photocatalyst mass per water volume ratio ($\text{TiO}_2/\text{water}$, $\text{m/v}\%$), assures the pollutants elimination from the permeate effluent.
- Filtration of the water with permeating pollutants through a highly asymmetric pore structure from the external to the internal membrane surface. The high asymmetry induces turbulent flow as the fluid passes from the layers of high to the layers of low pore size (nanosize) allowing better mixing and contact of the pollutant with the photocatalytic internal surface.

Furthermore, the performance of the developed PCMs for water purification was compared with that of commercially available polymeric nanofiltration membranes in order to define the most efficient candidates for up-scaled development. The NG-CVD/PCM presented the best rejection efficiency, operating, however, at high trans-membrane pressures and low water recovery rendering this membrane inappropriate for large scale photocatalytic filtration applications. The other 3 types of the developed PCMs (GOT4, N-TiO₂ and LBL-CVD) operated at extremely low energy consumption, ca. 10-12 times lower than that required by commercial nanofiltration membranes. By recycling the permeate effluent of the developed PCMs back to the feed an approximately 3-fold increase of the treatment period is required to achieve the rejection efficiency of a commercial NF membrane. The developed high flux photocatalytically active membranes have the capacity to treat identical volume of polluted water and bring it at similar quality expensing 7 times lower energy.

Inhibitory effect of water samples of the light emission of *Vibrio fischeri* (Luminescence bacteria) and the inhibitory effects of water constituents on Duckweed (*Lemna minor*) growth have been also selected for the risk assessment of the photocatalytic process (objective 7). The ECT-1023t nanocatalysts eliminated the toxic effect on *vibrio fischeri* of water containing 0.53 mM of phenol, and basic red after 3 hours of photocatalytic process, while four hours were necessary in the case of 2,4-dichlorophenoxyacetic acid. However, longer times were necessary for the complete reduction of toxic effects in water containing these pollutants using the anion doped TiO₂ nanomaterials as catalyst. In all cases, photocatalytic processes using ECT-1023t as catalysts were associated with a total elimination of the toxicity of azo-dyes, pesticides and phenols on *Vibrio fischeri* bioluminescence and *Lemna minor* growth.

WP5. Photocatalytic water detoxification II: Microcystin-LR, geosmin and 2-Methylisoborneol

One of the main targets of the CLEAN WATER project was the evaluation of the photocatalytic activity of the nanostructured catalysts for water detoxification from microcystin-LR (MC-LR), one of the most common and more toxic water soluble cyanotoxin compounds released by cyanobacteria blooms, as well as taste and odour pollutants released by cyanobacteria, geosmin (GSM) and 2-Methylisoborneol (2-MIB). In order to evaluate the photocatalytic degradation and mineralisation of MC-LR, GSM and 2-MIB by the TiO₂ photocatalysts, appropriate analytical methods were developed. The analytical method for the determination of MC-LR in water was based on the technique of high performance liquid chromatography (HPLC) with UV detection, while the method for geosmin and 2-MIB was developed by headspace solid phase microextraction (HS-SPME) coupled to gas chromatography with mass spectrometry (GC-MS). Optimisation and validation of methods developed was performed, in order to evaluate linearity, precision and limits of quantification. The limit of detection (LOD) for the former method was estimated from the analysis of spiked water samples at low concentration levels and represent the amount of MC-LR required to give a signal to noise ratio greater than three ($S/N > 3$). The LOD was found to be 0.005 mg/L. The limit of quantification (LOQ) was set to 0.1 mg/L, as this is the lowest validated level that fulfills the validation criteria. The limit of quantification (LOQ), defined as the minimum concentration of GSM and 2-MIB that can be quantified with acceptable accuracy and precision was found to be 5 ppt for both analytes, while the LOD at $S/N > 3$ was found to be 1 ppt for both compounds.

Furthermore, an innovative multi-walled carbon nanotube (MWCNT) electrochemical biosensor was developed for monitoring MC-LR in drinking water supplies. This novel approach, not foreseen in the initial workplan of the CLEAN WATER project, was devised relying on the combination of the work carried out on the functionalisation of carbon nanotubes with the MC-LR analytical determination. The development of a sensitive, specific and rapid method for MC-LR detection well below the World Health Organization (WHO) provisional concentration limit of 1 µg/L for MC-LR in drinking water was thus achieved for the first time. The electrochemical biosensor was developed using dense, vertically aligned, mm-long MWCNT arrays grown by water-assisted chemical vapour deposition on catalytically patterned Si substrates. High temperature thermal treatment (2500 °C) in inert environment was applied to anneal structural defects and enhance the crystallinity of the pristine MWCNTs. The MWCNT electrodes were subsequently functionalised by electrochemical oxidation in alkaline solution in order to produce oxygenated surface groups. A high degree of oxygen functionalisation was verified by cyclic voltammetry, micro-Raman spectroscopy, XPS, and electrochemical impedance spectroscopy (EIS). These oxygenated surface groups provided the anchoring sites for cross-linking agents that enabled the immobilisation of MC-LR onto the MWCNT electrodes. Conjugation of monoclonal antibodies specific to MC-LR in the incubation solutions provided the required sensor specificity for toxin detection. The biosensor performance was evaluated by EIS that demonstrated a marked increase of the electron-transfer resistance upon MC-LR and antibody conjugation. A linear dependence of the electron-transfer resistance on the MC-LR concentration was observed in the range of 0.05 to 20 gL⁻¹, which enables cyanotoxin monitoring below 1 g/L for MC-LR in drinking water.

The novel TiO₂ photocatalysts prepared in previous stages of the project (ECT-1023t, N-, NF- and GO-TiO₂) have been evaluated at laboratory scale for the destruction of MC-LR, GSM and 2-MIB using UVA, solar and visible light. Identification of the major reaction intermediates and final products during the course of the photocatalytic processes have been performed by the developed analytical procedures, while commercial Aeroxide® P25, Kronos VLP 7000 and control TiO₂ nanopowders were used for comparison. Under UVA and solar light illumination all photocatalysts were highly effective for the complete degradation of the target compounds, exhibiting similar photocatalytic activity with that of the benchmark catalyst (Figure 23). Under visible light illumination, N- and NF-TiO₂ presented higher photocatalytic activity for MC-LR degradation than that of commercial Kronos TiO₂, while P25 and control TiO₂ catalysts were completely inactive.

Further evaluation of the catalysts activity was based on total organic carbon (TOC) and inorganic ion measurements concerning the mineralisation extent of the tested compounds. It was proved that for MC-LR, mineralisation higher than 90% was achieved under UVA and solar light illumination using N- and NF- doped TiO₂. In the case of GSM and MIB the mineralisation was higher than 90% utilising the GO-TiO₂ catalyst under solar light. These results confirmed the ability of the prepared photocatalysts to effectively degrade and mineralise the target compounds under UVA and solar light. Analysis of the stable reaction intermediates and final products for the destruction of MC-LR have shown that they can result mainly from hydroxyl radical attack on the benzene ring of Adda and substitution and cleavage the Adda conjugated diene structure. While the Adda moiety alone is not toxic, the stereochemistry and hydrophobicity of the Adda chain play critical roles in the toxicity of MC-LR.

Based on our results, we concluded that the MC-LR photocatalytic degradation results in the destruction of the Adda moiety structure of MC-LR, which is responsible for its toxicity. The above are in agreement with toxicity tests results. All tested photocatalysts eliminated the toxicity of MC-LR or toxic intermediates/byproducts produced during the photocatalytic treatment of water samples, as evaluated by PPIA and *Vibrio fischeri* bioluminescence assays. Photocatalytic experiments using a number of scavengers for the visible light degradation of MC-LR in water by the anion doped TiO₂ indicate that under visible light reactive oxygen species are generated via the oxygen reduction pathway rather than the oxidative reactions of photogenerated holes producing hydroxyl radicals that prevail under UV light.

Furthermore, evaluation of the materials performance as a function of several water parameters and natural water samples has shown that the pH and water alkalinity are major factor influencing the photocatalytic degradation rate of MC-LR, while the presence of natural organic matter had a detrimental impact on the photocatalytic efficiency. Taking into account all results we can conclude that the tested photocatalysts are highly photoreactive under UVA and solar light for the destruction of the tested compounds and elimination of their toxicity and can be further applied in lab and pilot-plant scale photoreactors.

WP6. Photocatalytic water detoxification III: edocrine disrupting compounds

Evaluation of the efficiency of the innovative photocatalysts for water detoxification by endocrine disrupting compounds (EDC) was an important target of the CLEAN WATER project. To address this objective in the most effective way, we developed a systematic methodology to assess the efficiency of materials according to several factors (WP6), where global impact evaluations were added to the kinetic studies of degradation of the target molecules.

HPLC-UV and LC/MS/MS methods were developed for the analysis and quantification of endocrine disrupting compounds, bisphenol A (BPA) and 17-estradiol (E2) and their degradation by-products at different concentration levels. In addition, tetracycline (TC) representing the pharmaceutical category of emerging pollutants with diverse impact on the environment and human health was added to the examined compounds. Three distinct tests were applied for the evaluation of the materials toxicity: a biodegradation (Sturm) test, an acute toxicity test (*Pseudomonas aeruginosa*) and an endocrine disruption test (WachtFrog).

The effect of heterogeneous TiO₂ photocatalysis was thus evaluated not only in terms of degradation/mineralisation efficiency but also toxicity and improvement in the biodegradability of the water pollutant and its photo-products. A decrease of the toxicity during tetracycline photocatalysis was thus established that was not accompanied by an increase of the biodegradability. Together with the identification of the main intermediates and the reaction mechanism it was shown that the tetracycline by-products are less toxic than tetracycline and like tetracycline, not biodegradable. Selected TiO₂ nanomaterials (ECT-1023t, N-modified TiO₂ and GOT) were evaluated for the photo-degradation of BPA and E2 under different illumination conditions controlled by a newly designed solar reactor. Among the different nanocatalysts ECT-1023t was the most efficient in terms of BPA conversion and mineralisation under UV light, whereas N-modified TiO₂ showed weaker but hardly affected performance by the illumination wavelength. Monitoring of the reaction intermediates has shown that the distribution and the nature of intermediates depend on the catalyst properties as well as the irradiation conditions.

Most importantly, investigation of the endocrine disrupting effect on BPA degradation has shown that the by-products generated when using the ECT-1023t catalyst under UV light, do not present any estrogenic effect, contrary to the commercial Aeroxide® P25 catalysts, validating further the application potential of the new photocatalyst.

WP7. Development of laboratory UV-vis membrane photoreactors

The development of an innovative photocatalytic membrane reactor has been successfully implemented within WP7, currently protected by an EU patent (EP2409954- Photocatalytic Purification Device). Several operation and design parameters of the reactor, the most important being the flow capacity, the pressure in the cell, the irradiation intensity, the distance between the reactor cell and the photocatalytic materials, the accommodation of the photocatalytic materials, and the thickness of the water film flowing on the annular membrane side, were evaluated and optimised. Particular emphasis was given to the accessibility of the active material to irradiation through a special Lamp Testing Unit. Thereby, it was established that a

continuous flow photoreaction process based on photocatalytic membranes and appropriately stabilised photocatalytic materials could be effectively applied for water purification. The membrane reactor was extensively used for the evaluation of the efficiency of the photocatalytic ceramic membranes produced in WP3.

Furthermore, incorporation of the composite alginate/TiO₂ porous fibers together with the central photocatalytic ceramic membranes in the developed reactor resulted in a continuous flow hybrid photocatalytic/ultrafiltration water treatment process that led to a three-fold enhancement of the pollutant removal efficiency, while the permeability of the ceramic membrane was enhanced in the presence of the fibers by almost 20%. This performance was achieved with 26 cm² and 31 cm² of membrane and stabilised photocatalyst surfaces, respectively. These results are particularly promising for the up-scaling of both membranes and fibres and the achievement of much higher water yields since the methods applied for the materials development (CVD and dry-wet phase inversion in a spinning set-up) are readily scalable and not expected to add significant cost to the water treatment process.

WP8. Up-scaling materials and processes: Large scale evaluation - process engineering

Based on the evaluation of the catalyst performance in WPs 4, 5 and 6, and a screening of their photocatalytic activity under natural solar irradiation, the most efficient powder catalysts were selected and upscaled (ECT-1023t, EST1023t and N-TiO₂) (objective 6). These nanocatalysts were subsequently tested at pilot plant scale for the removal of selected target pollutants (phenol, 2,4 -dichlorophenoxyacetic acid, imazalil sulphate, bentazon and basic red dye) representing the main water pollutant groups studied during the process development (phenolic compounds, pesticides, herbicides and azo-dyes), while commercial Aeroxide® P25 was used as reference. A pilot plant for solar photocatalytic detoxification, based on the technology patented by PSA (Plataforma Solar de Almeria, CIEMAT, Spanish Ministry of Science and Technology) and Ecosystem Environmental Services, S.A. Company, was specially designed and installed to carry out the validation tests of the scaled up catalysts and processes for the removal of target toxics from water.

The optimum operating conditions (catalyst loading, catalyst reuse, and catalyst settling) were accordingly determined at pilot plant scale, while toxicity studies on *Vibrio fischeri* (Microtox® toxicity test) were carried out to assess water detoxification. Overall, the efficiency of the innovative TiO₂ photocatalysts (ECT-1023t and EST1023t) at pilot plant for the degradation and mineralisation of the water pollutants under natural solar irradiation was higher than the commercial catalyst, while toxicity studies verified faster detoxification of water during the photocatalytic treatment by these catalysts. In addition, the ECT-1023t and EST1023t catalysts presented significantly higher ability for reuse upon consecutive photocatalytic cycles and lower catalyst losses than P25.

This behaviour is mainly due to the ease of the ECT-1023t and EST-1023t catalysts to settle even inside the plant pipes once the water flow stops. For this reason, the amount of these catalysts in the mixing tank decreases up to the second-third cycle. However, these catalysts are not strongly attached to the pipes or the tube inner walls

and can be easily re-suspended once the solution flow is restored and continue being active for the photocatalytic process.

Furthermore, the synthesis process for the best catalysts at pilot plant scale has been designed and the production cost has been evaluated. To assess the economic and technical feasibility of the produced technology, a solar photocatalytic plant for the treatment of waste waters from the cleaning of fungicide solutions in a banana packaging plant, a real societal problem in Canary Islands, which is a major banana producer in EU and at the same time dedicates many economic and energy resources to desalinate water due to water shortages. Cost analysis of the installation and operation of the designed solar photocatalytic wastewater treatment plant has been accordingly performed to be compared to other technologies.

The photocatalytic ceramic membranes that exhibited the best performance during their testing in were selected for up scaling. Besides the photocatalytic performance, the cost of up-scaled production, the easiness of up-scalability and the potential implications to the environment (i.e. waste effluents produced during manufacturing) were taken into account. Up scaling of the LBL-CVD/PCM, GOT4/PCM and N-TiO₂/PCM was accordingly performed by deposition of the photocatalytically active layers on both sides of pilot scale UF tubular alumina supports of ID 7 mm, OD 10 mm and length of 50 cm and nominal pore size of 5 nm and 10 nm. According to our patent concerning the novel photocatalytic purification device, involving PCMs and photocatalysts stabilised in the matrix of polymeric aerogel fibres, the up-scaled development (Figure 31) requires 24 PCM elements of 50 cm length in order to increase the reactor capacity to treat about 60 L/h of polluted water.

Leveraging of the new developments

Leveraging of the new developments achieved within the CLEAN WATER project in other application fields has been pursued by exploiting the new materials and reactor, i.e. air purification, solar energy conversion (dye sensitised solar cells) and hydrogen production. In particular:

Air purification

- The optimised NF-TiO₂ films were exploited as immobilised photocatalysts for the air purification and specifically in the photocatalytic oxidation of NO_x gas pollutants under UV and visible light. The films exhibited very efficient photocatalytic activity under visible light excitation with maximum percentage of NO removal equal to 24.2 %, one of the best reported up to now for visible light photocatalysis. Moreover, the NF-TiO₂ films presented excellent stability and reproducibility in successive light on-off experiments.
- The most promising photocatalytic materials (ECT-1023t, GOT composites and N-TiO₂) embedded into polymeric aerogel type hollow fibers were applied for NO_x and volatile organic compounds (VOCs) abatement in air using the developed reactor in a continuous flow photocatalytic air treatment process where the gas stream is forced to flow through the pore structure of the light transparent fibres in contact with the photocatalysts.

Dye sensitised solar cells

- The mesoporous NF-TiO₂ films with different fluorosurfactant ratio were utilised as photoelectrodes in dye sensitised solar cells (DSCs) with optimum photovoltaic efficiency of 3 %, a promising result if we take into account the relatively small (2.5 µm) film thickness that is far below that of conventional DSC photoelectrodes (~15 µm). Most importantly, these DSCs have shown a large photopotential of more than 800 mV, which is among the highest ever reported for iodide/triiodide based electrolytes.
- The most active GOT composites were utilised as counter electrode (CE) in DSCs. Cells fabricated with N719 dye in combination with LiI/I₂ and tertbutyl pyridine-based electrolytes, were submitted to thermal annealing/light soaking to induce degradation giving very promising results on the thermal stability of cells, while process optimisation is underway to compete the performance of conventional Pt-CEs.

Hydrogen production by photocatalysis

Hydrogen is a promising energetic vector that can be produced by clean processes such as water splitting. In this process only water, solar energy and a photocatalyst are required. The GOT composite are currently under evaluation for water splitting, since commercial TiO₂ photocatalysts containing carbon (such as Kronos vlp7000) have already proved to be effective materials for this process.

Potential Impact:

Nowadays, the world is facing formidable challenges in meeting rising demands of clean water as the available supplies of freshwater are decreasing due to extended droughts, population growth, and more stringent health-based regulations. Besides the shortages of potable water, the presence of chemicals with serious adverse health effects, even at extremely small concentrations, as well as sporadic epidemics from waterborne infectious diseases, have imposed serious considerations for the quality of drinking water emphasising the need for advanced treatment methods. Recently, the EU Commission Services launched a new directive where new Environmental Quality Standards (EQS) for hazardous priority substances have been defined within Europe. In particular, pesticides and phenols are referred, with admissible thresholds lower than 0.5 microgram per litre in water. This legislation aims at:

- (1) overall reduction in human exposure to chemical pollutants as a result of water, seafood, meat and milk consumption;
- (2) minimisation of human impact in sensitive eco-systems and biodiversity;
- (3) improvement of soil quality irrigated from natural water sources; and
- (4) increase of the sludge quality for disposal in agricultural lands.

Thus, implementation of adapted technologies to comply with EU legislation for these specific pollutants is needed.

The need for strong support to research activities aiming at developing new environmental technologies towards sustainable solutions of environmental problems has been accordingly recognised as a strategic priority in FP7 Cooperation Work Programme 2008: Environment, projected in the activity 6.3 Environmental Activities. Close coordination and shared information between different Themes of the Cooperation Specific Programme regarding their contribution to environmental technologies has born the Cross-thematic approach implemented through the joint call between Theme 6 Environment and Theme 4 Nanosciences, Nanotechnologies, Materials and New Production Technologies (call identifier FP7-ENV-NMP-2008-2), on the topic “Nanotechnologies for water treatment”. This action aimed at supporting research and technological development in the field of water treatment by applying developed or adapted nanoengineered materials to promising separation, purification and/or detoxification technologies. The expected impact of the specific topic involves the development and uptake of innovative and cost-efficient water treatment technologies benefiting from progress and advances made in nano-sciences, materials and technologies.

The general aim of the CLEAN WATER funded under the latter call was the development of efficient and viable water detoxification technology exploiting solar energy and recent advances in nanoengineered titania photocatalysts and membranes for the destruction of extremely hazardous compounds in water, including novel emerging pollutants (toxins, hormones) of high environmental and health impact. This target has been implemented by combining a wide range of diverse research activities ranging from the development of titania based nanomaterials and membranes to reactor engineering and analytical methods for the detection of recalcitrant water

pollutants as well as pilot plant scale studies and cost analysis materials and processes for water purification.

- The integrated R&D efforts of the consortium members resulted in the synthesis of highly reactive TiO₂ photocatalysts (ECT-1023t and EST-1023t) with markedly improved performance for water detoxification under solar light exceeding that of commercially available titania photocatalysts. Furthermore, the CLEAN WATER project provided significant advances in the development of innovative visible light responding nanocatalysts based on anion (N, F, S, C) doped TiO₂ with tailor designed physicochemical properties and advanced composites of TiO₂ with carbon nanomaterials (carbon nanotubes and graphene oxide) with unique reactivity under visible and solar light. Validation of the selected photocatalysts for the photodegradation and mineralisation of a wide range of water pollutants (phenolic compounds, pesticides, herbicides, azo-dyes as well as caffeine and diphenhydramine) at both laboratory and most importantly pilot plant scale together with the determination of the optimum operating conditions (catalyst loading, catalyst reuse, and catalyst settling) and toxicity evaluation renders these nanocatalysts very promising for photocatalytic water treatment under solar light. Apart from the ensuing advances concerning the state of the art synthesis of TiO₂ photocatalytic nanomaterials and the concomitant high impact on the potential of heterogeneous semiconductor photocatalysis as an advanced oxidation process, the newly developed photocatalysts based on the corresponding production cost analysis can be directly applied in solar photocatalytic wastewater treatment plants using slurry photocatalysts.

The project has also strong societal impact by addressing a serious and emerging environmental problem as significant efforts by the consortium partners were devoted to the quantification, monitoring and detoxification of specific pathogenic pollutants including cyanobacterial toxins, geosmin and endocrine disrupting compounds as well as phenols, pesticides and azo-dyes in water supplies and natural waters, touching upon direct societal needs for the control of water quality.

- In particular, there has been increasing concern of human health impacts of cyanobacteria (blue green algae) in drinking water reservoirs worldwide. Cyanobacteria not only produce taste and odour compounds but also have the ability to produce lethal toxic compounds, called cyanotoxins, which were found responsible for several incidents of wild and domestic animal poisoning as well as human injury and death due to toxic cyanobacteria blooms. Hepatotoxic cyclic peptide toxins (microcystins, MCs) are the most widespread cyanotoxins that are present in diverse environments. MCs are cyclic heptapeptides that are produced by cyanobacteria belonging to the genera *Microcystis*, *Anabaena*, *Plankothrix*, *Nostoc* and *Snowella*, and it is likely that more genera of cyanobacteria will be identified as microcystin producers in the future. About 80 MC variants have been identified so far in natural water samples and cyanobacterial cultures, with microcystin-LR (MC-LR) being the most common and most toxic variant. Environmental awareness has recently arisen on Endocrine disrupting compounds (EDC) that can interfere with the normal endocrine function of wildlife and possibly humans by mimicking or antagonising the effects of hormones, by altering the pattern of synthesis and metabolism of hormones and by modifying hormone receptor levels. Due to the large variety of suspected EDC, it is probable that humans and animals are exposed not to a single agent, but a mixture of multiple endocrine disrupting agents. EDC are suspected of entering rivers, streams

and surface waters through the effluents of wastewater treatment plants (WWTP). Previous works have shown that TiO₂ photocatalysis has the potential to degrade efficiently EDC compounds under UV light. However, use of UV-visible photocatalysts for EDC photodegradation at low concentration (µg/L) together with the identification of the reaction intermediates and their toxicity remains a major challenge. The innovative TiO₂ based nanocatalysts developed within CLEAN WATER have been verified to be very effective in water detoxification by the most hazardous cyanobacterial microcystin-LR, the taste and odour pollutants geosmin and 2-methylisoborneol as well as the endocrine disrupting compounds (17-estradiol, bisphenol-A and tetracycline) and their by-products during the photocatalytic reaction. The outcome of this research is of high importance for the destruction, detection, and the understanding of these emerging environmental contaminants that have been classified as chemical and biological warfare agents.

A major impact of the CLEAN WATER project is foreseen by the development of double side photocatalytically active ultrafiltration membranes operating at high flux and low trans-membrane pressure with high photocatalytic and rejection efficiency for water pollutants combined with enhanced antifouling and hydrophilicity as well as minimal generation of toxic condensates in their retentate side. Implementation of this challenging task enabled the development of an innovative continuous flow photocatalytic membrane reactor (EP2409954- Photocatalytic Purification Device) incorporating the photocatalytic ceramic membranes and the novel nanomaterials immobilised on alginate polymeric fibers. Thereby, a major target of the CLEAN WATER project has been accomplished i.e. the merging of advanced oxidation processes and in particular TiO₂ photocatalysis with nano/ultrafiltration membrane technology in a sustainable water purification device. This innovative approach has the potential to “leap-frog” the application of TiO₂ photocatalysis and membranes for enhancing water quality through the development of an advanced technology that offers multiple functions in water treatment (separation, disinfection, organic destruction, and anti-biofouling). The basis for an Advanced Oxidation Photocatalytic Membrane Process has been thus established in a versatile continuous flow disinfection and oxidation technology that can be scaled without loss of efficiency. The developed reactor affords degradation of organic pollutants in three photocatalytically active surfaces and combines the retention efficiency of nanofiltration or ultrafiltration with the high efficiency of UV-Vis active photocatalysts.

Step-up changes in water treatment technologies are thus envisaged in terms of improving treatment performance and reducing energy requirements as well as scale up of the materials and procedures, attractive for industrial applications in water supplies. The combined photocatalytic-membrane process can be fruitfully applied in the following markets:

- Water cleaning: offering efficient and cost-effective treatment for color, taste, and odour issues in municipal drinking water supplies with low operating cost, and minimal waste production.
- Water reuse: offering high-performance destruction of recalcitrant organic compounds in municipal water, to enable safe, sustainable and environmentally friendly municipal and industrial water reuse.

- Remediation: offering the most efficient and cost-effective methods for non-selective removal and clean-up of contaminated sites from a wide range of organic contaminants with different health, safety and compliance considerations.

The technical challenges involved in developing a viable water detoxification technology for the destruction of extremely hazardous toxins and pollutants in water based on nano-engineered photocatalytic materials and membranes were very high. Uptake of such a task was confronted by combining and integrating the professional skills and the participation of experts from diverse scientific fields, including chemical and environmental engineers, chemists, physicists and a variety of materials scientists. By grouping skills from six EU member countries and a leading expert in photocatalytic water treatment from USA, the consortium brought together in a multidisciplinary approach partners specialised in advanced oxidation processes, environmental engineering, TiO₂ photocatalysis, membrane manufactory, and water supply and distribution ensuring the development of effective and competitive technology that will undoubtedly contribute to strengthening European competitiveness in the water sector.

Main dissemination activities and exploitation of results:

Dissemination of the project foreground was keenly pursued within the borderline of the project partnership and most importantly beyond the Consortium, aiming to attract the interest of third-party organisations, both European and international, employing the following routes:

- Dissemination through publications and communications in peer-reviewed scientific journal and proceedings of relevant international and national conferences as well as EU funded workshops. This activity resulted up to now in 48 publications in prestigious journals in the field, e.g. Applied Catalysis B: Environmental, Journal of Hazardous Materials and Water Research together with several editorials and 152 presentations in Water and AOT related conferences and workshops worldwide.
- Dissemination through the creation of a dedicated Clean Water web site providing the channel for information flow both within and outside the Consortium.
- Active participation in the Nano4water Cluster, a coalition of several research projects, funded by the European Commission under FP7 on Nanotechnology-based Water Purification Methods <http://nano4water.eu/index.php?id=34> and the corresponding dissemination Workshops.
- Significant contribution to the creation of EPF (European Photocatalysis Federation) and Release of CLEAN WATER to the website of EPF (please see <http://www.photocatalysis-federation.eu> online).
- Contacts and collaboration with potential end-users.

A number of achievements concerning both materials and processes accomplished by the CLEAN WATER consortium are of particular importance for further dissemination and exploitation:

- The best performing bare TiO₂ photocatalysts under solar light i.e. the ECT-1023t and its analogue EST-1023t for which a patent has been filed, which are highly competent photocatalysts in powder form.
- The anion doped and N modified TiO₂ visible light responding nanomaterials, especially upon immobilisation on rigid substrates (e.g. thin films, fibers, coatings) for water detoxification.
- The optimised graphene oxide TiO₂ (GOT) nanocomposites both as powder and immobilised photocatalysts under solar light.
- The optimised carbon nanotube-TiO₂ composites, which are very efficient photocatalysts in the form of films and, therefore, more appropriate for flat-plate photoreactors.
- The photocatalytic ceramic membranes prepared by either CVD or sol-gel spin coating (the most easily manufactured being those produced by the Layer by Layer CVD technique).
- The patented continuous flow photocatalytic purification device that combines photocatalytic ceramic membranes and the photocatalytic nanomaterials immobilised on alginate polymeric fibres.
- The new analytical methods developed for emerging environmental pollutants including harmful cyanobacterial toxins (microcystin-LR), bad odour and taste compounds (geosmin, 2-methylisoborneol), endocrine disruptors (17 β -estradiol, bisphenol-A) and pharmaceuticals pollutants (tetracycline, DPA) as well as the novel

(multi-walled carbon nanotube based) electrochemical biosensor for direct MC-LR detection in water.

Moreover, the fundamental concepts on nanostructured materials synthesis, functionalisation, and bio-recognition can be applied in the preparation of other nanostructured ceramic support materials, membranes, nanotubes, photovoltaics, fuel cells, sensors with high surface area, monitoring devices for biological and chemicals warfare agents, and surfaces with outdoor and indoor self-cleaning and disinfection properties. Potential markets also include chemical, pharmaceutical, and environmental industries (catalysis, chemical synthesis, electrochemistry, separations). In fact, leveraging of the new developments achieved within the CLEAN WATER project has been already pursued by the consortium members by exploiting the new materials and reactor in other application fields, i.e. air purification, solar energy conversion (dye sensitised solar cells) and hydrogen production with very promising results.

Project website:

<http://www.photocleanwater.eu/>

CLEAN WATER consortium

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