EC Project

INNOWATECH

Innovative and integrated technologies for the treatment of industrial wastewater

Specific Targeted Research Project
(Contract n° 036882)

Thematic Priority 'Global Change and Ecosystems'

Publishable Final Activity Report

Period covered: 01.11.2006 - 31.03.2010

Date of preparation: 2nd May 2010

Start date of project: 01.11.2006

Duration: 41 month

Project coordinator name: Dr. Antonio Lopez

Consiglio Nazionale delle Ricerche
Istituto di Ricerca Sulle Acque
Sede di Bari
Via Francesco De Blasio, 5
70132 Bari
Italy

Phone: +39-080-5820550
Fax: +39-080-5313365
e-mail: antonio.lopez@ba.irsa.cnr.it

Table of Contents

1. SUMMARY DESCRIPTION OF PROJECT OBJECTIVES

The main objective of INNOWATECH has been to investigate, assess and enhance the potential of promising technological options (i.e., technologies, processes and concepts) for the treatment of industrial wastewater. The intended aim of the project was to provide effective solutions to end-users for the treatment of a wide range of wastewaters. The presented solutions have been based on the integration of the investigated options and improvements in existing technologies with respect to system components, operation and control. Specific objectives have been:

- Investigating and enhancing the performances of promising wastewater treatment options, namely: aerobic granulation, advanced oxidation processes (AOP) integrated with biological processes and membrane-based hybrid processes (i.e., membrane contactors and membrane chemical reactors);
- Achieving fundamental and technological knowledge advancements necessary for advanced wastewater treatment application in different industrial sectors;
- Assessing the economic and environmental sustainability of the considered wastewater treatment options;
- Outlining integrated tailor-made solutions for end-users in different industrial sectors;
- Transferring the developed know-how to potential end-users inside and outside the project;
- Contributing to enhancing the EU Water Industry competitiveness.

In order to achieve such objectives, coordinated research activities have been planned for treating, by the selected technological options, wastewaters produced by different sectors such as Food-, Pesticides-, Pharmaceutical- and Chemical-Industry. In addition, mature landfill leachates have been included because of their inherent treatment difficulty (i.e., scarce biodegradability and high qualitative complexity) and so can be considered a sort of “benchmark” in the sector.

The results from the parallel activities have been merged to define solutions for end-users which are appropriate across other industrial sectors. A major goal of the project was the definition of treatment needs within a consensus framework appropriate for a wide range of wastewaters based on the particular features of the options investigated. The approach enabled the consideration of technology-industrial wastewater links to be made beyond those directly investigated such that single processes, or combination of processes, may have potential applications in areas which have not been investigated in the project.

A summary of relevant problems encountered and the respective solutions proposed and investigated in INNOWATECH is provided in the table below.

Problems	Solutions
Inefficient biological treatment lacking in operational flexibility and stability as well as high sludge production	Systems based on aerobic biomass granulation
Recalcitrant and/or toxic compounds impairing wastewater biodegradability	Advanced oxidation processes integrated with biological processes
Lack of technologies for selective removal or recovery of raw materials and/or priority organic pollutants	Membrane hybrid technologies such as Membrane Contactors and Membrane Chemical Reactors
Non-ideal combination and adaptation of treatment options for specific processes	LCA and LCC Methodologies and models for evaluating economical and ecological sustainability as well as systems integration

In INNOWATECH, the investigated innovative and/or promising technological options have been selected on the basis of their potentiality for treating different kinds of wastewaters whose features are common to several and vast industrial sectors and/or because of their new treatment-concept.
In conclusion, INNOWATECH aimed at providing effective technological solutions for the treatment of industrial wastewater. Such solutions are vital for supporting and enhancing the European competitiveness of different industrial sectors, including the water technology sector.

WP1: Aerobic granulation

Technologies utilizing aerobic granular sludge are a relatively new option with only a few published studies available to date. In particular, application to industrial wastewaters has not been significantly investigated such that the specific influences of process parameters important for industrial applications are yet to be clarified. Accordingly, more insight is needed with regards to granule formation and composition as well as an understanding of how to scale up results from laboratory studies to practical industrial scale. Therefore, in this WP1, granule formation has been investigated at micro-organisms, granule and reactor level.

The specific objectives were:

- Obtaining insight in the structure of aerobic granules by using FISH techniques on sliced granules;
- Investigating the influence of particulate and polymeric COD (such as fats, proteins, starch, suspended solids) on granule morphology and removal pathways;
- Optimising the simultaneous COD, N and P removal in highly contaminated wastewater (e.g. slaughterhouse effluent);
- Studying the influence of high temperatures (30°C-55°C) on granule formation and conversion processes;
- Studying the influence of toxic compounds on granule activity;
- Investigating and optimising treatment of landfill leachate with a Sequencing Batch Biofilter Granular Reactor (SBBGR) in combination with ozonation;
- Investigating and optimising treatment of different wastewaters (e.g. from slaughterhouse and from food industry) following appropriate technologies (such as the commercial technologies -UniFed and the Nereda^{TM} system)

WP2: Coupling advanced oxidation processes with biological treatment

Many industrial wastewaters are recalcitrant to biological treatment requiring expansive and complicated downstream polishing. In recent times consideration has been started to be given towards the integration of advanced oxidation processes (AOP) with enhanced biological processes as a means to overcome this barrier. Accordingly, the aim of this work package has been to provide optimized technical solutions exploiting the combination of highly effective chemical oxidations and cost-efficient biodegradation processes.

The specific objectives were:

- Optimization of biological treatment coupled to ozone (BIOZO concept) for landfill leachate treatment.
- Definition and optimization of the integration of AOPs (photo-Fenton, O3 and/or UV/H2O2) with membrane bioreactor (MBR) with a specific focus on microbiological characterization.
- Investigating the efficacy of the treatment of wastewater contaminated with recalcitrant components originating from synthesis process from pharmaceutical industry and from pesticide industry with a solar Fentons process coupled to a biological fixed film reactor.

- Systematic assessment of the photodegradability of selected model compounds representative for non-biodegradable and/ or toxic contaminants.
- Development of a novel immobilized photochemical catalyst on polymeric membranes for enhanced AOP efficiency.

WP3: Membrane based intensification of wastewater treatment processes

Membrane based processes are commonly utilized for industrial wastewater treatment such that many recent developments in membrane first found application in industrial wastewater treatment. Accordingly the aim of this work package was to investigate the potential of two novel hybrid membrane processes for future uptake into the industrial wastewater treatment sector with specific focus on the treatment of hazardous priority pollutants. The two technologies were:

- A Membrane Chemical Reactor (MCR), which combines a photo catalytic reactor with a membrane filtration unit to retain the TiO_2 catalyst.
- A Membrane Contactor (MC), which utilizes a coated membrane for the reactive extraction of phenols with caustic soda.

In both cases the work focused on developing the technology for industrial wastewater treatment and so specific objectives were:

- The development of lab- and pilot-scale treatment units,
- The evaluation of their performance and their technical limitations,
- System optimization and scale-up.

WP4: Tailor-made solutions for end users

The development of novel technologies or treatment trains can only be successful if achieved within an appropriate economic and ecological framework. Accordingly, the aim of this work package was to find the ecologically most sustainable and economically most feasible treatment system for a given treatment case from a holistic perspective, i.e. considering all consequences of building and operating the system.

The specific objectives were:

- Life-cycle assessments of existing treatment systems - Develop computational models and a basic database for case studies, including waste treatment.
- Modeling and assessment of the new treatment technologies as part of treatment systems**.**
- Preliminary economic evaluations.

Once the overall objective and especially sub-objective 2 was successfully reached, a further objective was pursued:

- Identification of additional end-user cases not studied in the project.

2. SUMMARY OF THE ACHIEVED RESULTS

The activities carried out have generated relevant and innovative results which, if appropriately exploited, will enhance the European (Water) Industry's competitiveness. These results can be summarized as: **new concepts**, **processes** and **technologies** for wastewater (WW) treatment with benefits regarding the stability of the effluent quality, energy and operational cost savings, and the protection of the environment. More specifically:

- The further development of aerobic granular biomass based systems together with accurate biomass characterization, through new or adapted protocols, have enabled the demonstration of the efficacy of the technology towards industrial wastewater treatment (e.g., food industry WW). The novel technology was shown to require a smaller footprint and procude less excess sludge compared to traditional alternatives.
- When treating complex wastewater (e.g., mature municipal landfill leachates or pharmaceutical WW), the integration of biological and chemical treatments results in synergistic effects that generate cost saving and increased treatment efficacy.
- Utilization of solar light in photochemical reactors enables chemical and energy savings without detriment to the effectiveness of the process for the treatment of wastewaters containing toxic pollutants such as pharmaceutical WW or liquid streams containing pesticides.
- Innovative methods for immobilizing photo-catalysts on the surface of commercial polymers have been developed. The obtained photo-catalysts work at near neutral pH greatly enhancing the technologies appropriateness for a range of wastewaters. Specific benefits were demonstrated with regards to reduced chemical sludge production and the ability to regenerate the catalyst under solar irradiation.
- Innovative silicone coated selective membranes were developed for use in the Membrane Contactor which was then optimized enabling the recovery of organic acids and bases economically appropriate for small- and medium-scale applications in the chemical industry.
- Key development issues required to utilize the membrane coupled photo-catalysis reactor were identified and overcome demonstrating the efficacy of the technology to a number of industrial wastewaters a resulting in a suggested design for the technology when applied to industrial wastewater treatment.
- Definition and application of conceptual models of existing treatment systems as well as the assessment of suitable software for LCA and LCC modeling of case studies was completed to compare the sustainability of the investigated technologies.

3. PROJECT CONSORTIUM AND COORDINATION

The project's consortium (Table 1) consisted of 17 partners: 16 from 8 European Countries and 1 from Australia. The partners have complementary roles and competences; they cover 5 universities, 3 research institutions, 6 specialised SMEs and 3 commercial organizations.

Table 1. The INNOWATECH Consortium

Partic. Role*	**Partic. N°**	Participant name	**Participant short name**	**Country**	**Date enter project**	**Date exit project**
CO	1	CNR - Istituto di Ricerca Sulle Acque	IRSA	Italy	month 1	month 41
CR	2	Aachen University of Technology	RWTH	Germany	month 1	month 41
CR	3	Technical University Delft	TUD	The Netherlands	month 1	month 41
CR	4	Swedish Environmental Research Institute Ltd	IVL	Sweden	month 1	month 41
CR	5	Cranfield University	CRAN	United Kingdom	month 1	month 41
CR	6	Swiss Federal Institute of Technology	EPFL	Switzerland	month 1	month 41
CR	7	Plataforma Solar de Almería	PSA	Spain	month 1	month 41
CR	8	Norwegian Institute for Water Research	NIVA	Norway	month 1	month 41
CR	9	SolSep BV	SOLSEP	The Netherlands	month 1	month 41
CR	10	Bayer MaterialScience AG	BAYER	Germany	month 1	month 41
CR	11	ITT Wedeco	WEDECO	Germany	month 1	month 41
CR	12	Austep S.r.l.	AUSTEP	Italy	month 1	month 41
CR	13	Albaida Recursos Naturales y Medio Ambiente	ALBA	Spain	month 1	month 41
CR	14	AnoxKaldnes	ANOX	Sweden	month 1	month 41
CR	15	Water Innovate Ltd	WAT-INN	United Kingdom	month 1	month 41
CR	16	DHV	DHV	The Netherlands	month 1	month 41
CR	17	Advanced Wastewater Management Centre	AWMC	Australia	month 10	month 41

*CO = Coordinator   *CR = Contractor

The project is coordinated by Consiglio Nazionale delle Ricerche (CNR) – Istituto di Ricerca sulle Acque (IRSA). The coordinator contact details are:

Dr. Antonio Lopez
Consiglio Nazionale delle Ricerche
Istituto di Ricerca Sulle Acque
Sede di Bari

Via Francesco De Blasio, 5
70132 Bari
Italy

Phone: +39-080-5820550
Fax :   +39 080 5313365
e-mail: antonio.lopez@ba.irsa.cnr.it

4. METHODOLOGIES, APPROACHES AND RESULTS

To achieve its objectives, the project has been structured in six WP_i (work-packages): WP1 (Aerobic Granulation), WP2 (Coupling Advanced Oxidation Processes with Biological Treatment), WP3 (Membrane based intensification of wastewater Treatment Processes), WP4 (Tailor made solutions for end-users), WP5 (Dissemination and exploitation) and WP6 (Project management). In WP1, WP2 and WP3 different industrial wastewater or liquid waste streams representing relevant industrial activities were treated by selected promising and innovative technologies to solve the inherent treatment difficulties of each stream. Through an iterative process, ecological sustainability and economic feasibility of the tested and iteratively improved technologies have been assessed in WP4 by life cycle assessment (LCA) and life cycle costing (LCC) methodologies to outline tailor made solutions to end-users. In WP5 results from the project have been disseminated and exploited inside and outside the project. WP6 manage the whole project with the connection between the WPs illustrated in Figure 1.

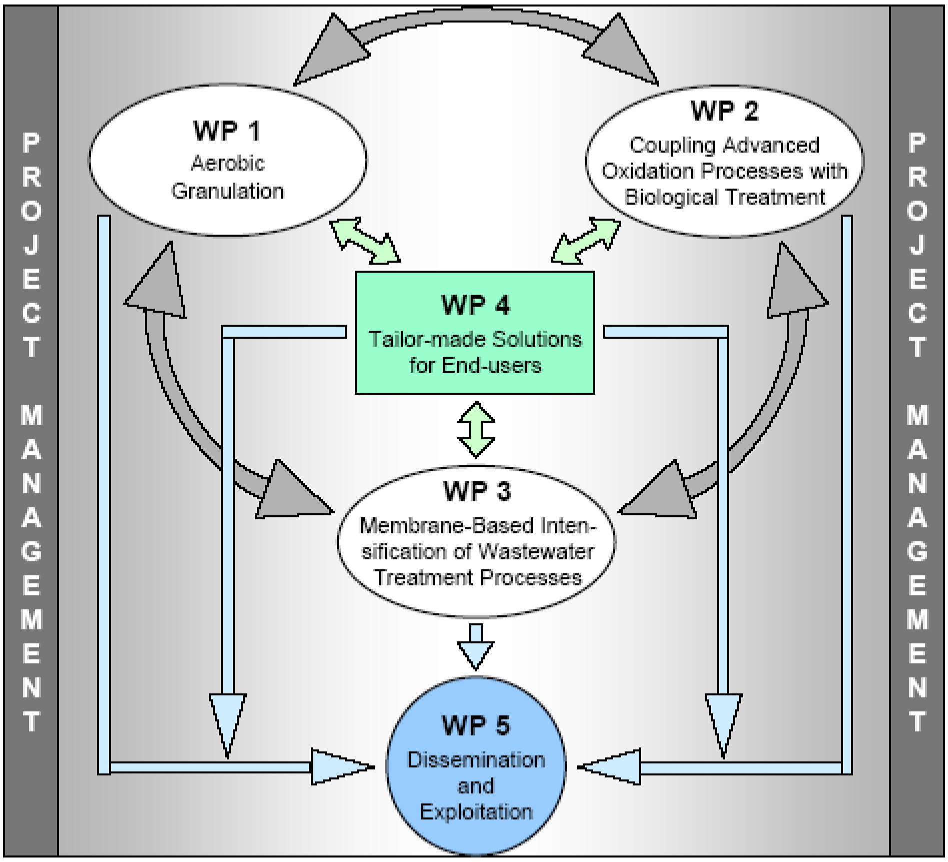


Fig.1: The INNOWATECH work packages and their main interconnections

WP1: AEROBIC GRANULATION

BACKGROUND

Among the novel biological technologies recently developed for wastewater treatment, perhaps the most promising are systems based on aerobic granular biomass. In such systems, the microorganisms grow in granules, instead of flocs, characterized by high settling velocity allowing greater biomass retention in the reactor, with interesting repercussions in terms of substrate conversion capacities, area requirement, sludge production and operative costs. Aerobic granular sludge has been developed in laboratory systems and first applied to municipal wastewater with very limited consideration given to its application towards industrial wastewater treatment. However, the attributes described above also apply for industrial wastewaters such that aerobic granular sludge systems offer opportunities due to their compactness and low energy requirements. In fact, industrial effluents usually contain complex substrates, toxic pollutants and particular pH and temperature conditions which can greatly affect granule formation and reactor performance. Consequently, the focus of this WP was to understand the capabilities and limitation of utilizing aerobic granules for this new application area. To achieve this aim the WP was subdivided into a number of key questions that needed to be addressed concerning:

- The effects of complex polymeric COD, elevated temperature and toxic compounds on granular sludge formation and stability;
- The effectiveness of coupling ozone with an aerobic granular reactor (SBBGR system) for treating a recalcitrant wastewater (illustrated as a mature municipal landfill leachate);
- Specific investigation into the microbial composition and structure of granular biomass under the different options.
- Assessment of the best management option of granular sludge produced during real wastewaters;

To achieve the above within an industrially relevant framework three different configurations of aerobic granular reactor (Nereda, SBBGR and Unifed system) were utilized for the treatment of a range of wastewaters including landfill leachate, slaughterhouse effluent and food wastewater

METHODOLOGIES AND RESULTS.

Effects of complex polymeric COD, elevated temperature and toxic compounds on granular sludge formation and stability

The activity was largely performed on lab scale aerobic granular sludge systems which where operated as SBR processes with a typical cycle consisting of: anaerobic feeding/effluent discharge (like in a sludge blanket reactor), anaerobic reaction time, aerobic reaction time and settling period. The reactors where fully automated and provided with on-line off gas measurements. In addition, soluble compound concentrations where monitored by off-line analysis and the formation of granular sludge was studied by Image Analysis.
To directly investigate the impact of the nature of COD on the process both particulate (PP) and soluble starch (SS) was used for studying the formation of granular sludge sources. The results obtained showed that aerobic granular sludge can be maintained on solely particulate substrate, although settling characteristics decreased. In both cases, starch was adsorbed onto the granules and

hydrolysed on the granule surface. This led to an extended feast phase during the aeration period (total aeration availability of external substrate with PS and approximately 2/3 of the aeration period with SS) resulting in the generation of finger-type structures and the growth of filaments. A very low growth yield in the particulate starch reactor (0.22 gCOD/gCOD for PS and 0.24 gCOD/gCOD for SS) was observed which indicates that at least a significant part of the starch will be removed through a non heterotrophic catabolic mechanism. The impact of this suggests that slowly biodegradable substrates will potentially retard nutrient removal (N and P) compared to operation with soluble substrates. The reason for this is that the substrate will not penetrate in and be stored in the regions inside the granules where it could be used for denitrification. Instead, most of the substrate stays on the outside of the granule, together with oxygen and will be oxidised directly after hydrolysis. Only the hydrolysed and stored part during the anaerobic feeding could contribute to denitrification. Similarly, for phosphate removal it is possible to conclude the same, since phosphate accumulating organisms also need a substrate rich anaerobic period in which they can consume enough substrate to outcompete other heterotrophs (as in normal biological P-removal). Also this will not be reached when the ratio suspended COD/dissolved COD or slowly biodegradable COD/readily biodegradable substrate is too high. Therefore in practice, it would be advantageous to remove suspended solids from the influent or have a pre-fermentation in a buffer tank.

To understand the impact of temperature, laboratory scale aerobic granular sludge reactors were operated at 30, 45 and 55°C which were compared with previous studies performed with granular biomass at 20, 15 and 8°C. During the experiments aerobic granules were formed at all the tested mesophilic temperatures (30-45°C), and could be maintained at the thermophilic temperature tested (50°C). Biomass in the granular reactor appears to be more stable at elevated temperatures than reported for activated sludge in literature as sludge bulking and excessive biomass wash-out did not occur. Additionally, enhanced stability was also observed in regards to phosphate inhibition as a function of temperature although nitrogen removal inhibition was similar to that observed in traditional plants. Overall the adaption of aerobic granules appears to provide a greater stability at elevated temperatures and so require less temperature control than traditional plants.

Regarding toxic compounds, the effects of salt, pH and 2-fluorophenol (2FP) on ammonia oxidizing bacteria (AOB) and on phosphate accumulating organisms (PAO) in aerobic granules were evaluated. Short term effects of salt, pH and 2FP experiments were performed in batch at room temperature (20ºC). Results were compared with activated sludge and crushed granular sludge. Ranges of 0-50 g NaCl/L were tested for salt effect, 5-10 for pH effect and 0-200 mg/L for 2FP effect. The long term effects of salt on aerobic granular sludge was also studied and was carried out in a laboratory scale aerobic granular sludge reactor. From the short term laboratory scale experiments with salt, pH and 2FP it was concluded that AOB and PAO in granular sludge are less affected by these inhibitive compounds than in activated sludge and crushed granular sludge. This suggests that the compact granular structure provide microorganisms with a beneficial protection from toxicity. However, AOB are much more sensitive to toxicity than PAO. For all the ranges tested for each compound, PAO were always active, except for 50 gNaCl/L, while AOB were not. From the long term laboratory scale experiments with salt some preliminary conclusions can be drawn. Neither PAO nor AOB were really affected by 10 g/L NaCl. Moreover, for concentrations up to 40 g/L, AOB still had some activity, allowing the conversion of ammonium to nitrate. Overall, at long term, PAO seemed to be more sensitive to increasing salinities than AOB which could be related to the accumulation of nitrite in the process.

Effectiveness of coupling ozone with an aerobic granular reactor

An innovative process consisting of a pre-treatment step for ammonia removal via struvite ($MgNH_4PO_4$) precipitation followed by ozone enhanced biological degradation carried out in a SBBGR system (Sequencing Batch Biofilter Granular Reactor) was tested at laboratory scale (Figure WP1.1 – right side). The pre-treatment unit consisted of a clariflocculator equipped with a mixer, two pumps for dosing chemicals (i.e., H_3PO_4, NaOH) and a pH controller, operated in batch mode. The operating sequence involved initially slowly adding the required amount of MgO powder to the leachate followed by H_3PO_4 with NaOH added when the pH dropped to a set value. Once all the necessary amount of phosphoric acid had been added, the content of clarifier was stirred slowly until equilibrium after which the mixing was stopped and the contents allowed to settle. The chemically enhanced biological treatment unit consisted of a biological (based on SBBGR system) and chemical (based on ozone dosage) oxidation compartment (see Figure WP1.1). SBBGR is a periodic biofilter in which the biomass grows mainly as granules characterized by very high density; these granules are entrapped in the pores produced by packing the reactor with a filling material which allows greater biomass retention in the reactor to be obtained (up to one magnitude order higher than that recorded in conventional biological systems). The SBBGR used in this project consisted of a cylindrical reactor partly filled with biomass support material (wheel shaped plastic elements) packed between two sieves and aerated by air injection through porous stones placed close to the upper sieve. An external loop allowed wastewater re-circulation through the filling material in order to obtain a homogeneous distribution of substrate and oxygen. Activated sludge from the municipal treatment plant of Bari (a town of Southern Italy) was used as an inoculum of SBBGR. The chemical oxidation compartment consisted (see Figure WP1.1 – left side) of pump P_O which circulated the biologically treated wastewater from the SBBGR through a glass bubble column for ozone contact. Ozone was supplied through a porous distributor with the ozone produced from pure oxygen by means of an ozone generator (model: Modular 8HC, WEDECO, Germany). The column was supplied with a residual ozone destroyer and ozone meter.

The operation of the chemically enhanced biological treatment unit was based on the succession of treatment cycles each consisting of four consecutive phases: filling, biological degradation, biological degradation + ozonation, and drawing. During the filling phase, a fixed volume of supernatant from the clariflocculator was added to the liquid volume retained by SBBGR from the previous treatment cycle. In the biological degradation phase, during which the ozonation unit remained switched off in order to permit the biological removal of biodegradable pollutants, the liquid in the reactor was continuously aerated and recycled through the biomass supporting material. In the successive phase (i.e., "biological degradation + ozonation" phase), the biological degradation was enhanced by activating the ozone compartment (i.e., by switching on pump Po and the ozone generator). During this phase, two liquid flows were simultaneously present in the plant: the first (operated by pump Po) was aimed at producing biodegradable compounds by means of the partial chemical oxidation of recalcitrant pollutants in ozone reactor, while the second (operated by pump P_R), was aimed at removing these products in the biological unit. Finally, the treated wastewater was withdrawn by gravity from the biological compartment (by means of the motorised valve, $V_{M,}$ see Figure WP1.1) and the plant was ready to start a new treatment cycle. Three treatment cycle per day were carried out. The plant was fed with a real leachate coming from a mature municipal landfill located in Apulia, a region of southern Italy.

The experimental activities were split in three periods:

- Period A- Pretreatment + SBBGR unit
- Period B - Pretreatment + SBBGR unit + Ozone
- Period C - SBBGR unit + Ozone

Pre optimization of the ozone unit revealed that maximum efficacy was obtained by shortening the ozonation phase time with a commensurate increase in ozone mass flow rate. Once optimized the ozonation phase time, additional runs were then performed for evaluating the applied ozone dose influence on the plant performance.

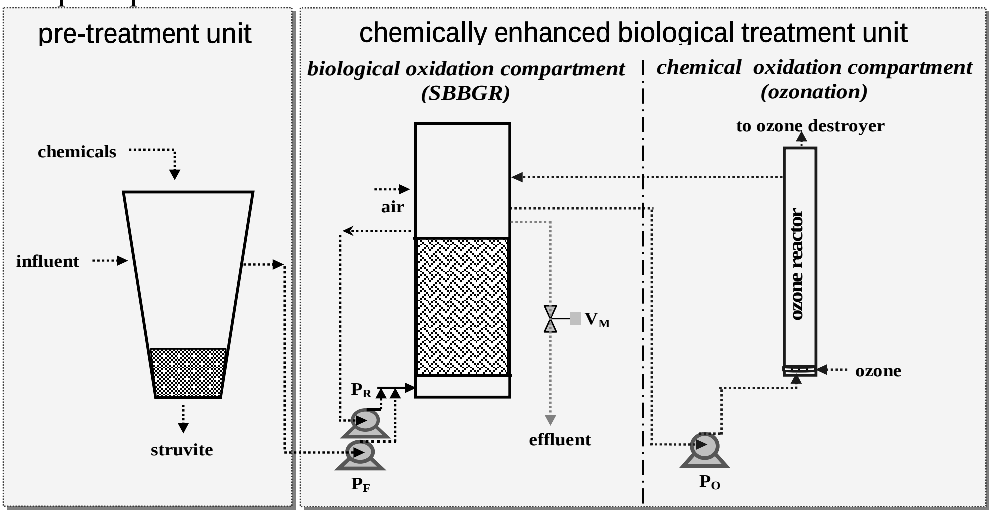


Figure WP1.1. Sketch of the lab-scale plant used in the project.

Table WP1.1. Plant performances under optimized operative conditions (average values).

Parameter		**Period A**	**Period B**		**Period C**
HRT (d)		3	3.5	3.5	12
Ozone dose ($gO_3/L_{influent}$)		0	2	0.5	0.5
Ozonation time (h)		-	0.5	0.5	0.5
COD	influent [mg/L]	8,700	8,700	8,200	9,500*
	effluent [mg/L]	4,500	160	500	485
	removal efficiency [%]	48	98	94	95*
DOC	influent [mg/L]	2,700	2,700	2,500	3,950*
	effluent [mg/L]	1,750	141	380	290
	removal efficiency [%]	35	95	85	93*
BOD_5	influent [mgN/L]	1,400	1,400	1,200	3,800*
	effluent [mgN/L]	3	3	0	5
	removal efficiency [%]	100	100	100	100*
NH_4	influent [mgN/L]	2,900	2,900	2,600	1,680
	effluent [mgN/L]	2	2	1	4
	removal efficiency [%]	100	100	100	100
NOx	influent [mgN/L]	0	0	0	0
	effluent [mgN/L]	0	0	0	6
	removal efficiency [%]	-	-	-	99
TSS	influent [mg/L]	470	470	390	220
	effluent [mg/L]	65	20	30	30
	removal efficiency [%]	86	96	92	86
Surfactants	influent [mg/L]	70	65	54	18
	effluent [mg/L]	10	1	2	1.5
	removal efficiency [%]	86	98	96	92
Colour removal	[%]	2	99	95	98

* It includes also the external carbon source (i.e., glucose) added to the leachate

The results indicate that the pre-treatment of leachate by struvite precipitation followed by SBBGR (Period A) resulted in low COD and DOC removals (i.e., 48% and 35%, respectively) due to a high recalcitrant COD fraction (Table WP1.1). During period B (i.e., when an ozonation step was inserted in the SBBGR treatment) much higher removal efficiencies were observed than during period A in terms of COD, DOC, TSS and colour highlighting the benefits of incorporating ozone into the treatment scheme. For instance, by dosing 2 and 0.5 g $O_3/L_{influent}$ the plant was able to meet the Italian limits for discharging into water bodies and sewer system, respectively. Finally, operation during Period C (i.e., when the pre-treatment unit was not used) indicated that the chemically enhanced biological treatment unit was able to remove carbon and nitrogen by using a longer HRT (i.e., about 4 times higher).
Among all the other results, it is worth highlighting that during the whole investigation, the chemically enhanced biological treatment unit generated a very low sludge production (i.e., lower than 0.05 g $TSS/gCOD_{removed}$) due to the high age (θc >200 d) and concentration (22-35 $gTSS/L_{bed}$; VSS/TSS: 0.4-0.5) of the biomass in SBBGR. Figure WP1.2 shows a photo of a biomass sample drawn from SBBGR bed where it is possible to see the presence of the granular biomass. Overall, the novel treatment scheme investigated in the current WP demonstrated an improved performance compared to traditional biological treatments followed by physic-chemical methods which have been considered as the most appropriate treatment for years.

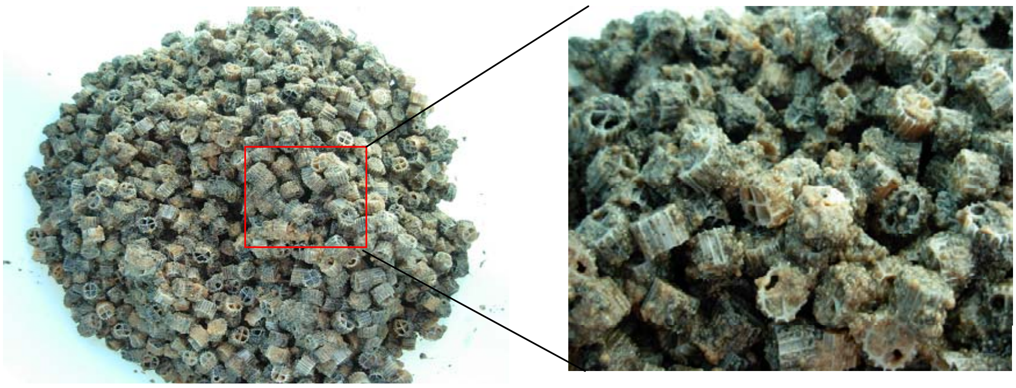


Figure WP1.2. Photograph of the biomass sample drawn from the bed of SBBGR system.

Microbial composition and structure of granular biomass

Fluorescence in Situ Hybridization (FISH) was chosen as the elective screening tool to identify, visualize and quantify bacterial species and to investigate the biomass composition during granule development. FISH was applied with confocal laser scanning microscopy in combination with specific staining procedures directed towards visualization of the EPS composition and presence of specific intracellular storage inclusions. The analysis was performed on two granular biomasses: from the SBR treating soluble and particulate matter operating at high temperatures and from ozone enhanced biological degradation carried in a SBBGR system for treating a mature municipal landfill leachate.

FISH enabled the identification of most Bacteria and it highlighted the presence of important microbial functional groups (ammonia and nitrite oxidisers, GAOs and PAOs etc.) in mature granules. In contrast, high temperatures (30-50°C with acetate as carbon source) produced compact and round shaped granules, with a diameter of ~2 mm, dominated by a single bacterial group (*Alphaproteobacteria* at 30 and 40°C and *Betaproteobacteria at* 50°C) (Figure WP1.3) compared to the fluffly granule structures previously reported with the particulate starches. In addition, the alphaproteobacterial cocci, retrieved at 30°C and 40°C, behave as GAOs but were interestingly found to be not affiliated to the known alpha GAOs. A significative number of *Archaea* was also observed at 30°C in the granules core (8% of total cells).

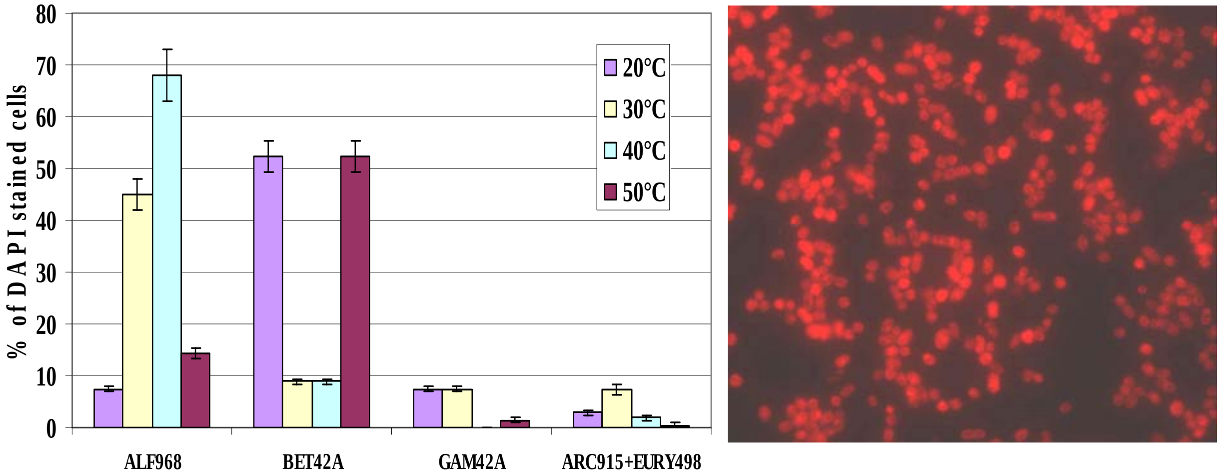


Figure WP1.3. Microbial composition of granular biomass from SBR system operating at different temperatures, estimated by FISH and typical alphaproteobacterial cocci dominating the granular biomass at 30 and 40°C .

Similarly, molecular characterization of the biomass cultivated in the SBBGR mapped the changes microbial and EPS composition as the flocculent sludge (activated sludge used as inoculum) evolved into a granular biomass (granule diameter: 2-3 mm). The biomass composition determined by FISH before and after ozone compartment activation (i.e., Period A and B of activity A.2) is reported in Figure WP1.4. As expected, due to the low ammonia concentration in the pre-treated leachate, no ammonia oxidisers (representing almost 20% of *Betaproteobacteria* in the activated sludge used as inoculum) were retrieved in the SBBGR biomass. In spite of the complex recalcitrant composition of the influent, the system produced a granular biomass with an efficient degradation capabilities. The granulation occurred when ozonation was inserted in the treatment cycle (Period B) of SBBGR system indicating that the inclusion of ozone generated either a significant reduction in the inhibition effect of available toxic compounds or to produced higher amounts of EPS favouring biomass aggregation (mainly composed by α- and β-glucans). Most of the granular biomass was detectable by FISH with bacterial probes (always ≥ 60% of the total cells) and was almost completely identified by group specific probes. This finding is in agreement with those typically recorded with activated sludge samples characterised by a significative lower biomass concentration (3-4gTSS/L against 30 gTSS/L of granular reactor) and sludge age (lower than 30 d). The detectability of bacteria by FISH is often utilised as a simple "gross parameter" to assess the overall physiological state of bacterial communities and found to be in agreement with reactor performances and with conventional respirometric tests applied for microbial activities measurements in previous experiences.

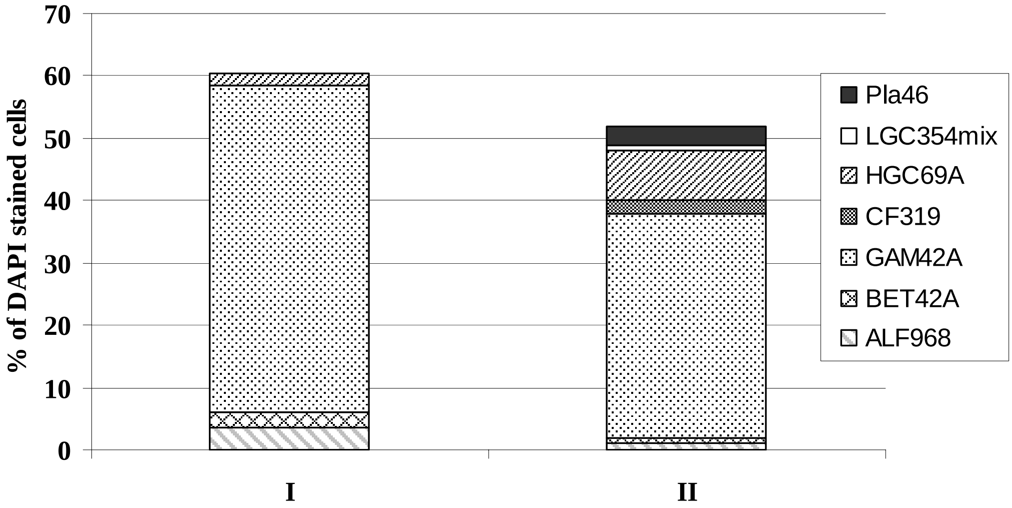


Figure WP1.4. Microbial population dynamics, estimated by FISH with group specific probes, in the SBBGR system treating landfield leachate. The binding of the specific probes is reported as percentage of the total DAPI stained cells. Samples refer to period A (I) and B (II) of activity A.2.

During Period C (i.e., when the chemically enhanced biological treatment unit was used for both carbon and nitrogen removal), relevant changes of the bacterial populations were observed (see Figure WP1.5). In fact, the granular biomass was characterised by a higher bacterial diversity and remarkably the system recovered nitrification (confirmed by FISH) after prolonged stress condition exposure (around 1.5 years). FISH also revealed, in accordance with the operative data, the simultaneous presence of denitrifying bacteria (mainly belonging to *Thauera/Azoarcus* spp. group).

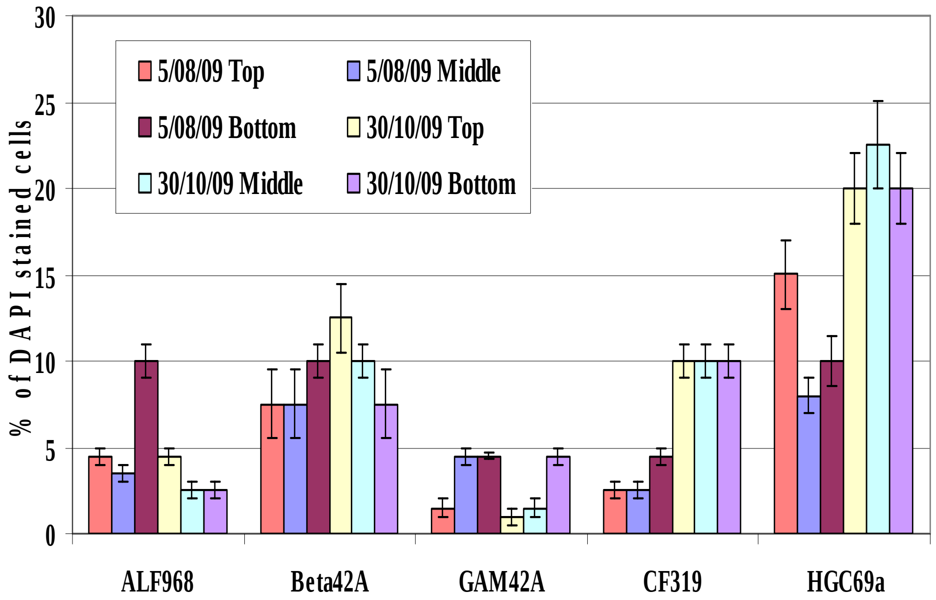


Figure WP1.5. Biomass composition at three different bed heights of SBBGR system for each sampling date during period C of activity A.2.

The research activity carried out within the project represents the first characterization of granular biomass involved in treatment of industrial effluents. Considering the stringent characteristics of the analysed influent (i.e. landfill leachate) or operating condition (i.e. high temperatures) of both granular biomass systems, the mixed microbial cultures involved in the biodegradation processes were highly selected and composed by few different bacterial species. However both technologies finally produced mature granules under steady state conditions with different structure and microbial/EPS composition depending on the operative conditions used.

Microbial characterization during the trials with the Unifed system treating slaughterhouse wastewater were conducted using microarrays to monitor the function of microorganisms. The opportunity to identify a gene or group(s) of genes up or down regulated during granulation provides an improved fundamental understanding of the granulation process as well as information about which gene(s) and/or organisms are potentially important during granulation.
A flocculant and granular sludge (initially floccular but transitioned to granular) were seeded with the same sludge, enriched for EBPR and operated in parallel while maintaining EBPR performance. During the period of reactor operation (160 days) an archive of nucleic acid samples was collected and established for further analysis. The RNA samples were processed and applied to a NimbleGen microarray platform, allowing for the differences in gene expression of approximately 64000 genes to be monitored between the flocculant and granular sludge's. Analysis of microarray data was performed using the Genespring software. Within this software program several different parameters and filtering methods were explored and investigated to optimize the extraction of relevant data. Results indicate more than 100 genes, associated with the Cluster of Orthologous (COG) categories, *Cellular Processors* and *Metabolism* are up-regulated in granular sludge compared to flocculant sludge. Within these two major COG categories, five functional categories, *Cell envelope biogenesis, Ion transport*, *Signal transduction mechanisms, Amino acid transport and metabolism* and *Co-enzyme metabolism*, contain the majority of up-regulated genes

The interpretation of these results continues to be explored and investigated using various BLAST and search algorithms to identify interesting genes, their functions (COG) and which metabolic pathways (KEGG) they are involved in and how important they potentially could be during the granulation process

Assessment of the best management option of granular sludge produced during treatment of real wastewaters

Investigation of the effectiveness of granular biomass cultivated in Nereda system for treating food industry effluents

Two industrial wastewaters (a beer brewing wastewater and a food wastewater) have been investigated for the application of granular sludge cultivated in Nereda system at full scale. The major finding was the need for pretreatment to reduce solids loadings onto the granular beds by incorporating processes like dissolved air filtration or tilted plate settler. Granular sludge formation in the Nereda systems proved was rapid without the need of special start-up procedures. Operational challenges identified in the laboratory with polymeric organic substrates (such as starch) leading to a poorer granulation were not observed in the food industry application. The application of aerobic granular sludge based processes appears appropriate for such wastewaters as the industrial company expanded the trial to other sites. To illustrate, the quality of the effluent produced was sufficient for direct reuse of effluent in the food processing factory indicating the satisfactory effluent characteristics of the plant.

Assessment of the best management option of granular sludge produced in the Nereda and SBBGR systems

Sludge produced in the SBBGR and Nereda systems during the treatment of municipal landfill leachate and food industry effluent were analyzed and compared with regards to organic micropollutants, heavy metals, nutrients content and dewaterability.
The sludge produced by SBBGR system was characterized as having a high phosphorus concentration (due the presence of struvite in the sludge), low SV/ST ratio (that confirms the good stabilization) and good dewaterability. Heavy metals analysis showed that this granular sludge exceeded the limits of the directive 86/278 for sludge reuse on land. As a consequence this sludge was not suitable for agricultural application consistent with it being generally classed as unsuitable due to the "bad" origin of the sludge.
The sludge produced in Nereda system (food wastewater) was benchmarked against sludge from an Activated sludge process treating the same wastewater enabling a direct comparison. Results indicate that the granular sludge was richer in organic matter and phosphorus but poorer in nitrogen. In addition the granular sludge was seen to be more dewaterable than the flocculant sludge. The experimental analyses to assess the sludge quality showed that conventional activated sludge was characterised by higher surfactants, phthalates and alkyl-phenols/ethoxylated content with respect to granular sludge. Specifically, anionic surfactants and phthalates concentrations appeared not to be compliant with the proposed limit value for sludge utilization in agriculture reported in the 3rd draft European working document (European Commission, 2000). Nereda sludge was generally cleaner than conventional activated sludge enabling the potential for use in agricultural. All the characterized sludge samples can be classified as "non hazardous" and their codes in the *"European Waste Catalogue and hazardous waste list (2002)"* are 19 08 05 for the Nereda sludge and 19 08 12 for the SBBGR sludge.

<u>Investigation of the effectiveness of granular biomass cultivated in SBR reactors (Unifed system) for treating slaughterhouse wastewater</u>

Lab scale SBR operation

Initial activity focused on the use of laboratory SBRs fed with slaughterhouse wastewater optimised for the generation of aerobic granules. In order to obtain aerobic granules, a strategy of progressively reducing the settling time was applied to the reactors. This approach is commonly used and has been demonstrated to enhance granulation. However, during the application of this strategy, a reduction in biomass within the reactors occurred. An increase in particle size was only observed when the biomass concentration decreased from 3g MLSS/L to levels lower than 1g MLSS/L. Although both the 90th and the 50th percentiles increased, suggesting an increase in the size of the granules present, the biomass concentration never recovered.

Biodegradable COD removal was achieved with an efficiency of 99% even when low levels of biomass were present. For instance, during one run (Figure WP1.6A), the volumetric exchange ratio (VER) was set and maintained at a constant 33%. However, N removal deteriorated over time due to a decrease of biomass in the SBR, causing an accumulation of NH_4^+ in the reactor thus inhibiting the bacteria present. This particular system could not be recovered and was stopped after 80 days of operation. During another run (Figure WP1.6B) the initial VER applied to the SBR was 17% in order to avoid NH_4^+ accumulation in the reactor. During the first 25 days of operation, 90% N removal was achieved. The wastewater loading was slightly increased, increasing the VER to 25%. However, the system could not cope with this increase, partially because the biomass concentration was also decreasing, and N removal decreased. Although VER was reduced again, the performance did not substantially improve and the biomass concentration reached very low levels. This run was stopped after 70 days of operation.

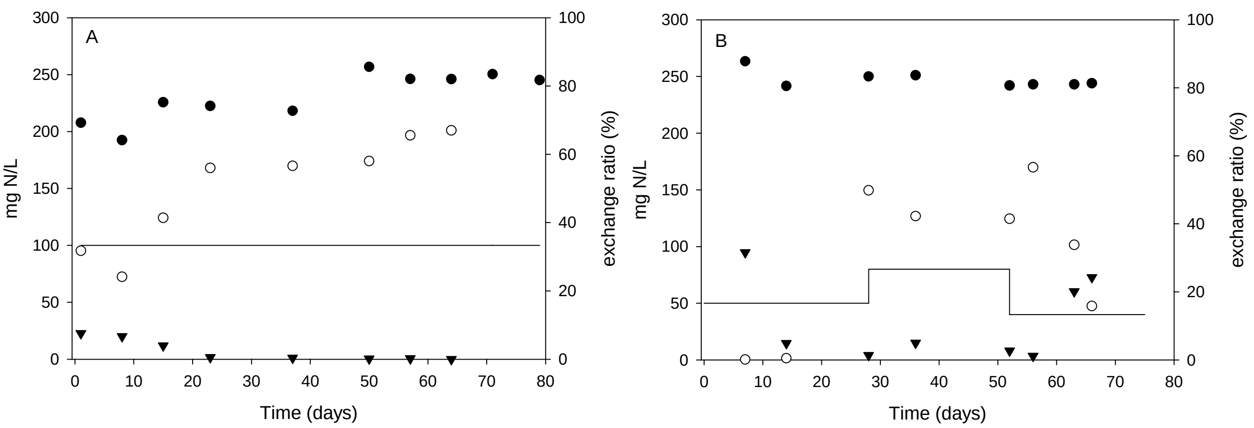


Figure WP1.6. Nitrogen removal performance for SBRs seeded with 100% floccular sludge: A- 1st round; B-2nd round. ● N-NH4$^+$ influent, ○ N-NH4$^+$, ▼ N-NOx, — exchange ratio.

In order to overcome the above mentioned problems a different start up strategy was applied, using a mixture of granules and flocculant sludge. Several combinations of granular sludge with flocculant sludge were used to start 11 aerobic granular sludge reactors for the treatment of slaughterhouse wastewater. The results showed that this type of seeding strategy substantially reduced the start-up time of aerobic granular sludge reactors for the treatment of this nutrient rich

wastewater. Importantly there was no net biomass loss observed in any of the reactors and 90% COD and 85-95% nitrogen removal was achieved during the granulation period. Additionally, several reactors achieved excellent phosphorus removal. A patent has been lodged that describes this start-up procedure.
Furthermore, studies on the effect of starvation conditions in aerobic granules treating slaughterhouse wastewater were performed. These results showed that aerobic granules could maintain their structure and microbial activity even after 1 month without wastewater supply. Additionally, their external morphology was better preserved under anaerobic starvation conditions.

Pilot-scale SBR operation

A fully tested and operational pilot scale SBR incorporating an automated cycling pattern with stable SBR operation was achieved and demonstrated. The biggest challenge, which was not overcome, was the wastewater characteristics of the prefermenter side-stream which fed the pilot plant. This side-stream from the prefermenter provided the bulk of VFAs required for the process. However, it also provided the bulk of readily degradable non-VFA COD which resulted in uncontrolled heterotrophic growth. This unwanted COD was particulate in form. Periods of granular development were experienced during the project when relatively low non-VFA COD was present from the prefermenter. However, these periods could not be maintained. Granular development within this system was promoted primarily by VFA concentration rather than washout of poor settling sludge (although this did play a role in the process). The measured increase in particle size was the net result of an increase in particle size due to granulation minus the loss of developed particles in the effluent (due to the capture of the developing particles within the flocculant biomass and washout during decant). During periods of observed granule development, the prefermenter produced relatively high VFA concentrations (for granule development) and low non-VFA COD (available carbon for opportunistic floccular growth), resulting in a net increase in particle size.
Decreasing the settling time to washout poor settling biomass always resulted in a loss of BNR activity but no increase in particle size due to the fast replenishment of flocculant biomass which was being washed out. The unwanted particulate COD settled poorly, which was most likely a function of both the particulate size (median size 10-20 μm) as well as the presence of fats in the raw feed water. Separation of the unwanted particulate COD was attempted by optimising the prefermenter feeding strategy (both HRT and location of feeding in tank) as well as including mechanical separation (Induced Air Flotation unit). However, these attempts were largely unsuccessful. The periods when granule development did occur indicated that the SBR design and operation was sufficient to obtain granules. The problem was simply obtaining the correct wastewater characteristics to maintain this in the long-term.
Another major challenge was not discovered until towards the end of the project. At this time the HRT of the SBR was reduced to 18 h (previously operating at 29-42 h). It was found that during the summer, this low HRT resulted in SBR operating temperatures of 36-39 °C due to the high temperature of the bulk feed stream from the anaerobic pond. At these temperatures, nitrification is severely inhibited such that nitrogen removal in the SBR was significantly reduced. While this was partly an artifact from the transfer of this feed stream to the pilot-plant via a black pipe, the wastewater exiting the anaerobic pond during summer still reaches >36 °C in summer. Thus, even if the granulation process was successful, only limited nitrogen removal could be achieved during summer periods. It is unclear what affect the loss of nitrogen removal would have on the stability of any mature granules developed.
Under the current operating conditions present at the slaughterhouse, development and operation of a granular SBR for wastewater treatment would not be possible without significant investment in pre-treatment of the wastewater. Cooling of the raw wastewater prior to entry to the full-scale DAF would significantly improve the fat and solids removal efficiencies which could provide the

conditions required for more optimal prefermenter operation and thus permit stable granular SBR operation.

Conclusions

- Technology utilizing aerobic granules was demonstrated to be effective at treatment industrial wastewaters providing enhancements compared to the current state of the art in terms of treatment performance, operational stability against toxin and temperature, sludge production and footprint.
- A number of key issues were identified that need considering when adopting aerobic granular based technologies:
  - Feed containing high levels of a particulate COD cause granule deterioration and retard nutrient removal through principally reacting at the granule surface although this does not prevent successful operation of the technology
  - Inclusion of a ozonation step greatly enhanced treatment performance without causing any deterioration in the granular reactor
  - When non VFA COD concentrations are high, pre treatment may be required to stabilize the granular reactor
- During the project the first full scale industrial applications of this process where implemented as a consequence of the work reported here. Based on the positive results several new implementations are currently investigated.

WP2: COUPLING ADVANCED OXIDATION PROCESSES WITH BIOLOGICAL TREATMENT

BACKGROUND

The biological treatment of industrial wastewaters is very often inhibited in the presence of solvents, salts, intermediates and synthesis products which can are non-biodegradable and/or toxic to microbial consortia and environmental systems. Moreover, the simultaneous presence of high fractions of easily biodegradable carbon (e.g., solvents) and lower amounts of recalcitrant organics (e.g., drugs, pesticides and other Xenobiotic Organic Compounds, XOCs) can pose serious limitations to the use of physico-chemical treatment such as oxidation or adsorption processes. For these reasons the selection and testing of specific treatment trains for the complete removal of refractory compounds from industrial wastewaters is needed. The present state of the art highlights the opportunity of either enhancing biodegradability through oxidative pre-treatments, including an oxidation treatment as a final polishing step, or integrated treatments. It has been demonstrated that the use of advanced oxidation processes (AOPs) can break down a wide range of molecules due to the on-site generation of sufficient hydroxyl radicals (•OH), a highly potent, extremely reactive chemical oxidant, to oxidize these compounds and purify water. In the current study a number of options were investigated to understand the potential of utilising AOPs with biotreatment. Treatment schemes included:

- Biofilm ozonation system for treatment landfill leachates
- Membrane bioreactors with AOPs (O3 or UV/H2O2) for treatment of pharmaceutical wastewaters
- Immobilised biomass reactor with solar photo Fentons for treatment of pharmaceutical and pesticide wastewaters
- Heterogeneous photo Fentons system

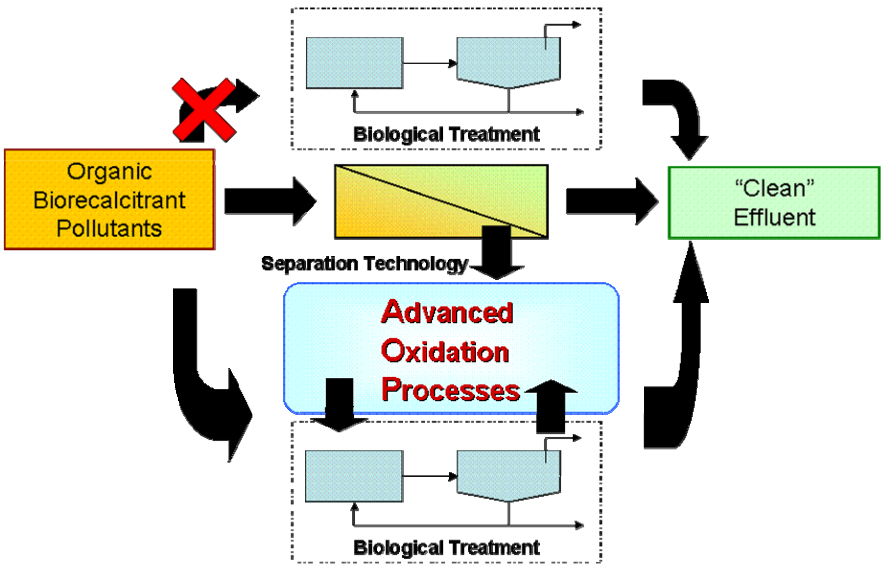


Figure WP2.1. Schematic summary of the treatment stages investigated within WP2.

METHODOLOGY AND RESULTS

Combined biofilm-ozonation system (BIOZO) developed treating landfill leachate

The BIOZO concept combines controlled ozonation with biological landfill leachate treatment in the secondary treatment step. Results obtained by GC-ToF-MS were used to assess the efficiency of the combined system in terms of PAHs removal efficiency. A novel, staged moving-bed biofilm reactor design (STRAKINES process) was developed and implemented in the laboratory- and pilot-scale experiments. Application of the novel system enhanced the removal of N and XOCs (PAHs) by means of controlling bacteria heterogeneity through the reactor stages. A methodology to assess the size of reactor compartments using reaction kinetics data was developed leading to the use of a continuous-flow biofilm system, in which, plug-flow conditions were approximated in the pre-denitrification zone by employing three continuous stirred tank reactor compartments. The sizes of the pre-anoxic biofilm reactor stages were assessed using data obtained in batch nitrate-nitrite uptake tests, and its efficiency is contrasted against data obtained with single stage arrangement in a laboratory-scale experiment. It was demonstrated that organic substrate and nitrogen removal efficiencies can be improved using reactor compartments, as a result of higher reaction rates and because bacteria can become more effectively acclimatised to utilise a broader range of organic substrates, thereby further increasing the reaction rates in the system.

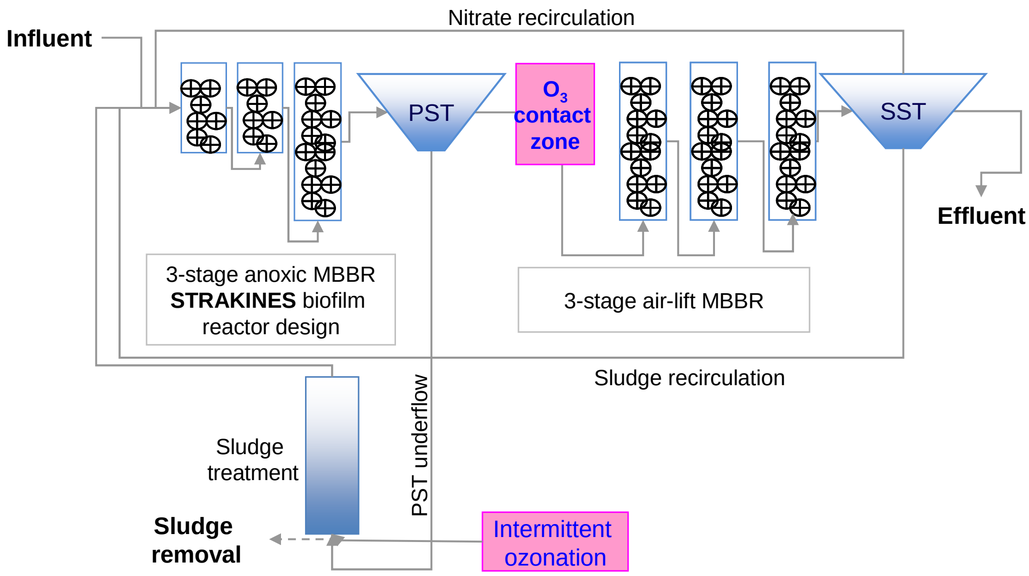


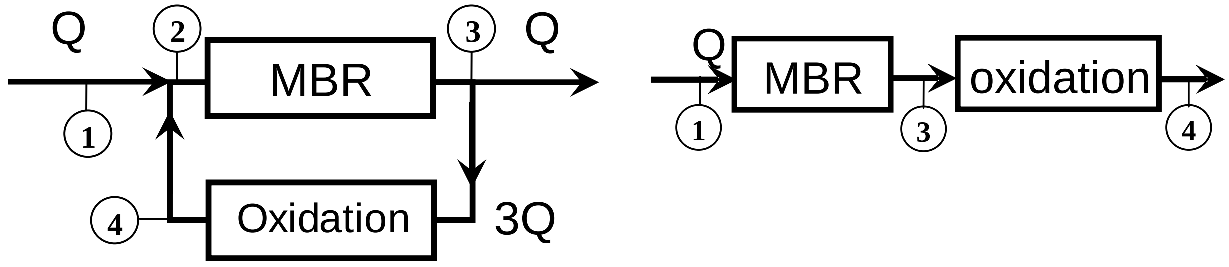
Figure WP2.2. The BIOZO process–Biofilm system (STRAKINES anoxic reactor design) combined with ozonation.

Most of the PAH removal took place in the pre-anoxic zone, thereby decreasing toxicity exhibited by PAH on autotrophic nitrifier bacteria in the aerobic zone. Results obtained in the laboratory-scale, continuous-flow system suggested that, in the anoxic reactors, nitrogen removal can be limited by the low influent biodegradable substrate concentrations, whereas ammonia oxidation, via nitrite and nitrate, was shown to be adversely impacted by the high alkalinity buffer and high ammonia concentrations, in the aerobic unit. In the presence of high concentration of PAHs compounds, coupling controlled ozonation with biological treatment showed to be effective with an ozone dosage of approx. 0.5 mg/L O_3. This dose decreased the effluent soluble COD concentration and pH profile in the aerobic reactors, improving the biodegradable COD production from inert compounds and consequently induced chemical nitrification. The specific cost of ozonation was evaluated as 0.36–0.73 € m^{-3} with 911 mg L^{-1} average effluent soluble COD measured in the biofilm system. The results suggest that, at full-scale, the system can ideally be implemented in treating municipal wastewater, in which the scavenging effects and hence the ozone dosing requirement are significantly lower than, for instance, in landfill leachate. Controlled ozonation was tested by installing it in the nitrate recirculation line and, subsequently, between the pre-anoxic and aerobic zones (see Figure WP2.2), in the pilot-scale system. Ozonation installed as it is shown in Figure WP2.2 demonstrated to be superior in terms of COD, PAH and nitrogen removal efficiencies. It was additionally demonstrated the potential of intermittent sludge ozonation (0.05 g O_3 $gTSS^{-1}$ d^{-1}; duration of ozonation: 20 min d^{-1}) as a means to decrease PAH concentrations in sludge wasted and to improve nitrogen removal in the BIOZO system.

The BIOZO configuration can effectively outperform the *state-of-the-art* solution, i.e. ozonation as a tertiary polishing step, as a result of the recirculation streams in the secondary step and of the more effective biological barrier of oxidation by-products formed by the aerobic and anoxic zones. Intermittent sludge ozonation is demonstrated to decrease the PAH solids concentration in the sludge produced.

Integrating membrane bioreactors (MBR) and chemical processes (AOPs) for treating pharmaceutical wastewaters.

In the presence of high concentrations of organic compounds, chemical pre-treatments can only be cost-effective if highly selective towards target compounds. On the other hand, when an oxidation process is used as final polishing step, the presence of organic by-products into the final effluent can only be avoided by favoring their complete mineralization setting a high reaction time and, consequently, with increased operational costs. A possible alternative is the integration of the biological treatment with an oxidation process aimed at improving the biodegradability of refractory compounds. This option may have a strong potential in terms of minimization of oxidation by-product release if these can be removed in the biological step. In this view, membrane bioreactors (MBR) offer unique opportunities in terms of suspended solids-free effluent, possible selection of specialized biomass, flexibility and compactness. These features make MBR particularly suited to be integrated with O_3 and UV/H_2O_2 as it is well known that the performance of ozonation is negatively affected by suspended solids that act as scavengers towards hydroxyl radicals (i.e., the reactive free radicals formed by ozone decomposition in water).
To test the validity of such suggestion the integration of an AOP (O_3 or UV/H_2O_2) with an MBR as with as either a combined or post treatment configuration was tested (Figure WP2.3). The performance of each were also compared against standard treatment configurations such as Sequencing Batch Reactor (SBR) plus adsorption onto Granular Activated Carbon (GAC) or SBR plus Fenton oxidation process. All the tests were performed using lab-scale plants to treat different pharmaceutical wastewaters. Separate optimisation of the biological and chemical processes under continuous operation were carried out to assess the treatability of the wastewater by the individual treatment steps. Finally, the effectiveness of the MBR/oxidation integrated process was verified.



(a) **(b)**

Figure WP2.3. Scheme of the investigated integrated wastewater treatment system (a) and the polishing treatment train (b) employed for comparison. Q = 1.6 L/d. Legend: 1=raw wastewater; 2=MBR influent; 3=MBR effluent (oxidation feed); 4=oxidation effluent.

The biodegradability of different wastewaters was evaluated through a standard Zahn–Wellens test. Additionally, the wastewater composition before and during the test was assessed in terms of parent compounds and main metabolites by LC/MS. The biodegradability of the parent compounds were also evaluated by performing Zahn–Wellens tests on synthetic solutions. The results identified the masking role of the bulk organic matrices in relation to specific pharmaceuticals (naproxen, acyclovir, and nalidixic acid). Detailed analysis revealed that the biodegradation of high concentrations of organic solvents and other biodegradable compound tended to ‘‘hide” a lack of removal of the target compounds. This can cause severe environmental drawbacks in many cases in which the treated wastewaters are normally discharged into centralized sewage treatment plants. The proposed approach, i.e. the adoption of a standard biodegradability test coupled with LC/MS, allowed assessment of the real potential of a biological treatment to remove refractory substances may be masked by major fractions of biodegradable compounds. The above approach indicated that only nalidixic acid was completely refractory to biological treatment although preliminary oxidation tests showed that the degradation of the acyclovir left a persistent by-product in the effluent.

Enhanced removal of organic compounds from a real pharmaceutical wastewater resulting from the production of acyclovir (an anti-viral drug) was obtained by employing a membrane bioreactor and an O_3 polishing step. The biological treatment alone reached an average COD removal of 99%, which remained stable with inclusion of the ozonation step. Similarly, in the case of acyclovir treatment the MBR produced 99% removal with a further 99% removal of the residual concentration in the MBR effluent when the AOP was applied. For several of the 28 organics identified in the wastewater the removal efficiency of the MBR treatment improved from 20% to 60% as soon as the ozonation was placed in the recirculation stream. The benefit of the integrated system, in comparison to the polishing configuration was evident for the removal of a specific ozonation by-product. The latter was efficiently removed in the integrated system, being its abundance in the final effluent 20-fold lower than observed when ozonation was used as a polishing step. In this configuration, the same performance of the integrated system in terms of by-product removal could only be obtained when the ozonation was operated for more than 60 min. This demonstrates the effectiveness of the integrated system compared to the polishing configuration.

In the case of nalidixic acid (an antibacterial drug), both O_3 and UV/H_2O_2 were tested, in integrated and polishing configurations. The treatment of simulated and real wastewaters with MBR alone resulted in COD removals of 85-95%, but the target compound concentration remained constant due to its very low biodegradability. The nalidixic acid concentration greatly decreased in the final effluent when the ozone step was placed in the MBR recirculation stream, with almost 80% removal efficiency. Moreover, COD removal in the MBR was unaffected by the integration with ozonation. Similar performances were obtained adopting UV/H_2O_2 instead of O_3. As for by-products removal, it was found that for most compounds the integrated MBR-AOP system was more effective than the conventional set-up in which an oxidative polishing step (by O_3 or UV/H_2O_2) was employed after the MBR.

Overall, the investigations showed that integrated MBR-AOPs systems provide additional benefit over the current *state of the art* treatment configurations, as they remove the by-products formed during the oxidation step. The other removal performances (COD, organics) are comparable to those of the standard treatment configurations.

Combining biological (Immobilized Biomass Reactor) and chemical processes (solar photo-Fenton) for the treatment of pharmaceutical wastewaters and streams containing pesticides.

Treatment of pharmaceutical wastewater.

In this context there are two main possible approaches: photo-Fenton can be employed as a pretreatment or as a polishing step, depending of the water characteristics. Photo-Fenton, due to its intrinsic characteristics (acid pH, residual H_2O_2), cannot be integrated directly with a biotreatment, but must be incorporated in series. The key issue when using such processes is to minimize residence time and reagent consumption (H_2O_2) in the more expensive photo-Fenton stage by applying an optimized coupling strategy. To investigate this all photo-Fenton experiments were carried out under sunlight in a compound parabolic collector (CPC) solar photocatalytic pilot plant. The biological system selected was an immobilized biomass reactor (IBR) of 200 L total volume.

The pharmaceutical wastewater treated contained 38 mg/L of nalidixic acid (NXA) with a DOC of. 725 mg/L, a COD of 3400 mg/L and a NaCl concentration of 5 g/L. A Zahn-Wellens biodegradability test indicated that the wastewater had a significant degree of biodegradable substances (80 %) but nalidixic acid was biorecalcitrant. Consequently, a combined system composed by a biological treatment (IBR) and an AOP (solar photo-Fenton) was applied at pilot plant scale for the decontamination of the wastewater. The first step was the treatment of the water in the solar photocatalytic pilot plant operated in batch mode until complete elimination of NXA was observed (28 % mineralisation, 350 min and 65 mM of H_2O_2). Subsequent biotreatment reduced the DOC to 30 mg/L after 6 days. This treatment was not considered suitable.

The next step was the treatment of the water in the IBR operated in batch mode. After 3 days of biotreatment, 96% of the initial DOC was removed. However, NXA concentration remained constant until the end of the process. After the biological treatment, the biotreated wastewater was treated by photo-Fenton (20 mg/L of Fe^{+2}, pH = 2.7). NXA was completely degraded at around 25 minutes of illumination time and 12 mM of H_2O_2 consumed, reaching a DOC of around 20 mg/L. The overall efficiency of the combined IBR/solar photo-Fenton treatment in terms of elimination of DOC was over 97%. The initial wastewater, intermediates formed during degradation by biotreatment and subsequent photo-Fenton were investigated by Liquid Chromatography-Time of Flight-Mass Spectrometry (LC-TOF-MS). Only after photo-Fenton treatment, NXA and analogous compounds were totally eliminated, and no further intermediates detected. Figure WP2.4 shows the evolution of the chromatograms in the different stages of the combined system. It reinforces the proposed approach, i.e. the adoption of biodegradability test coupled with LC/MS, allowed assessing the real potential of a treatment in case of wastewaters where the refractory substances may be masked by major fractions of biodegradable compounds.

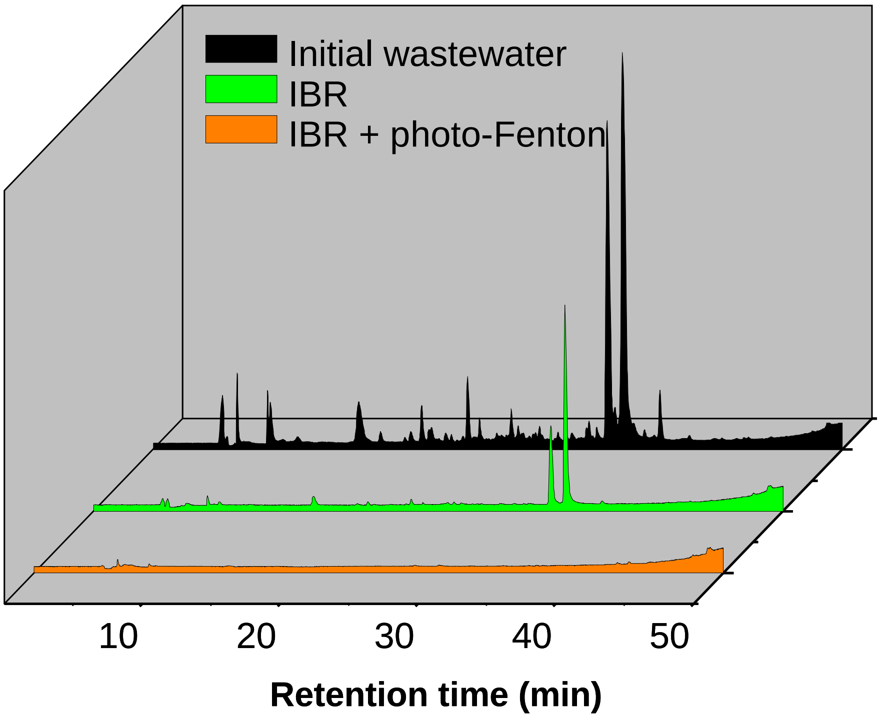


Figure WP2.4. LC-TOF-MS chromatograms obtained by the analysis of a wastewater sample before and after the application of biological and photo-Fenton treatments.

Treatment of wastewaters containing pesticides

The integration of solar photo-Fenton process and a conventional bio-treatment has been described as a feasible option for the degradation of industrial wastewaters containing non-biodegradable and/or toxic compounds. One step forward intended in the research developed during the project was the scaling-up of the combined technology, since industrial applications are still scarce. In this case photo-Fenton and IBR was carried out under sunlight at industrial scale. The total volumes were 2500 L (1060 L irradiated) in the case of the solar photocatalytic plant and an immobilized biomass reactor (IBR) of 2500 L.

ALBAIDA RESIDUOS S.L. is a company that selectively collects the empty plastic pesticide containers used in the greenhouses of the area of El Ejido (Spain) for recycling. These containers are shredded and washed, producing water contaminated with pesticides. This water has usually been treated by solar photo-Fenton since the start-up of the plant in 2004. However, this photocatalytic plant has been upgraded in the frame of the INNOWATECH project, including the installation of an IBR. The treatment of this wastewater was performed by the combination of a solar photo-Fenton pre-treatment and a subsequent biological process. This approach was selected since preliminary pilot and laboratory tests showed that wastewater containing commercial pesticides presented high toxicity and low biodegradability. The proposed operational strategy was extending the photo-Fenton process until 40 - 50 % of mineralization before discharging the partially oxidized solution in the IBR. The solar photo-Fenton was always performed in batch mode at pH adjusted to 2.8 and with 20 mg/L of Fe^{2+}, while the biological reactor was operated both in batch and continuous mode. The overall efficiency of the coupled system in terms of initial DOC elimination was 84 % (37.5 % photo-Fenton and 46.5 % IBR). The identification and quantification of the pesticides present in real wastewater during the combined system was performed by LC-TOF-MS based on the use of an accurate-mass database. The concentration of all pesticides decreased gradually throughout the process (the greater part during the photo-Fenton process) and after the biological treatment the majority was totally removed except for two of them (pyrimethanil and thiacloprid) that were found in the range of μg/L. This information is summarized in table WP2.1.

Table WP2.1. Main pesticides detected in real wastewater sample by LC-TOF-MS using an accurate-mass database: % reduction in the combined system and final concentration.

Compound	% Reduction in the combined system	Final concentration (μg/L)
Imidacloprid	96.4	25
Dimethoate	99.4	5
Pyrimethanil	82.3	160
Thiacloprid	84.2	88
Carbofuran	100	< 0.1
Metalaxyl	100	< 0.1
Spinosyn a	100	< 0.1
Bupirimate	100	< 0.1
Fenamiphos	100	< 0.1
Azoxystrobin	99.4	3
Malathion	100	< 0.1
Tebufenozide	100	< 0.1

Overall, the performed investigation showed that the combination of biological and chemical processes for treating biorecalcitrant wastewater provide additional benefit over that of *the state of the art*. The success of the current investigation led to the investigated scheme being further developed and implemented at industrial scale. This represents the first time the combination of solar photo-Fenton and biotreatment has been applied industrially for the treatment toxic wastewaters.

Heterogeneous photo-Fentons system

Performance of bio-treatment under typical conditions of photo-Fenton treatment

A coupled photochemical (photo-Fenton) and biological system (packed-bed immobilized biomass reactor) was set up for treating model compounds. Initial trials utilized solutions of p-chlorophenol. The aim of the investigation was to evaluate the performance of bio-treatment under typical conditions of photo-Fenton treatment (residual iron, residual H_2O_2, acidic pH). Table WP2.2 gives the characteristics of solutions which were treated by bio-coupling. The influence of pH, the H_2O_2 concentration and residual iron were studied.

Table WP2.2. Characteristics of different solutions (a-f) which were tested for biocoupling..

Experimental conditions	A	B	C	D	E	F
pH	7.0	2.5	3.5	5	7	7
Residual Fe (mM)	0.36	0.36	0.36	0.36	0.36	0.36
Residual H_2O_2 (mM)	0	0	0	0	2.3	4.6

Figure WP2.5 depicts the yields of organic matter degradation achieved in the bioreactor under the conditions shown in Table WP2.2. It The presence of H_2O_2 (Figure WP2.5 – left side) was not observed to be negative towards biological activity since TOC degradation was similar both in presence and in absence of H_2O_2. Figure WP2.5 (right side) shows the performance of the biological treatment for pre-treated solutions at different pHs. As it can be observed the biological treatment was efficient in the range of pH 3.5-7 during an operation period of 8 days. These results indicate that in the case of accident of pH regulation the fixed biomass has a good resistance to pH shocks.

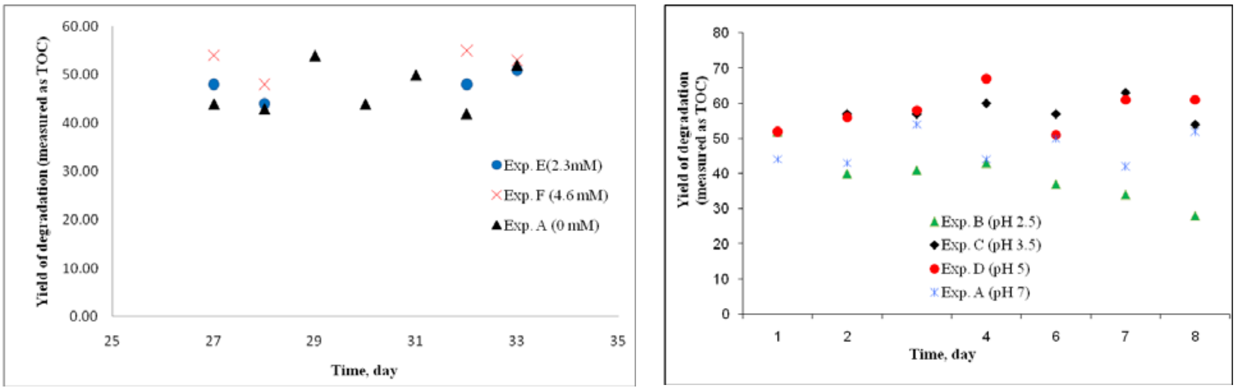


Figure WP2.5. Influence of hydrogen peroxide (left) and pH (right) on the performance of biological treatment..

<u>Assessment of the photodegradability by photo-Fenton of selected models compounds representative for non-biodegradable and/ or toxic contaminants.</u>

The effect of physico-chemical properties on the reactivity via photo-assisted Fenton catalysis was assessed for several *para*-substituted phenols (*p*-nitrophenol, *p*-chlorophenol, *p*-hydroxybenzaldehyde, phenol, *p*-methoxyphenol, *p*-hydroxyphenol in order to cover a wide range of electronics effects. As an attempt to determine a quantitative structure reactivity relationship, Electronic descriptors (Hammett constants (σ), frontier molecular orbital energies (E_{HOMO}), electronic and zero point energies (E, E_{ZERO})), electrochemical descriptor (half wave potential for the oxidation of phenols to phenoxyl radical ($E_{1/2}$)), and other descriptors (acidity constants (pKa), maximum absorption wavelength (λ_{max}), 1-octanol/water partition coefficient (K_{ow})) were correlated with the initial Fenton and photo-Fenton degradation rates (r_0). Biodegradability measurements (BOD_5) before and after photo-Fenton treatment of p-substituted phenols were also performed in order to determine if the degradation intermediates are more biodegradable than parent compounds and to assess the effect of substituent on biodegradability.

Linear relationships were obtained between the initial Fenton and photo-Fenton degradation rates and electronic descriptors (Table WP2.3) indicating that the electrophilic nature of hydroxyl radical. However *p*-chlorophenol and *p*-hydroxybenzaldehyde showed higher photo-Fenton degradation rates than ones predicted by the model implying the presence of weaker bonds in these molecules.

Table WP2.3. Correlation coefficients (R2) obtained after linear regression in the plots of initial rates of degradation versus different descriptors.

	σ	K_{ow}	E_{HOMO}	$E_{1/2}$	E_{zero}	pK_a
Fenton degradation[a]	0.949	0.711	0.961	0.977	0.995	0.723
Photo-Fenton degradation[b]	0.975	0.679	0.996	0.847	0.986	0.662

[a] *p*-chlorophenol excluded
[b] *p*-chlorophenol, *p*-hydroxybenzaldehyde excluded

Investigating heterogeneous photo-Fenton systems
Heterogeneous photo-Fenton systems were developed using iron oxide coated modified polymer films. It involved a study on catalyst preparation by a sequential procedure: first, the polymer surfaces (polyvinyl fluoride PVF) were functionalized by different techniques (vacuum-UV, oxygen radiofrequency plasma, photo-Fenton, TiO_2 photocatalysis) to improve iron oxide adhesion to the polymer, then iron oxide coating was performed by forced hydrolysis of $FeCl_3$ (5g/L) in aqueous media. The TiO_2 photocatalytic surface treatment (TiO_2 aqueous suspensions 1g/L, solar simulation, pH 5) followed by iron oxide coating (Figure WP2.6) was found to lead to the most efficient and stable photocatalyst (PVF^f-TiO_2-Fe oxide).

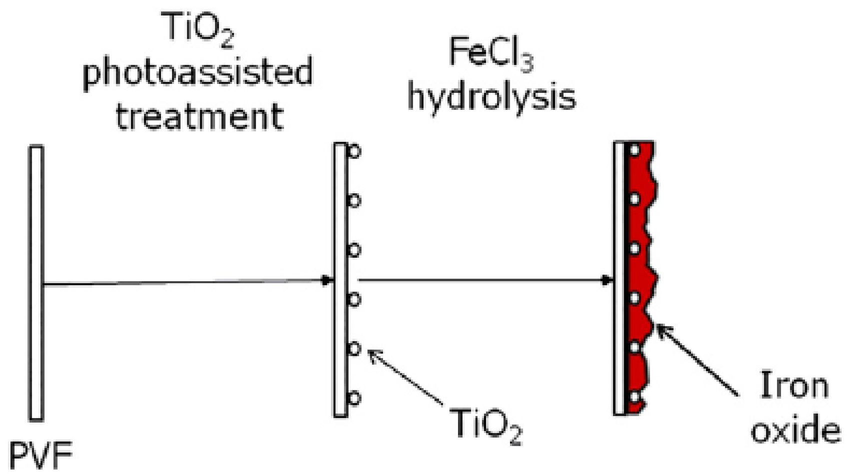


Figure WP2.6. Flow diagram of PVFf-TiO2-Fe oxide preparation procedure (not to scale).

Surface characterization has shown that oxygenic functional groups (C=O, C-OH…) formation on polymer surface and TiO_2 particles concomitant deposition occurring during the functionalization step, were involved in the high efficiency of PVF^f-TiO_2-Fe oxide. The degradation of real pollutant such as acyclovir, nalidixic acid (NXA), pesticides mixtures were achieved by PVF^f-TiO_2-Fe oxide under different conditions (lab/pilot scale, in presence and absence of salt).

The degradation of acyclovir and NXA (0.18mM) was achieved by PVF^f-TiO_2-Fe oxide in presence of H_2O_2 (3.2mM) under solar simulation at laboratory scale. The initial pHs (about 6) were not adjusted and iron leaching was followed: the homogeneous photo-Fenton contribution was found to be low. Acyclovir was slowly degraded (30%) during the irradiation time (240 min) but NXA was totally removed in less than 120 min treatment with a concurrent mineralization of 35 % based on TOC measurements. Besides, 50 repetitive NXA degradation runs were performed at lab scale showing an outstanding long-term stability of PVF^f-TiO_2-Fe oxide. Figure WP2.7 shows that NXA acid was efficiently degraded by PVF^f-TiO_2-Fe oxide/H_2O_2 adapted in a compound parabolic collector (CPC) photoreactors under natural solar light radiation. NXA was rapidly degraded under these conditions and about 35% of organic matter was mineralized although the operational pH was controlled by addition of base. This result shows the high efficiency of PVF^f-TiO_2-Fe oxide even at neutral pH in the case of NXA. In contrast a model mixture of commercial pesticides were slowly degraded (less than 50%) by PVF^f-TiO_2-Fe oxide /H_2O_2 in CPC photoreactors showing that this process is not efficient for all kind of wastewaters.

In the studies performed with the PVF^f-TiO_2-Fe oxide, important synergistic effects of iron oxide and TiO_2 were observed constituting a significant contribution *to the state of art*. As part of the work a new method to prepare supported photocatalyst under solar light illumination was explored which could decrease the costs of preparation procure.

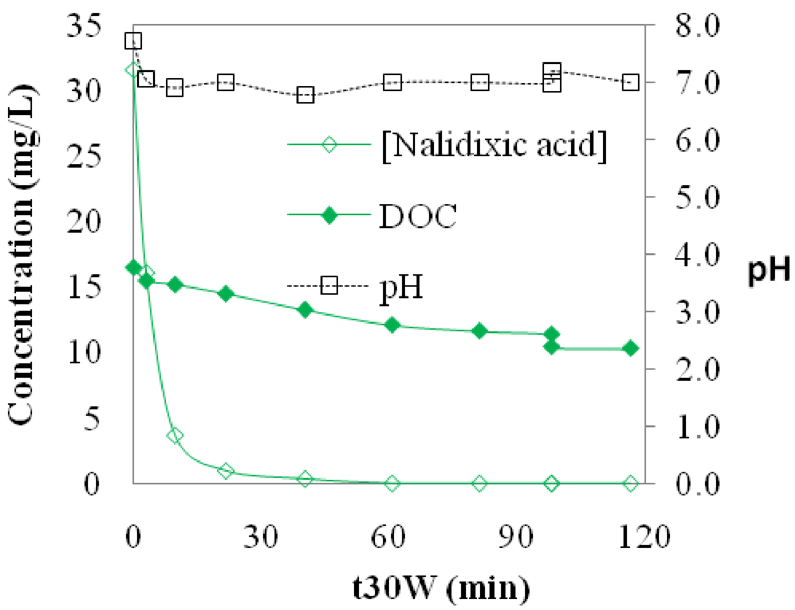


Figure WP2.7. Variation of substance (empty symbols) and TOC (filled symbols) normalized concentrations during degradation of NXA in presence of H2O2 in pilot CPC photoreactors at controlled neutral pH..

CONCLUSIONS

- Coupling advanced oxidation processes with biological treatment was observed to be an effective strategy for enhanced removal of recalcitrant compounds and represents an improvement in the current start of the art. Illustration of treatment scheme include:
    1. The development of a biofilm-ozonation system (BIOZO) where the ozonation was found to be most effective between the pre-anoxic and aerobic zones. Intermittent sludge ozonation was demonstrated to decrease the PAH solids concentration in the sludge produced
    2. Integrated MBR-AOP systems are more effective than conventional set-ups in which an oxidative polishing step is used after the MBR through the degradation of oxidation by-products
    3. Photo-Fenton process can be effectively applied as a finishing step after a biotreatment for the decontamination of wastewater containing biorecalcitrant non toxic compounds.
    4. Industrial wastewaters containing biorecalcitrant toxic compounds in the range of hundreds of mg/L can be successfully treated by solar photo-Fenton coupled with biotreatment.
- Characterization based on standard biodegradability test coupled with LC/MS investigations enables assessment of residual concentrations of refractory compounds in mostly biodegradable matrices overcoming the masking effect of the bilk organics
- Fenton and photo-Fenton degradation is faster when the electronic density of the aromatic ring is high favoring electrophilic radical attack on the ring. The degradation rates are higher when half wave potential is low.
- An innovative method for immobilizing iron oxide on polymer films was developed. The new photocatalyst (PVFf-TiO2-Fe oxide) can be installed in solar compound parabolic photo-reactors.

WP3: Membrane based intensification of wastewater treatment processes

BACKGROUND

Membranes represent a relative common technology used in industrial wastewater treatment especially where difficult to treat wastewaters are encountered and/or water recycling and resource recovery are being considered. Consequently, there is a track record of novel membrane processes first gaining acceptance for industrial wastewater treatment. Perhaps the most significant example of this has been uptake of membrane bioreactors which integrate biological treatment with a membrane. However, the efficacy of the technology is constrained by the biodegradability and ultimately, toxicity of the wastewater to be treated: the technology is unable to treat toxic or recalcitrant organic matter which limits its appropriateness to some industrial wastewaters. In cases where biological systems can not operate it is common to utilize chemical processes. Consequently, there is an opportunity to utilize membranes in combination with chemical reactions to achieve equivalent benefits to when integrated with biological processes in terms of intensification, footprint, robustness and treatment quality. The current work package investigated two possible future technologies:

- A Membrane Chemical Reactor (MCR), which combines a photo catalytic reactor with a membrane filtration unit to retain the TiO_2 catalyst.
- A Membrane Contactor (MC), which utilizes a coated membrane for the reactive extraction of phenols with caustic soda.

Similar technologies have been used for other applications, typically very dilute systems and whilst these provide some insights direct translation is not possible as they represent a 5-6 orders of magnitude decrease in organic concentration to be treated compared to the current situation. As with all novel technology it is important to understand the true potential they offer and as such the work outlined here develops a clear design approach suitable for industrial wastewater treatment (and recovery) enabling there potential to be properly considered.

Membrane Chemical Reactor (MCR) Membrane Contactor (MC)

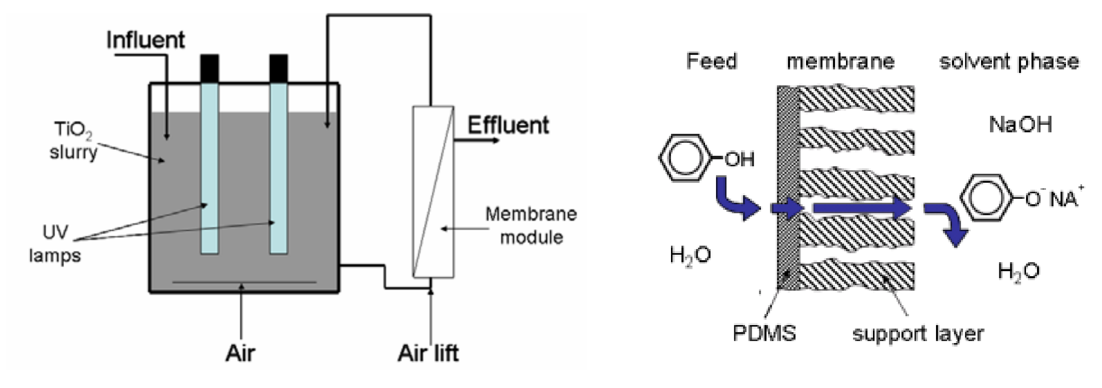


Figure WP3.1 Schematics of the MCR and MC

Membrane Chemical Reactor

The current state of the art in advanced wastewater treatment is represented by membrane bioreactors (MBRs) for intensive bio-treatment and advanced oxidation processes (AOPs) for intensive chemical treatment. However, the efficacy of the technology is constrained by the biodegradability and ultimately, toxicity of the effluent: the technology is unable to treat toxic or recalcitrant organic matter. It is against this background that the merits of a novel membrane chemical reactor should be assessed. The MCR combines a membrane filtration process unit with an advanced oxidation process (figure WP3.1 – left side). The pollutants, adsorbed on the surface of the catalyst (titanium dioxide, TiO_2), are oxidized by a photo-catalytic reaction triggered by UV lamps. A filtration membrane retains the TiO_2 particles.

Investigations into integrating membranes and photo-catalysis focus on low strength applications such as pesticide removal where μg/L-mg/L levels are considered. The current industrial application extend this but contemplating the treatment of organics at up to 6-7 orders of magnitude higher concentrations. Consequently, utilization of existing design guidance must be considered within the current framework and is unlikely to be directly transferable. The work undertaken in this WP addressed this but considering the key design issues in relation to the treatment of a range of industrial wastewaters.

<u>Catalyst selection</u>

The catalyst performance was assessed during laboratory trials in spent metalworking fluids. Three different commercially available TiO_2 media were studied with Degussa P25 being chosen as the most photo-catalytically active on the bases of the results obtained here as well as the information reported in the literature.

<u>Membrane Fouling</u>

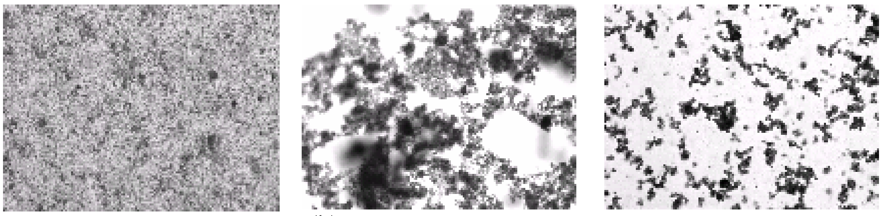
For all tested wastewaters, significant fouling was recorded in the original MCR pilot plant (single mixed reactor), such that regular restoration cleans were required which could potentially limit the operational feasibility of the technology. The operating time between cleans varied between just over 2 days and 10 days depending on the wastewater at a permeate flux of 10 $l.m^{-2}.h^{-1}$. Critically, clean TiO_2 particles (in clean water) do not foul the membrane. Further, a significant reduction of the membrane fouling was observed during the tests carried out with longer retention time in the reactor and consequently with better treatment of the wastewaters. These results suggest that sustainable operation of the process is dependent solely on the successful operation of the photo-catalytic stage of the process.

<u>Treatability of wastewaters</u>

In the MCR, an advanced oxidation process takes place and the main degradation mechanism is the reaction of organic pollutants with $^{\cdot}OH$ radicals. The potential of different wastewaters to be treated by $^{\cdot}OH$ radicals was initially evaluated using a UV/H_2O_2 process in a simple laboratory set up (collimated beam apparatus). 80 – 90% COD removals were achieved for pharmaceutical, textile and laundry wastewaters as well as spent metalworking fluids, demonstrating their treatability by advanced oxidation technologies. In contrast to that, the treatment of nalidixic acid solution and landfill leachate was found to be generally limited with less than 40 % COD removal. This suggests that these two wastewaters are not readily degraded by the $^{\cdot}OH$ radicals, and consequently the MCR would not be the most suitable application for their treatment. Further the degree of aggregation of the TiO_2 particles, which plays a role in the treatment efficiency (with higher degree of aggregation effectively limiting the treatment), was found to be dependent on the solution in which they were dispersed.

Catalyst aggregation

It was suggested that the aggregation of the TiO_2 particles could be a limiting factor in the MCR system as the surface available for the absorption and so for the reaction is reduced. Literature indicates that for bigger particles the mass transfer coefficient is reduced and also that the rate of the oxidation reaction with TiO_2 as the photo-catalyst increases with decreasing particle size. This means that reducing the particle size not only leads to a bigger available surface, but also to increased mass transport of the pollutants to the surface and to higher reaction rates. It is reasonable to assume that wastewaters that produce large flocs will tend to be poorly treated. An investigation of particle aggregation of TiO_2 dispersed in the different wastewaters was conducted using an optical microscope. Different degrees of aggregation of the TiO_2 particles could be observed. In DI water (a), the dispersant in which the flocs observed were the smallest, particles of a few microns were measured. These were much bigger than the nominal size of the TiO_2 particles reported at about 25 nm. As shown in figure WP3.2 Bigger aggregates were found with acid orange 7 (b), a dye, than with a landfill leachate and spent metal working fluids (c). Further results suggest that aggregation is linked to characteristics of the wastewaters, whereas the type of the compounds present appear to have a bigger impact than the general physico-chemical characteristics of the wastewaters. In any case, aggregation of the TiO_2 particles in the reactor should be minimized by sufficient mixing of the slurry.



(a) (b) I

Figure WP3.2 Variation in TiO_2-organo aggregate size for (a) clean, (b) coated with a dye and (c) coated with metal cutting fluid

Membrane configuration

Comparison of two membrane configurations, a side-stream multi-tubular polymeric membrane (MTp) and a submerged hollow fibre (HF) revealed a clear advantage for the side-stream configuration with significantly higher critical fluxes measured for the MTp membrane in comparison to the HF membrane. This trend was found to be the same for all the wastewaters tested here. A comparative study was also carried out on the MTp membrane with circular channels and a multi-tubular ceramic membrane with square channels (MTc). In this case, the polymeric membrane was found to generally perform better than the ceramic membrane. Overall, the side-stream multi-tubular membrane is the preferred configuration for this application as it consistently performed better than the submerged system. Moreover, it was shown that the material of the membrane is important with better performance observed with the polymeric than with the ceramic membrane.

Reactor design

Initial results obtained with a mixed reactor design equipped with low pressure UV lamps showed that an intensification of the photo-catalytic stage was needed in order to achieve better treatment and to limit membrane fouling. Subsequently, results obtained in the new MCR based on an annular reactor with a narrow gap containing medium pressure revealed significant increase in the treatment efficiency as well as lower fouling. However this configuration could only deliver this level of performance at low flows and high energy consumption. Further optimization was therefore orientated towards increasing the throughput of the treated wastewaters and lowering the energy consumption. To optimize the UV source, trials were carried with three sets of low pressure UV lamps with different wavelengths of 365 nm (UV-A), 310 nm (UV-B) and 254 nm (UV-C) and a comparative study of the three types of lamps for the treatment of a range of wastewaters revealed the UV-B lamps to be the most suitable. The final system configuration was comprised of a series of three mixed reactors each containing four low pressure UV lamps. Using nalidixic acid as the treated solution, the reactors in series achieved a 38% removal of the organic content in comparison to the annular reactor that achieved 32% removal of the organics with a greater energy input and a lower flow rate. These two values corresponded to energy per order (E_{eo}) of 325 and 3317 $kWh.m^{-3}$ for the reactors in series and the annular reactor respectively. These results clearly show the benefit of the reactors in series design with a one order of magnitude reduction in the energy while improving the overall treatment.

Membrane Contactor

A key task arising mainly in the chemical industry is the separation of phenols (representing the class of organic acids) from process water. This stream is often well-defined and thus of significant value. The usual approaches for removing dilute organic compounds from water all suffer from serious drawbacks. In this case:

- Liquid-Liquid Extraction: Due to its comparatively polar nature, phenol is poorly soluble in non-polar solvents. However, the choice of a mildly polar solvent leads to increased contamination of the aqueous phase with solvent, which leads to a new separation problem.
- Stripping: The high boiling-point and reasonable solubility in water renders phenol poorly strippable.
- Nanofiltration: The low molecular weight of phenol implies low separation efficiency.
- Biological Treatment: This class of methods is only applicable to wastewater with low phenol content and low concentrations of salt.

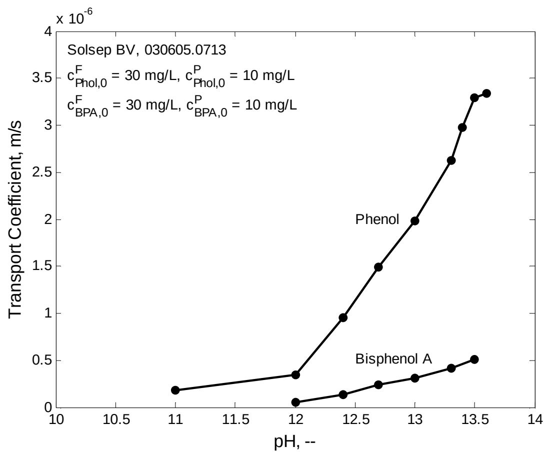
Other process options include reverse osmosis, activated carbon adsorption and wet oxidation, which share prohibitively high costs. Further, a recycle of separated compounds is often not feasible. As a solution to this problem, we examine the reactive extraction of phenol in a coated membrane contactor (figure WP3.1 – right side). The solvent is an aqueous solution of sodium hydroxide. As with the MCR the novelty of this technology requires basic design information to be derived in order to assess its suitability for industrial wastewater treatment. Accordingly, the work carried in this WP focused on determination of the key design and operating descriptors for the process so that an economic assessment of its potential could be conducted.

Membranes

The key element of the novel technology is a asymmetric membrane with a dense hydrophobic coating on top of a hydrophilic support to inhibit mixing of the feed and stripping fluid while phenols permeates. Phenol is a weak acid and reacts rapidly with caustic soda to form sodium phenolate, which is made available in the porous layer. Depending on the pH-value of the caustic solution, phenol reacts immediately to phenolate after passing the dense coating. Thus, the reaction maximizes the driving force across the selective coating (figure WP3.3 – left side). The membrane developed during the project shows high permeability for phenol (3.5E-6 m/s) as well as bisphenol A (5E-7 m/s), and is stable under such conditions for more than a year as was shown by gas permeation tests.

Operation

Permeability was found not to depend solely on the stripping pH, but also on the phenol concentration levels in the feed and permeate. An increase in phenol concentration in the permeate decreases the mass transfer enhancement effect of the caustic stripping solvent. Further, if significant amounts of (neutral) organic compounds become available (i.e. due to enrichment of phenol), the phenol permeability rises significantly. The likely cause is polymer swelling. Whenever the phenol permeability increased due to swelling, water flows across the membrane to equilibrate differences in osmotic pressure was also detected. The water flow rates were sufficiently low so that the phenol permeability remained unaffected.



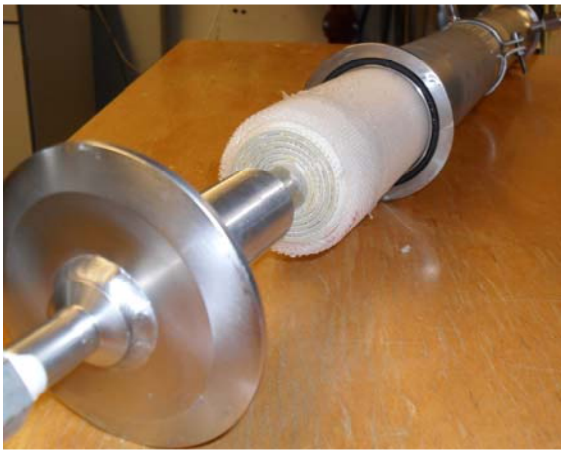


Figure WP3.3 Influence of pH on mass transfer (a) and a photograph of one of the tested membrane elements.

Scale-up

Stripping solvents generally have a huge take-up capacity relative to the feed stream. This translates to long residence times in mass transfer devices to achieve appropriate loading. Such devices preferably exhibit low permeate hold-up, no fluid maldistribution and no significant additional mass transfer resistances (i.e. in boundary layers). Hence, a significant part of this subproject was concerned with the design and optimization of a 4-end spiral wound membrane module (contactor prototype; see figure above WP3.3 – right side).

In such modules the channels between two layers of membrane are defined by spacer nets. For this purpose, we specifically designed tests to investigate fluid flow and mass transfer. At relevant operating conditions, the boundary layer mass transfer coefficients was always higher than 5E-6 m/s, usually in the order of 2E-5 m/s. Dispersion tests indicate that woven spacers do not counteract maldistribution. The tracer did not spread as observed for extruded spacers, with channel liquid between their filaments. Hence, thin extruded spacers with their filaments arranged parallel and perpendicular to the main direction of flow are most advantageous, because they avoid dead spots in corners. The copper dissolution method, which is based on a surface reaction limited by diffusion, was employed to study flow patterns inside modules induced by baffles. These experiments show only minor differences, so that the simplest design is preferred.

Economics and ecological impact

A life cycle case study reveals the positive impact of the membrane contactor system on the environment if the concentrate can be reused. The reduction of bisphenol A is ecologically advantageous well beyond economic viability. Whether the membrane contactor is economically competitive depends mainly on separation targets, volumetric flows and proper process integration. As a rule of thumb, the separation targets should not be overly strict (max. 1 order of magnitude) to keep up driving force. Moreover, only flows up to 10 m^3/h appear economically feasible. As mentioned before, the scale-up investigations revealed that the simplest module design is preferable. Thus, relatively cheap membrane elements can be used for such applications. As membrane area is a major cost issue, this is a very important conclusion.

CONCLUSIONS

- Novel hybrid membrane processes were seen to be effective for the treatment of industrial wastewaters. Key design information obtained from the project with regards to employing the technologies for industrial wastewater treatment include:
  - The key operational difficult with the MCR process relates to the photo-catalytic stage where sufficient reaction of the coated TiO_2 is required prior to membrane filtration to prevent rapid fouling at low to moderate fluxes.
  - Aggregate formation during the adsorption of the target organics onto the TiO_2 has a significant influence over the operation of the process
  - Annular reactors are a suitable methods for ensuring the effectiveness of the photo-catalytic reaction but are unable to treat high flow rates
  - Effective treatment at appropriate flow rate is possible through the use of tanks in series.
- Novel membrane contactors were seen to effectively remove and recover phenol from industrial wastewater stream. Key design information obtained from the project with regards to employing the technologies for industrial wastewater treatment include:
  - The inclusion of a dense hydrophobic coating enabling a reactive extraction of phenol to occur without excessive bleeding of other components.
  - Permeability depends on both pH and initial phenol concentration
  - Extruded spacers with their filaments arranged parallel and perpendicular to the main flow are the most suitable design to avoid dead spots.
  - Simple module designs are suitable for such applications greatly reducing membrane costs and increasing the economic scale of operation.

WP4: TAILOR-MADE SOLUTIONS FOR END USERS

METHODOLOGY

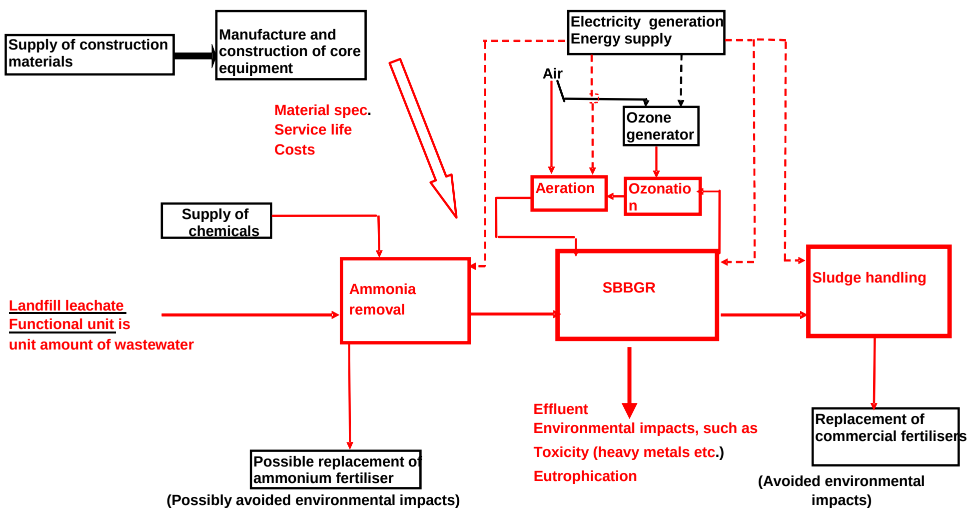
Modelling methodology

For the purpose of modelling the wastewater treatment systems in order to carry out life-cycle assessments and life-cycle-cost calculations, and in order to be able to design suitable treatment systems for other wastewaters than those studied experimentally, the unit processes of the treatment systems were divided into two categories:

- Core processes, defined as processes which are part of the treatment system as such. Their performance may be affected by changes of the properties of the treated wastewater.
- Peripheral processes, i.e. processes which deliver commodities such as energy or chemicals to the wastewater treatment system (upstream processes), or processes which treat wastes or other outputs from the treatment system (downstream processes). The performances of the peripheral processes are not affected by changes of the properties of the treated wastewater. They only react to changes by supplying more or less of their commodity or treating larger or smaller quantities of outputs.

The distinction between core and peripheral processes is illustrated in Figure WP4.1 with an example from work package 1: treatment of landfill leachate in a sequencing batch biofilter granular reactor (SBBGR).

Figure 1. ***Modelling example from WP1. Treatment of landfill leachate in a SBBGR. Core and peripheral processes.***
- Red text and lines: Core processes modelled mechanistically or statistically.
- Black text and lines: Peripheral processes described by linear life-cycle inventory data.



The aim of the modelling of the core processes was to be able to predict as far as possible their performance as a function of the conditions and the composition of the wastewater. This required software with mathematical functions more advanced than simple first-degree linear equations. A graphical interface was also required. Unless a mechanistic model of the process could be used to derive a mathematical model, the latter would have to be derived from experimental data collected during statistically planned experiments. In either case, the data collected during the experimental investigations had to be adequate for the purpose of confirming or deriving a mathematical model and for the purposes of life-cycle assessment and life-cycle costing.

For each treatment technology studied in the WP1, 2 and 3, WP4 started the modelling work by sending a simple flowchart of the process and a list of suggested parameters to be measured during the experiments to the task leader. In those cases where modelling was possible the model was built with the software Matlab with Simulink. Each part of the treatment process was developed as a separate process module which could be removed or added anytime and anywhere in the treatment process. The Simulink model calculated the core process data, which were then exported to the selected LCA software for inventory calculations.

In those cases where modelling was not possible the experimental data were used to calculate preliminary designs of real treatment plants. These calculations were quite simply performed in Excel.

Methodology assessment

The environmental assessments were carried out with the LCA methodology. The methodology was coordinated together with the EU funded project NEPTUNE (contract No. 036845). The goal of the LCA:s in both INNOWATECH and NEPTUNE was holistic environmental performance ranking (optimisation) of different wastewater treatment technologies and to assess the new treatment technologies in comparison to existing ones. The functional unit is 1 m^3 of “standard” wastewater, i.e. in the case of INNOWATECH real industrial wastewater. The upstream system boundary is thus the influent to the wastewater treatment plant. The downstream system boundary is the receiving water, to which the effluent from the treatment is assessed as an emission.
The inventories of the core processes were imported to the LCA:s from the MatLab models or the Excel calculation sheets as “locked” or “static” modules, which were connected to inventories of the peripheral processes. This “static” model was then processed as any other life-cycle assessment.
Data for the peripheral processes were collected from the literature or from available databases, mostly from Ecoinvent (*Ecoinvent 2004*).
The following existing impact categories were used as performance indicators in the assessments:

- Global warming
- Acidification
- Nutrient enrichment/eutrophication
- Photochemical oxidant potential
- Ecotoxicity (aquatic and terrestrial; via soil, water and air)
- Human toxicity (via soil, water and air)
- Resource consumption
- Waste generation

All these impact categories were included according to the EDIP97 methodology [*Wenzel et al., 1997*], which was also used by NEPTUNE.
The basis of the assessment of each technology per se was to compare the impacts caused by the wastewater treatment to the impacts avoided by the treatment. The avoided impacts were calculated by assuming that the wastewater was discharged untreated to a receiving watercourse. The impacts that would be caused by such a discharge were calculated from the composition of the wastewater using the EDIP97 methodology. The avoided impacts were then calculated as the difference between the impacts from the discharge of the untreated water and from the discharge of the treated water. Figure WP4.2 illustrates the calculation principle.

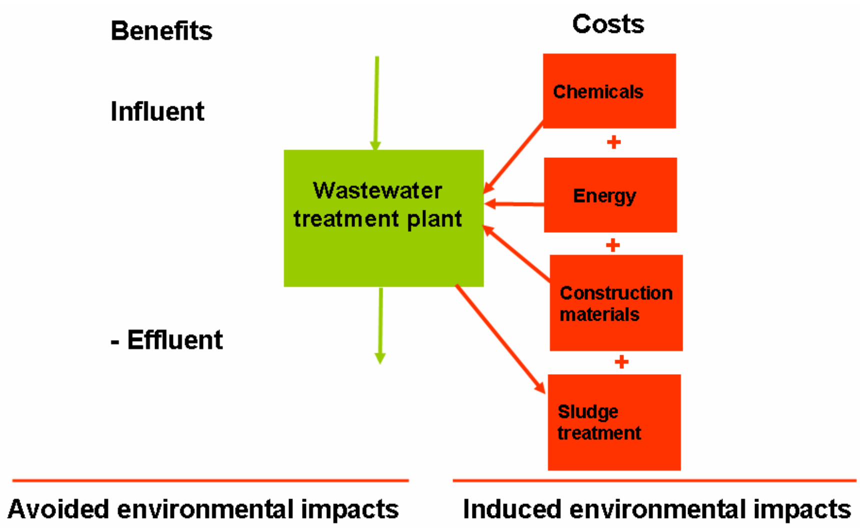


Figure WP4.2 Environmental efficiency – Environmental cost/benefit assessment

Avoided impacts were primarily nutrient enrichment, oxygen consumption and toxicity from organic matter and toxicity from metals in the wastewaters. In those cases where organic compounds in the wastewater had been synthesized from fossil raw materials (crude oil and natural gas) their degradation to carbon dioxide contributed to global warming as well.

The cost/benefit assessment of figure WP4.2 requires recalculation of the different potential environmental impacts listed above to a common scale. This was done by normalisation. In the EDIP97 methodology normalisation is carried out by dividing each impact potential from the life cycle of a product or a process, e.g. the global warming potential as kg CO_2 equivalents caused by released greenhouse gases, by the entire potential impact of that category from a specified region during a specified reference year [*Wenzel et al., 1997*]. The potential impacts from entire regions are given as kg impact equivalents per person and year. The normalised values of all impact potentials from the life cycle of the product or process are thus expressed as person-equivalents(pe)·years. The person equivalent can be regarded as the annual impact of an average person in the specified region.
For the purpose of cost assessments a life-cycle cost (LCC) approach was used. The core processes were assessed with capital cost calculations and with calculations of maintenance, labour and other operating costs. The costs were periodized as lifetime annuities, i.e. as a regularly paid constant annual amount over a limited period of time. It is the same as the net present value multiplied by an

annuity factor. The net present value is the sum of all costs and receipts at a given point of time, discounted with a specific discount rate.
First, the net present value was calculated:

$$LCCtot = \sum_{t=0}^{t=n} \frac{C_t}{(1+r)^t}$$

where n is the considered economic life, r is the interest rate and C_t are the calculated total costs at time t.
These costs were then multiplied by an annuity factor:

$$LCC / year = LCCtot * \frac{r}{1-(1+r)^{-fn}}$$

where fn is the economic life of the core process facility.
The annuity could then be related to the functional unit, which in all assessments was 1 m^3 of wastewater to be treated, i.e. effluent water directly from industries.
For the peripheral processes no cost calculations were carried out. Their costs were part of the operating costs and entered the assessments as prices of commodities or fixed treatment costs for wastes, like sludge.
The progress compared to available technology was assessed by comparing the environmental and economic performance of the new technologies to reference cases. In these reference case studies treatment plants were designed with available technology to treat wastewaters used by the WP1,2 and 3 in their R&D work. These plants were then assessed with LCA and LCC methodology in the same way as the new technologies. Table WP4.1 summarises the reference cases.

Table WP4.1 The reference case studies and the corresponding new technologies

New technique	Existing (reference) technique	Wastewater studied
Sequencing Batch Bioreactor with granular biomass (Nereda) (WP1)	Activated sludge design by DHV and IVL based on actual plant data, costing by ANOX	Food industry wastewater
Biozo system (WP2)	5-stage SBR with nitrification/denitrification, design from a real plant	Landfill leachate from Norway
Struvite precipitation + SBBGR + Ozone (WP1) SBBGR = Sequential Batch Biofilter Granular Reactor	Activated sludge with nitrification/denitrification, design by ANOX	Landfill leachate from Italy
• MBR + Ozone (WP2) MBR = Membrane Bioreactor • Photo-Fenton /IBR (WP2) • Membrane contactor + IBR (WP2+3) IBR = Immobilised Biomass React. • Membrane-chemical reactor (WP3)	Moving-Bed Bioreactor (MBBR) + Powdered activated carbon removal, design by ANOX	Pharmaceutical industry wastewater

RESULTS

Modelled and assessed systems

For the new treatment technologies models, designs and assessments could be prepared as summarized in table WP4.2.

Table WP4.2 Modelling and assessments of new treatment technologies - Overview

Technology	MatLab model	Treatment plant design	LCA	LCC
WP1				
Nereda		X	X	
Struvite + SBBGR + Ozone		X	X	X
WP2				
Biozo		X		
MBR + Ozone		X	X	X
Photo-Fenton/IBR	X	X	X	X
WP3				
Membrane contactor	X	X	X	
Membrane-chemical reactor				

It was possible to construct mathematical models from the experimental results (photo-Fenton) or from mechanistically derived equations (membrane contactor) in two cases. The photo-Fenton model is rather limited in scope. It was derived for the pharmaceutical-wastewater treatment case by regression analysis and relates degradation of nalidixic acid, consumption of hydrogen peroxide and degradation of DOC (dissolved organic carbon) to the illumination time.

For the five technologies SBBGR + ozone, Biozo, MBR + ozone, photo-Fenton/IBR and membrane contactor preliminary designs for real treatment plants could be prepared from the project results. For the Nereda technology a design was already available at the start of the project.

The results of the assessments of the individual technologies have been reported to each work package concerned. In this report from work package 4 the result of a comparative study of several technologies when used to treat a common wastewater is described.

The common assessment case - Treatment of a pharmaceutical wastewater by new technologies and by the reference technology

A wastewater from a pharmaceutical industry was used as a standard treatment case for comparative assessments of the investigated technologies. The wastewater has a matrix of synthetic but biodegradable organic compounds, but also contains a non-biodegradable substance known as nalidixic acid (1-ethyl-1,4-dihydro-7-methyl-4-oxo-1,8-naphthyridine-3-carboxylic acid). Nalidixic acid is an antibiotic used to treat urinary infections in both animals and humans. It has an estimated low PNEC value (predicted no-effect concentration) in the environment, which means that it is assigned a high ecotoxicity potential in the EDIP97 methodology. The wastewater is furthermore saline and slightly acidic. Table WP4.3 describes its properties.

Table WP4.3 The standard wastewater treatment case

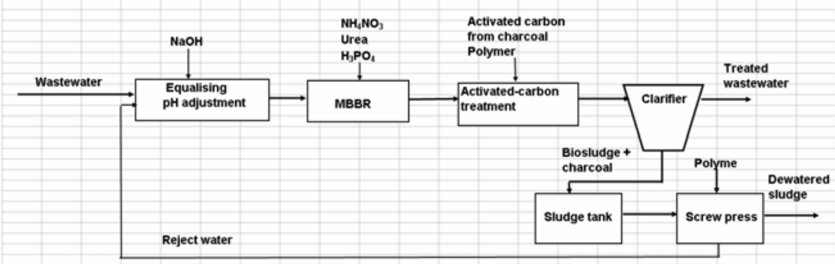
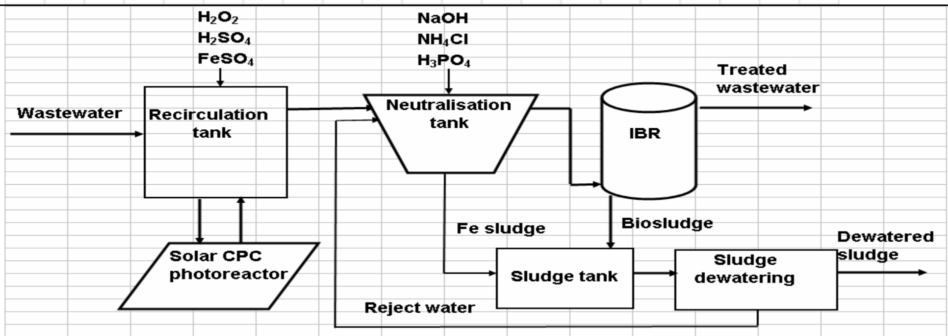
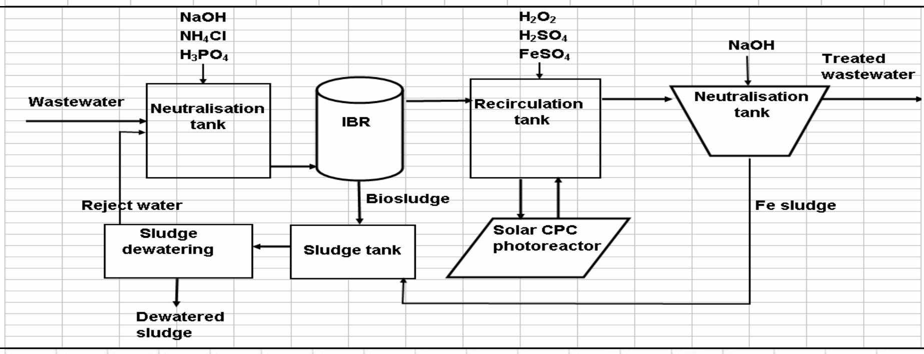
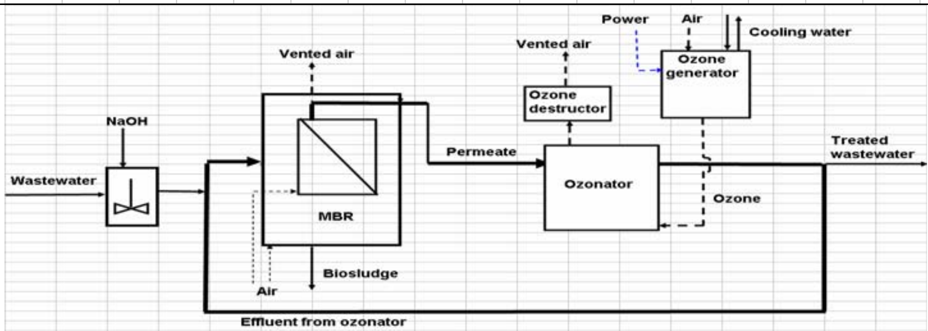
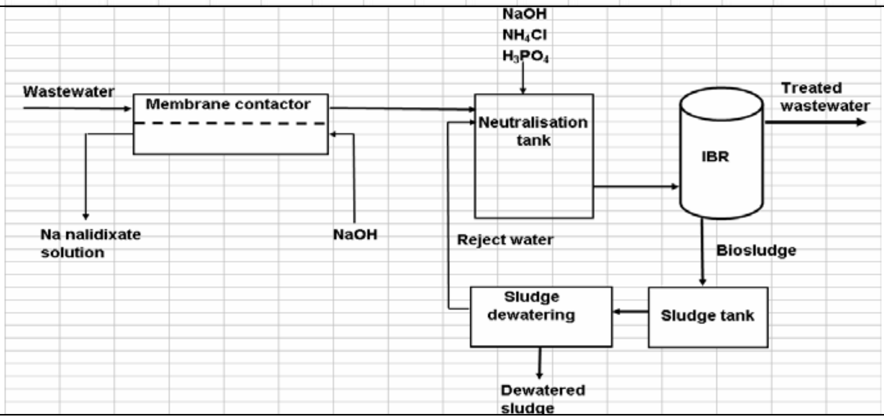
Parameter	**Value**	**Unit**
Wastewater flow	5	m^3/day
Nalidixic acid	0,045	kg/m^3
N-tot (N in the nalidixic acid)	0,005	kg/m^3
DOC	0,78	kg/m^3
COD	2,7	kg/m^3
TSS	0,50	kg/m^3
VSS	0,26	kg/m^3
PO_4^{3-}	0,01	kg/m^3
pH	4	
Cl^-	2,8	kg/m^3
SO_4^{2-}	0,16	kg/m^3
Na^+	2	kg/m^3
Ca^{2+}	0,02	kg/m^3
Conductivity	7	mS/cm

The treatment technologies, which could be tested on the standard case, are listed in table WP4.4. Some of them are designs based directly on experimental results from the other work packages. Other designs have been put together from literature data or experience or by combining data modules from different work packages.
All treatments were assumed to take place in the same geographical setting as follows:

- Supply of chemicals: Europe in general
- Supply of electricity: Southern Europe (Spain)
- Receiving water for the wastewater: Fresh-water course.

Since the plant designs are preliminary, and there is some uncertainty concerning the material standard of ordinary equipment like holding tanks, aeration tanks, pumps etc. the best approximation for the purpose of this comparative assessment is to exclude the construction material for these items and just include the construction material for special equipment like solar collectors, ozone generators + destructors and membrane contactors. The error introduced in the comparisons by this approximation is in our judgment within the uncertainty of the data at this point.

Table WP4.4 The technologies tested on the common case

Fictitious case MBBR + PAC Reference case Design with existing technology	
Studied case in WP2 Photo-Fenton + IBR	
Studied case in WP2 IBR + Photo-Fenton	
Studied case in WP2 MBR + Ozone	
Fictitious case Membrane-contactor + IBR MC model from WP3 IBR data from WP2	

The treatment results are reported in a traditional way in table WP4.5. The important function of the treatments is to remove organic compounds in general and nalidixic acid especially. Removal of nitrogen and phosphorus is not an important issue, and in this respect the results are varying. The increase of nitrogen in the MBBR + AC case is caused by an intentional excess dosage of nitrogen nutrient for the biology.

Table WP4.5 Treatment results for the nalidixic acid wastewater – Traditional reporting

	Nalidixic acid removal, %	COD/TOC removal, %	Nitrogen removal, %	Phosphorus removal, %
MBBR + PAC	90	88	-120	70
Ph-F + IBR	98	98	8	98
IBR + Ph-F	98	99	8	96
MBR + ozone	96	98	0	ca. 30 %
MC + IBR	98	96	8	96

In figure WP4.3 the treatment results are reported in a holistic way, i.e. both avoided impacts and impacts induced by operating the treatment plants and supplying them with commodities are taken into account. Other impacts than emissions of nutrients and COD with the treated wastewater, such as the greenhouse gas effect (global warming) and acidification, are also considered. All impacts have been normalised to a common scale, milliperson equivalents * years following the procedures and using the normalisation references of EDIP97. The avoided impacts have been calculated as illustrated in figure WP4.2.

Only impacts from emissions have been taken into account in figure WP4.4. Data on quantities and classification of generated waste from the commodity supply are uncertain, as are the normalisation references for wastes. All treatment technologies generate inert wastes to landfills, mostly overburdens from mining, and radioactive wastes. Use of the data from the inventories and the EDIP normalisation references for wastes seems to put an unreasonably high emphasis on wastes, however. We have thus limited this assessment to a comparison of avoided and induced emissions.

All the treatments avoid potential eutrophication from removed COD and potential ecotoxicity from removed nalidixic acid. A small potential greenhouse gas effect is also avoided. The organic compounds in the wastewater are synthetic and presumably of fossil origin. Their degradation in nature would thus contribute to the greenhouse gas effect. This avoided greenhouse gas effect is, however, induced again, when the wastewater is treated biologically or oxidatively, and when the biosludge is incinerated.

If our estimate of the ecotoxicity potential of nalidixic acid is accepted the highest-valued benefit of the treatments is the removal of an ecotoxic emission to water. This does not seem unreasonable since that was the reason for special treatment of this wastewater in the first place. Figure WP4.3 also suggests that if nalidixic acid would have been a completely harmless compound, the use of advanced treatment technologies would hardly have been environmentally warranted. Much or most of the benefit of high COD removal would have been neutralised by the impacts of potentially toxic emissions from the commodity supply. Potentially ecotoxic emissions to water and impacts of potential human toxicity in soil seem to be the kind of induced impacts, which infringe most on the sustainability, if we regard all environmental impacts as equally important. The normalised sums of induced acute and chronic ecotoxic emissions to water from the supply of electricity and chemicals amount to between 10 % and 40 % of the avoided ecotoxic impact, if we consider all kinds of ecotoxic emissions at any location equally important. The reported ecotoxic emissions from

generation of electricity and manufacture of chemicals are mostly metals. The impact on soil from substances, which are potentially toxic to human beings, are rather highly emphasized by the EDIP normalisation. The origin of this induced impact is emission of various hydrocarbons, notably benzene, to air. The inventories of emissions of organic compounds from the commodity supply chain are probably not complete. The induced toxic emissions may thus well be underestimated.
There is at this point a technical uncertainty in the results. The treatment plant designs are based on laboratory or short-period pilot-plant trials. The MBBR + PAC (reference case) and the MC + IBR cases were calculated from projected data from other applications. There is obviously a potential for improvements and optimisation. The MBBR reactor for instance was designed primarily with safe operation of the biology in mind, but could probably be better adapted to such small flows as 5 m^3/day, which would save a lot of electric power.

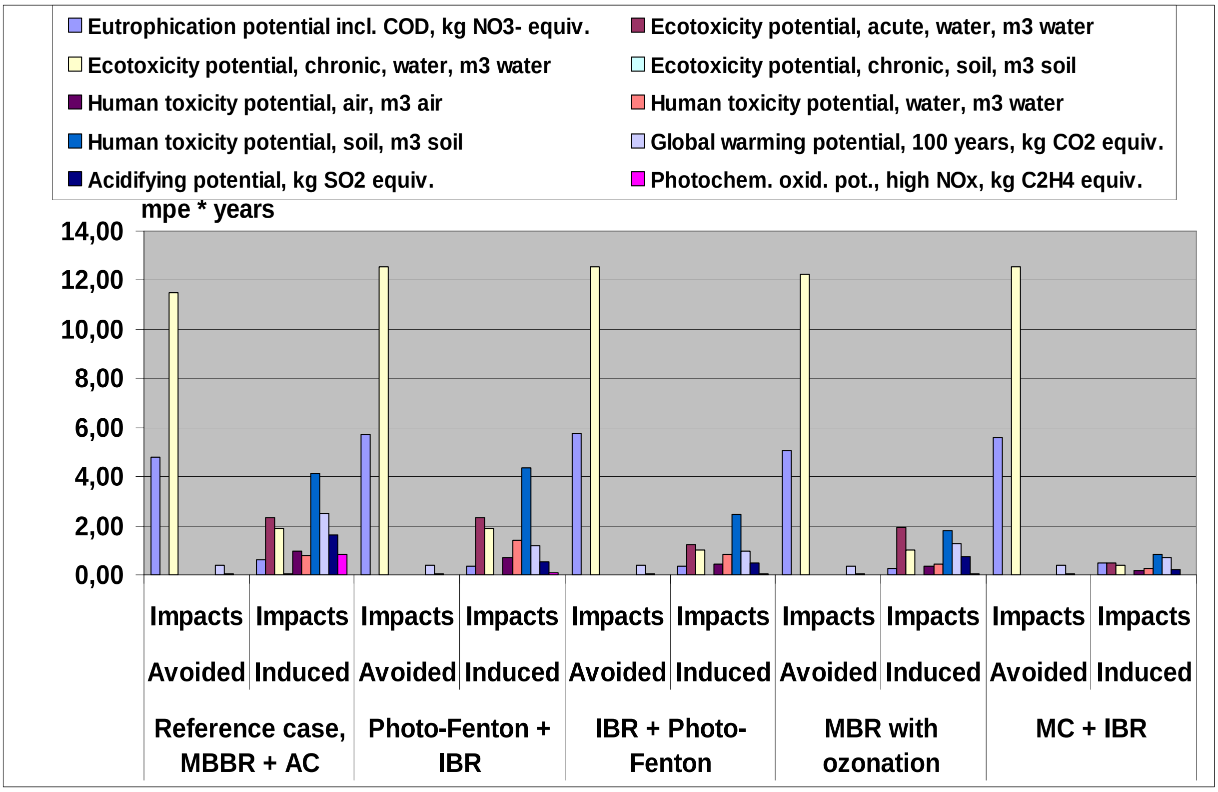


Figure 4.3. Treatment results for the nalidixic acid wastewater – Holistic reporting

CONCLUSIONS

Despite the uncertainties discussed above, the result in figure WP4.3 looks promising. It seems that the new technologies can improve treatment results for toxic and recalcitrant water impurities without higher costs in the form of higher induced impacts from emissions. The result also demonstrates how data from different experiments can be used for modelling “tailor-made” solutions. The “tailor-made” MC + IBR case (never studied experimentally in INNOWATECH) utilised the fact, that the problematic pollutant was an organic acid, to design and assess a treatment with data from one work package and a model from another work package.

Software used

MATLAB/Simulink distributed by The MathWorks, www.mathworks.com, 2008-10-15

GaBi distributed by the Institut für Kunststoffprüfung und Kunststoffkunde, Universität Stuttgart, and PE International GmbH, Leinfelden-Echterdingen, www.gabi-software.com, 2008-10

Microsoft Excel distributed by Microsoft, www.microsoft.com, 2008-10-15

References

Wenzel H., Hauschild M.Z. and Alting L., *Environmental assessment of products, Vol. 1 - Methodology, tools, techniques and case studies*, 1997,544 pp. Chapman & Hall, United Kingdom, ISBN 0 412 80800 5, Kluwer Academic Publishers, Hingham, MA., USA.

Ecoinvent 1.2 (2004), R. Frischknecht and N. Jungbluth ed., Swiss Centre for Life Cycle Inventories, Dübendorf, Switzerland.

5 DISSEMINATION AND USE

PUBLISHED RESULTS

The following is a list reporting only the results published, or submitted or in preparation, in referred journals. The whole dissemination activities are reported in the Final Plan for Using and disseminating the Knowledge.

Malato S., Wolfgang G.; Peña P., Dona Rodrıguez J. M.
Selected Contributions of the 4th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA 4).
Catalysis Today, 129 (1-2), 1-2, 2007

Mosteo R., Gumy D., Pulgarin C.
Coupled Photo-Fenton - biological system: Effect of the Fenton parameters such as residual H_2O_2, Fe^{2+} and pH on the efficiency of biological process
Water Science and Technology, 58 (2008) 1679-1685

Lapertot M., EbrahimiS., Oller I., Maldonado M. I., Gernjak W., Malato S., Pulgarin C.
Evaluating Microtox as a tool for biodegradability assessment of partially treated solutions of pesticides using Fe^{3+} and TiO_2 solar photoassisted processes
Ecotoxicol. Environ. Saf., 69 (2008), 546-555.

Comninellis C., Kapalka A., Malato S., Parsone S. A., Poulios I., Mantzavinos D.
Advanced oxidation processes for water treatment: advances and trends for R&D
J.Chem. Technol. and Biotechnology 83:769–776 (2008)

F. Mazille, T. Schoettl, C. Pulgarin
Synergistic effect of TiO_2 and iron oxide supported on fluorocarbon films. Part 1: Effect of preparation parameters on photocatalytic degradation of organic pollutant at neutral pH.
Applied Catalysis B: Environmental (2009), 89, 635–644

F. Mazille, A. Lopez, C. Pulgarin
Synergistic effect of TiO_2 and iron oxide supported on fluorocarbon films. Part 2: Long term stability and influence of reaction parameters on photoactivated degradation of pollutants
Applied Catalysis B : Environmental (2009), 90, 321–329.

Blanco. J, Malato.S, Fernandez-Ibanez P., Alarcon D.. Gerniak W., Maldonado M.I.
Review of feasible solar energy applications to water processes
Renewable and Sustainable Energy Reviews, 13 (2009) 1437 -1445

C. Sirtori, A. Zapata, I. Oller, W. Gernjak, A. Agüera, S. Malato.
Decontamination industrial pharmaceutical wastewater by combining solar photo–Fenton and biological treatment.
Wat. Res. 43 (2009) 661-668.

C. Sirtori, A. Zapata, I. Oller, W. Gernjak, A. Agüera, S. Malato
Solar photo–Fenton as finishing step for biological treatment of a real pharmaceutical wastewater.

Env. Sci. Technol. 43 (2009) 1185-1191.
S. Malato, P. Fernandez-Ibanez, M.I. Maldonado, J. Blanco, W. Gernjak.
Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends.
Catalysis Today (2009), 147, 1-59.

Di Iaconi C., Pagano M., Ramadori R., Lopez A.
Nitrogen recovery from a stabilized municipal landfill leachate
Bioresource Technology, 101 (2010) 1732–1736.

De Sanctis M., Di Iaconi C., Lopez A. Rossetti S.
Granular biomass structure and population dynamics in Sequencing Batch Biofilter Granular Reactor (SBBGR)
Bioresource Technology , 101 (2010) 2152-2158.

G. Mascolo, L. Balest, D. Cassano, G. Laera, A. Lopez, A. Pollice, C. Salerno
Biodegradability of pharmaceutical industrial wastewater and formation of recalcitrant organic compounds during aerobic biological treatment.
Bioresource Technology, 101 (2010) 2585–2591.

A. Moncayo-Lasso, J. Sanabria, C. Pulgarin, N. Benítez
Simultaneous *E. coli* Inactivation and NOM Degradation in River Water via Photo-Fenton Process at Natural pH in Solar CPC Reactor. A New Way for Enhancing Solar Disinfection of Natural Water.
Chemosphere (2010), 77, 296–300

G. Mascolo, G. Laera, A. Pollice, D. Cassano, A. Pinto, C. Salerno, A. Lopez
Effective organics degradation from pharmaceutical wastewater by an integrated process including membrane bioreactor and ozonation.
Chemosphere (2010), 78, 1100-1109.

F. Mazille, T. Schoettl, A. Lopez, C. Pulgarin
Physico-chemical properties and photo-reactivity relationship for para-substituted phenols in photo-assisted Fenton system.
Journal of photochemistry and photobiology A: Chemistry (2010) - doi:10.1016/j.jphotochem. 2009.12.015

F. Mazille, T. Schoettl, N. Klamerth, S. Malato, C. Pulgarin.
Field solar degradation of pesticides and emerging water contaminants mediated by polymer films containing titanium and iron oxide with synergistic heterogeneous photocatalytic activity at neutral pH.
Water research (2010), in press.

F. Mazille, A. Moncayo-Lasso, D. Spuhler, A. Serra, J. Peral, N.L Benítez, C. Pulgarin.
Comparative evaluation of polymer surface functionalization techniques before iron oxide deposition. Activity of the iron oxide-coated polymer films in the photo-assisted degradation of organic pollutants and inactivation of bacteria.
Chemical Engineering Journal (2010), doi:10.1016/j.cej.2010.03.035.

Sixto Malato, Isabel Oller, Pilar Fernández, Manuel I. Maldonado.
Descontaminación de aguas residuales industriales mediante fotocatálisis solar.
FarmaEspaña Industrial, 10, 26-28, 2010

A. Zapata, I. Oller, C. Sirtori, A. Rodríguez, J.A. Sánchez-Pérez, A. López, M. Mezcua, S. Malato
Decontamination of industrial wastewater containing pesticides by combining large scale homogeneous solar photocatalysis and biological treatment
Chemical Engineering Journal (2010), doi:10.1016/j.cej.2010.03.042

C. Bayer, M. Follmann, T. Melin, T. Wintgens, K. Larsson, M. Almemark
The ecological impact of membrane-based extraction of phenolic compounds – a life cycle assessment study
Water Science and Technology, in press.

Plósz, B.G., Jantsch, T.G., H., Vogelsang, C., Lopez, A.
Ozonation as a means to optimise biological nitrogen removal from landfill leachate.
Ozone Science and Engineering, in press.

Plósz, B.G., Langford, K.H., Heiaas, H.H.,Macrae, K., Liltved, H., Lopez, A., Vogelsang, C.
Occurrence of xenobiotic organic micro-pollutants in landfill leachate and PAHs removal from the liquid and sludge phases in a biofilm system combined with ozonation.
Water Science and Technology, in press.

C. Sirtori, A. Zapata, W. Gernjak, S. Malato, A. Lopez, A. Agüera
Analytical assessment and fate of nalidixic acid and its main transformation products during the treatment of an industrial effluent by coupling solar photo– Fenton and biooxidation
Analytical Chemistry, submitted.

Plósz, B.G., Vogelsang, C., Bomo, A.M., Rossetti, S
Controlled stratification of microbial populations in biofilm systems by reactor stages: A novel optimisation method using reaction kinetics
Water Research, submitted.

De Kreuk, M.K., Kishida, N., Tsuneda, S. and van Loosdrecht, M.C.M.
Behavior of Polymeric Substrates in an Aerobic Granular Sludge System.
Water Research, submitted.

Jeremy J. Barr, Andrew E. Cook, Phillip L. Bond.
Investigation of granular segregation within a synthetic EBPR wastewater system.
In preparation

Jeremy J. Barr, Frances Slater, Toshikazu Fukushima, Philip L. Bond.
Bacteriophage-host interactions cause community and performance changes in a mixed-culture activated sludge system.
In preparation

Andrew E. Cook, Jeremy J. Barr, Katrina McMahon, Phillip L. Bond.
Differential gene expression in floccular and granular systems.
In preparation

De Kreuk, M.K., Pronk M., and Van Loosdrecht, M.C.M.
"Aerobic granular sludge formation under elevated temperatures"
In preparation

A. F. Duque, Pronk, M., M.K. de Kreuk, M.F. Carvalho, P.M.L. Castro and M.C.M. van Loosdrecht
Evaluation of salt and pH effects on aerobic granule activity
In preparation

A. F. Duque, Pronk, M., M.K. de Kreuk, M.F. Carvalho, P.M.L. , M.C.M. van Loosdrecht, P.M.L. Castro.
2-Fluorophenol effects on aerobic granule activity.
In preparation

M. Pronk, A. Duque, J. Bassin, R. Kleerebezem, M.C.M. van Loosdrecht
Long term effect of salt on formation, population and activity in an Aerobic granular sludge reactor.
In preparation

MacAdam J., Santaulària R.G., Pidou M., Jefferson B. and Parsons S.A
Evaluation of UV/H2O2 and UV/TiO2 advance oxidation processes as a treatment for industrial wastewaters.
Applied Catalysis B, in preparation

MacAdam J., Ozgencil H., Jefferson B., Pidou M. and Parsons S.A.
Treatment of spent metalworking fluids using biodegradation and advanced oxidation processes
Journal of Hazardous Materials, in preparation

Autin O., Pidou M., MacAdam J., Jefferson B., and Parsons S.A.
Optimisation of a Membrane Chemical Reactor for the treatment of industrial wastewaters
Applied Catalysis B, in preparation

Pidou M., MacAdam J., Jefferson B., and Parsons S.A.
Influence of membrane configuration in an MC-R for industrial wastewater treatment
Environmental Technology, in preparation

Pidou M., MacAdam J., Jefferson B., and Parsons S.A.
Evaluation of reactor configuration in an MC-R for industrial wastewater treatment
Applied Catalysis B, in preparation

Pidou M., MacAdam J., Jefferson B., and Parsons S.A.
Study of TiO_2 particles aggregation in the photo-catalytic treatment of industrial wastes
Water Research, in preparation

Pidou M., MacAdam J., Jefferson B., and Parsons S.A.
Study of interactions between TiO_2 and membrane materials with AFM
Applied Surface Science, in preparation