

PROJECT FINAL REPORT

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4.1 Final publishable summary report

4.1.1 Executive summary

In CeraWater honeycomb like ceramic nanofiltration membranes with strongly increased membrane area were developed. Anti-fouling layers were developed and applied on these membranes. The membranes were extensively characterized and filtration processes in drinking and industrial wastewater treatment were successfully developed and demonstrated in half-technical scale.

First technical focus was put on the development of ceramic nanofiltration (NF) membranes with strongly enlarged membrane area. Basis for development were existing NF membranes on 19channel geometry with a cut-off of 450 Da and a membrane area of 0.25 m²/membrane. By a step-wise adaption of NF coating the membrane area per element could be increased by a factor of 5, by a combination of 4 pie shaped developed membrane bodies a membrane are of 4 m² (length 1 m) was achieved, resulting in a multiplication of membrane area by a factor of 16. CFD calculations were essential tools in order to optimize membrane support geometry and layer composition in terms of pressure stability and mass transfer. Next to the given standard support material a new material was introduced. This material allows higher membrane performance and decreases membrane price on terms of material and handling costs. For optimizing membrane performance in applications of high fouling potential various anti-fouling technologies were developed and tested. An optimized anti-fouling coating was developed on the membranes of increased membrane area and tested in model fouling mixtures in real applications. The developed coating strongly decreases fouling tendency/flux reduction in application in the tested media.

A special focus within the project was put on the application testing of the developed membranes in drinking water production and treatment of different industrial waste waters.

4.1.2 A summary description of project context and objectives

The main objective of CeraWater was the development of honeycomb ceramic nanofiltration membranes (HCNF) coated with anti fouling layers and with strongly increased membrane area. A robust, sustainable and eco-friendly process scheme should be developed to make HCNF competitive against conventional water treatment processes. The new and advanced ceramic nanofiltration (NF) process should be demonstrated in half-technical scale.

In combination with a high surface to volume ratio this should make ceramic honeycomb NF membranes competitive with polymeric membranes in terms of economics and technical performance due to the following features:

- A NF coating should allow for instance the direct filtration of surface water for drinking water preparation by a “low volume, low energy” filtration process.
- The low fouling tendency of the ceramic material should lead to low operating costs and reduced membrane down time during membrane cleaning.
- The high mechanical stability should enable high pressure back-flushing of the membranes.
- The high chemical and thermal stability of the membrane material should allow the chemical or thermal regeneration and sterilisation by effective chemicals or hot steam if needed.
- Furthermore ceramic membranes should show considerably higher permeate fluxes in comparison to polymeric membranes. In addition to the high permeability and a low fouling tendency the membranes should be operated at low transmembrane pressures and low cross flow velocities.

CeraWater addressed a crucial point in terms of a more extended use of membrane filtration technologies in water purification: the ratio between active filtration surface and module size. Besides overall ordinary requirements in membrane filtration like long-term stability, appropriate membrane price, high selectivity, high flux/pressure ratio, low energy demand for cross-flow-filtration and low membrane cleaning frequency this parameter is of vital importance for the implementation of ceramic membrane technique in a large scale.

Therefore, CeraWater should deliver ceramic honeycomb NF membranes that will:

- Be able to strongly improve the energy efficiency and usability of high performance water purification processes
- Allow an efficient process set up to remove bacteria and viruses from waters to produce safe drinking water on-site
- Remove or at least reduce toxins from water
- Be applicable in industrial water separation processes to clean water or recover valuable materials
- Improve the competitiveness of the European water purification industry (membrane manufacturer and plant manufacturer).

To broaden the area of application, to create a second development of high value and to even increase development's benefit an intermediate step in membrane development should be implemented.

The first membrane dimension was a honeycomb like multi-channel tube with strongly increased membrane area (by a factor of 5 compared to existing 19 channel tubes), named **HCNF1**. The second membrane dimension was a honeycomb with an increased membrane area and optimized mass transfer

characteristics called **HCNF2a**. The membrane support of HCNF1 was developed by partner Rauschert Klosterveilsdorf (RKV) just at the start of the project and it was available for membrane and intermediate layer development. Due to a similar geometrical proportion this membrane development should deliver vital information for membrane development on the large honeycomb HCNF2a. Furthermore these membranes allowed an early start and a sustainable development of the anti fouling coatings.

Content and concept

CeraWater focused on the optimization of the honeycombs material (material, sintering temperature, pore size, pore size distribution etc.), the definition of an optimal geometry of the honeycomb support, the development of a suitable NF coating including anti fouling coatings, the characterization and the installation of the ceramic membrane in modules. The development of module and system design and optimal treatment process should enable the optimal design and the efficient use of the HCNF. The new geometry and properties have the potential to change the process design in order to exploit completely the potential in terms of energy and chemical demand.

The membrane development should be in very close cooperation with further experts in the field of membrane application and in the field of water and wastewater treatment. Process combinations should be evaluated and alternative coatings should be prepared.

Around this basic element further R&D activities in terms of layer and process development (for different applications), demonstration of feasibility, evaluation of systems scalability and more should be performed. Only such integrated approach including Life Cycle Assessment (LCA) enables an overall, positive contribution to one of the main global societal issues – access to safe and pure water

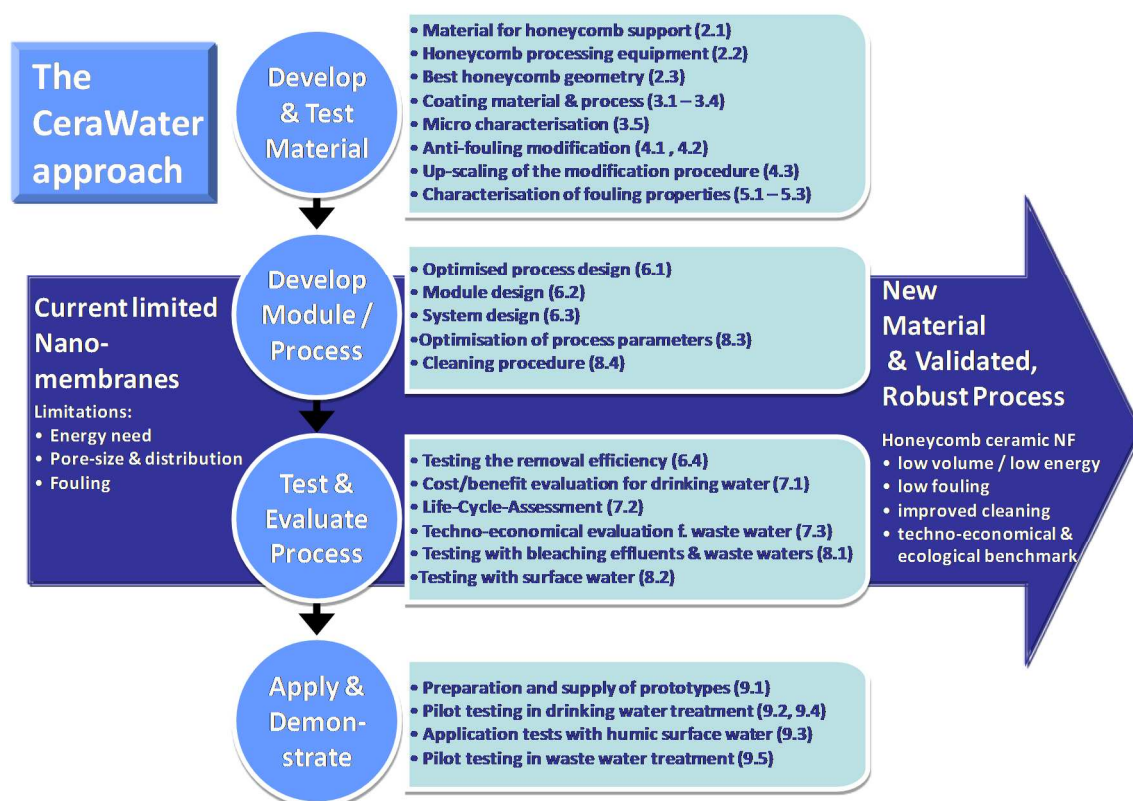


Figure 1: Workflow of project CeraWater

Although ceramic membranes have significant advantages compared to membranes made of polymers their use is limited to niche application due to their relatively high price per membrane area and restricted up-scaling of membrane area due to small membrane area per membrane element. Within the project the membrane area of an existing ceramic NF membrane element was strongly increased within two steps (HCNF1 and HCNF2a). The stepwise up-scaling of membrane area boosts the change of development success and increases the area of application. The developed membrane elements should be of high industrial relevance due to the combination of a large filtration area and nanostructured active membrane layer for selective separation on molecular level. Membrane's composition should be evaluated and simulated very carefully to obtain the desired cut-off on the one hand and a high permeability and stability on the other hand.

Membrane fouling processes, that are an important problem, strongly reduce membrane performance. Therefore the project focussed strongly on the improvement of fouling characteristics. Ceramic NF membrane materials have per se a low fouling tendency (due their strong hydrophilicity, low pore size and low surface roughness). This is particularly true for the NF layer of IKTS. In contrast to other filtration layers on the basis of slurry coating or colloidal sol-gel technique (slit pores), these layers are produced by a polymeric sol-gel technique that leads to cylindrical pores² that are much more fouling resistant. The project should additionally address the issue of fouling to develop even more fouling resistant membranes. More specifically the project looked into the potential of extra grafting of the membrane surface, in order to further decrease the membrane fouling capacity. Fouling is a result of the adsorption/deposition of specific feed components (as e.g. NOM³) on the active surface of the membrane. The grafting used in this project aimed at the replacement (partly or complete) of the OH- reactive groups on the membrane surface, by less-reactive groups, and this without too much altering the hydrophilic character and therefore the permeability of the membrane (by using short grafting groups as e.g. methyl groups). Consequently, this grafting should result in a still hydrophilic surface with strongly decreased interaction possibilities between foulants and membrane surface, and therefore in an anti-fouling action. The HCNF including its production technology should have the potential to be a core element for a large range of applications: production of drinking water from different origin (ground water, surface water), purification and water recuperation of a broad range of waste waters, recuperation of valuable compounds (e.g. metals) from waste waters, production of boiler water or other type of process waters, purification of produced water in oil fields, separation of nutraceuticals in the dairy industry etc.

The project focussed on drinking water and particular industrial waste waters. Bleaching stages discharge wastewaters which are not completely degradable by biological treatment processes have a detrimental impact on environment. Effluents streams are typically alkaline or acidic and contain significant amount of refractive compounds. Their treatment using membrane filtration and purified water reuse would reduce the fresh water use and the environmental impact of the pulp mills. This is a challenging task since acidic pulping effluents cause strong membrane fouling. Moreover the potential reuse of the clean water generated by the NF, some valuable compounds can be recovered from specific wastewaters, with the consequent economic benefits. Olive oil processing wastewaters were tested to evaluate the recovery of polyphenols for example.

The development of the filtration process fitted to the characteristics of the membrane to be developed should be a vital task to obtain the maximal membrane performance.

² Voigt, I. et al.: The pore structure of meso- and microporous TiO₂-membranes, Cfi/Berichte der DKG 79(2002)8. - S. E39-E44

³ natural organic matter

The application tests in two different areas of water treatment should explore the membrane ability for those separation processes and should give a required feedback to the membrane developers (in particular development of nanofiltration layer and anti-fouling coating) and allowed a contemporary adaption of membrane preparation.

Tab. 1: Scientific and technical objectives of CeraWater

R&D objectives of the call	CeraWater project
Modelling, rational design and development of innovative tailored nanostructured membranes with high hydraulic permeability, high selectivity, low fouling tendency, enhanced stability	Development of ceramic (highly stable), honeycomb (high packing density and high hydraulic permeability) (WP2), NF (high selectivity) membrane (WP3) with extra grafting for low fouling (WP4) combined with high permeability. Modelling and rational design of the honeycomb structure (WP2.2) and the anti-fouling grafting (WP4).
Development of robust processes for processing and up-scaling of the new membranes	Development of a robust and up-scalable (extrusion and sol-gel coating have proven to be robust and up-scalable production processes) production of the innovative ceramic honeycomb with anti-fouling grafting (WP2-4). Development of a module design and filtration process (WP6).
Demonstration of water treatment modules in relevant separation processes	Application testing and demonstration of new developed large-scale modules in drinking and waste/process water separation processes (WP8, WP9).
Assessment of risks and benefits of the new technology	Life cycle assessment, cost analysis, techno-economical evaluation and comparison with existing technologies (WP7).
Industrial relevance	Active participation of industrial partners: RKV (membrane manufacturer), VMW (end-user) and CYCLUS (OEM, end-user).

4.1.3 A description of the main S&T results/foregrounds

WP 2 Development of ceramic honeycombs with strongly enlarged filtration area (HCNF2) suitable for coating

The starting point of the CeraWater project, in case of the membrane material development, was the standard support of Rauschert (A-1) made of high purity aluminium oxide (> 99.7 %). Pure Aluminium oxide shows a very high chemical and mechanical resistance for example in contact with acidic or alkaline environments or in the treatment of abrasive materials. On the other hand it is also a very expensive material and requires very high temperature for processing.

The use of ceramic nanofiltration membranes for the treatment of different water streams suffers mainly from two important points. The relatively high price for one m² of membrane and the low filtration area/volume ratio of ceramic membranes. During the CeraWater project a new membrane material was developed by changing a bit the content of aluminium oxide. As a result a membrane support material ("CW") with improved characteristics like a larger pore size and a higher open porosity which help to reduce flux resistance in the support material was found.

The new ceramic mass has also a very low sintering temperature, a very important point for saving a lot of energy in the membrane production and therefore very important for the entire production costs. These new material was also used for coating experiments with the nanofiltration layers and showed excellent results which are later described into detail.

Table 1: Different properties of the supports made of the two general materials

Parameter	A-1 material	CW1 material
Composition	99.7 % Al ₂ O ₃	>96 % Al ₂ O ₃
Open porosity	28 – 32 %	42 %
Pore size	3 µm	4.5-5 µm
Sintering temperature	1700 °C	1400 °C

Regarding the filtration area/volume ratio one of the main project objectives was to develop membrane support geometries with strongly enlarged active membrane surface. As can be seen in figure 1 the starting point was the established 19 channel geometry with a membrane area of 0.25 m²/1.2 m membrane length and the 61-channel membrane with 0.5 m²/1.2 m. For the first developments in the project, the 163-channel membrane support with an outer diameter of 41 mm and an active filtration area of around 1.3 m²/m was used. The combination of the 163 channel design with the new membrane material was successfully tested for the nanofiltration coating and showed excellent results in respect of membrane flux and retention.



Figure 2: Different membrane support geometries made by RKV (From left to right: 19 channel-, 61 channel- and 163 channel design.)

Many competitors see a good option for enlarging the filtration area with ongoing enlargement of the membrane tube diameter. A known drawback of these method is the fact that with larger diameters the inner channels become more and more ineffective for the filtration.

Extensive calculations were performed on mass transfer through membrane support and pressure distributions as well as permeate flow across membrane support were calculated. Also the influence of intermediate layers was considered. Calculations showed that a high pore diameter of membrane support improves the mass transfer clearly. It could be shown that in case of nanofiltration and the given membrane structure the influence of the support is considerably stronger than the influence of the intermediate layers.

Theoretical support structures were used for the calculations to discover influence of membrane support and active layer and to identify maximal theoretical membrane support dimensions. Pressure distributions and simulated permeate fluxes were calculated for the existing membrane geometry HCNF1 and the developed geometry HCNF2a. The results show low loss of pressure during permeation of membrane support and high specific permeate fluxes. Furthermore these results could be practically confirmed by filtration tests with the developed membranes. Figure 3 shows the pressure drop in the cross section of HCNF2a membrane supports during filtration coated with a nanofiltration layer. It can be clearly seen, that in case of the NF layer the mass transfer resistance in the thin layer dominates the mass transfer resistance in the support structure leading to an efficient support geometry for this active coating. The calculated permeances of 36 l/m²hbar (

Table 2) match the results obtained in membrane characterization very good.

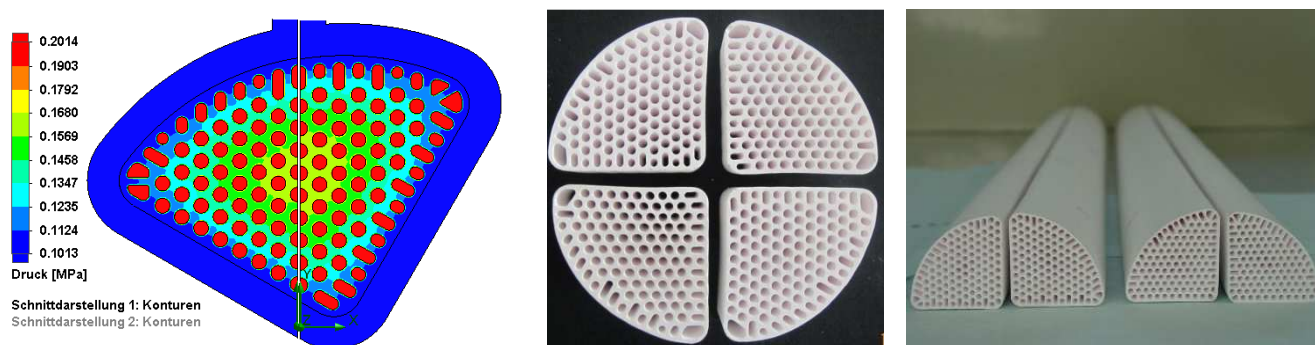


Figure 3: Pressure drop in the cross-section of new developed HCNF2a membrane geometry (with NF coating) and pictures of new quarter shaped membrane support design produced by partner RKV

Table 2: Calculated permeances and permeate flows for theoretical and real support geometries coated with NF layer.

Shape	Permeance	Permeate flow	
	[l/m ² h bar]	[l/h] Ref. Vol.	[l/h] L250
th 0.95 5 rows*	35.7	96.4	-
th 0.95 7 rows*	30.7	87.1	-
12x12 cells	28.4	75.9 * ²	8.6 * ³
HCNF1	33.8	58.5 * ²	7.1 * ³
HCNF2a	36.0	68.0 * ²	7.8 * ³

Calculation of mechanical behaviour

The calculations of mechanical behaviour were performed for the most interesting load case, the so called bursting pressure. This means a uniform pressure at the inside of all channels of the structure. These calculations were an important tool for mechanical optimization of membrane geometry. So the principal stress could be reduced from 22.2 MPa to 16.0 MPa (at a pressure of 20 bars) by a slight modification of the membrane geometry, leading to significant higher burst pressures of membrane elements.

The distributions of 1st principal stress give any ideas for an improvement of the design with respect to the mechanical behaviour. Especially the channels with a relatively great cross-section area at the edges of the structure (1st design) are unfavourable with regard to strength. For a better understanding the figures at the right side show the location of maximal stress within a considerably enlarged view of the resultant deformation. The light green area shows the unloaded structure. With this knowledge the decision was taken to split the channels into two separate channels. This means also a more homogeneous hydraulic diameter with respect to the channels of the structure. The flow behaviour especially the flow velocity is homogenized. A reduction of the maximum value of 1st principal stress from 22.2 MPa to 16.0 MPa is achieved at a pressure of 20 bars. But the comparisons with the well known 19-channel tube (5.8 MPa) and the 61-channel tube (10.7 MPa) show a tendency to higher stress in structures with much more channels. The goal should be a targeted design improvement especially of selected channels at the outside of the structure (radius, shape). The resulting membrane support geometry is shown in Figure 3. With a length of 1 m and 122 channels every element has an active filtration area of around 1 m² and all together around 4 m². The channels have an average diameter of 2.5 mm ideally for the filtration in drinking water applications. This new membrane geometry is now available from RKV. The design of the channels was optimized together with IKTS by finite element calculations (FEM) to enhance the burst pressure stability especially at the edges of the membrane.

Also the coating technique was adapted from the standard tube geometry to the quarter shape and first real membranes with different separation layers starting from microfiltration to ultra- and nanofiltration were prepared.

The next steps after the project are extended test of new sealing techniques to make smaller housings with the same membrane area to go on with the optimization of the area/volume ratio. The membranes will be tested in different applications in the field of drinking water production, wastewater treatment and other industrial filtration processes.

Highlights of the new membrane material and geometry:

- High energy savings through lower sintering temperature
- Larger pore size of 4.5-5 µm and higher porosity for optimized permeate flux
- Cost savings for the support production of up to 30 %
- Reduced contact sensibility of the new material allows a simplified sintering process
- New quarter geometry shows higher burst pressures as the established 163-channel design
- The standard coating process from the tube geometry was adjusted and successfully tested with the new geometry
- The new membranes will be available for different filtration applications in the micro-, ultra and nanofiltration range in the near future

WP 3 Development of NF coating on ceramic honeycombs

Nano filtration (NF) membranes made of ceramics are of many advantages regarding stability (chemical, mechanical, thermal) and flux in comparison to polymeric ones. Ceramic NF-membranes with a cut-off of 450 Da prepared inside of 1.2 m long 19-channel elements (0.25 m²) are state of the art. However, large-scale applications in water treatment are hindered by the high production costs of these membranes. A strongly reduced membrane price could be achieved by the development of ceramic NF-membranes on geometries of larger specific membrane area and reduced production costs.

The ceramic support material was optimized by systematic variation of grain size and materials composition. Support geometries of increased specific membrane area of 0.5 m² (61-channel tube (61-CT)), 1.25 m² (163-CT) and 4x1 m² (quadrant) were prepared by extrusion. All geometries were stepwise coated by slurry, colloidal and polymeric sol-gel technique. Coating technology and coating solutions were adapted to the different geometries. Final membranes and selected intermediate layers were characterized by pure water flux, polyethyleneglycol (PEG) retention and cut-off determination. Single samples were investigated by FESEM (field emission scanning electron microscopy).

A support material made of α -Al₂O₃ of a reduced sintering temperature and increased pore size of 4 μ m was developed in WP2. Several defects were detected in the intermediate layers after first coating trials. Only by stepwise optimizing of every single coating step a nearly defect free and smooth asymmetric support structure could be prepared.

After final coating with polymeric sol-gel technique ultra-thin NF layers of only 17 nm were observed inside the 163-CT. However, perfect cut-off values of 400 Da (163-CT) and 1,100 Da were determined. Results on cut-off measurements can be found in the membrane characterization part. Figure 4 shows a cross section of a HCNF1 structure.

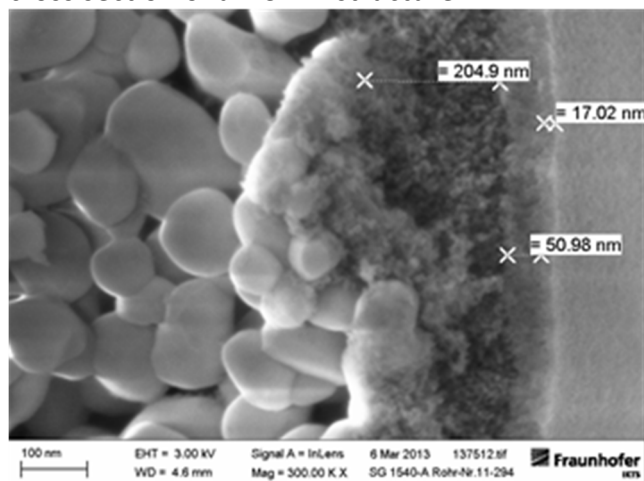


Figure 4: NF-membrane layer inside of HCNF1-structure (SEM-figure)

The worldwide first ceramic NF-membrane on elements of enlarged membrane area was developed and opens opportunity for large-scale application.

WP 4 Development and Test of Anti-Fouling Coatings

Efficient anti-fouling coatings were developed on the ceramic NF honeycombs in the project. Focus was put on fouling reduction for drinking water purification and applications in specific process streams correlated to WP8 and 9.



Task 4.1: Development of a flexible anti-fouling modification

The philosophy of membrane grafting to further reduce the already low fouling sensitivity of ceramic NF membranes is as follows: the membrane grafting replaces (totally or partially; on the complete pore surface or only on the outer membrane surface) the OH-groups abundantly available on ceramic NF membranes with other groups that are more inert towards interaction with foulants. To retain sufficient hydrophilicity of the modified membranes, the grafting groups utilised are small organic groups as methyls (M) or phenyls (P). In this project, 2 grafting procedures delivering highly stable hybrid organic-inorganic nanofiltration (NF) membranes are used: grafting using Grignard chemistry (GR, proprietary method of VITO) and grafting using phosphonic acids (PA, known in the art). Both methods lead to different membrane surfaces.

At the start of the project, VITO has successfully adapted the already known procedures of GR and PA grafting in order to graft also fine-porous NF membranes. Characterization of the different grafted membranes lead to the following conclusions:

- The water flux of MPA, MGR and PGR membranes is sufficiently high, and about 50 % of the water flux of the ungrafted membranes. PPA membranes are too hydrophobic.
- Retentions measured with different model neutral solutes (e.g. polyethylene glycol typically used for molecular weight cut-off measurements, and humic acids, meat peptone and laminarin gum as representative for foulants in surface and ground water) is similar as for the ungrafted membranes. Tests with real surface water confirm this.
- In more heavily fouled waters as real olive oil waste water, the retentions of the grafted membranes (measured on the basis of COD) were clearly higher. This is most likely due to the different fouling and concentration layers determining the separation behaviour (more details in WP5).
- The salt retentions of grafted membranes are typically lower than for ungrafted membranes due to the lower amount of OH groups and therefore lower charge on the pore surface.
- Fouling tests with model foulants in task 4.2 have shown that MGR grafting is the most optimal, and shows in many cases no irreversible fouling.
- MGR grafted membranes were subjected to cross-flow filtration during 24h using different corrosive media at different temperatures, to study their stability. The stability of grafting is sufficiently high to allow proper cleaning of the MGR membranes in real surface waters, and in different waste waters. In this respect we want to remark that the MGR membranes can be properly cleaned using less aggressive media (e.g. pH=10 instead of 12), as their fouling is strikingly lower.

Task 4.2: Optimisation of the modification for optimised fouling reduction in drinking water and specific process stream purification

At the start of the project an efficient procedure for fouling measurements was determined, assessing the irreversible fouling of a NF membrane by comparing its water flux before and after fouling with a specific foulant mixture (ratio of water fluxes used). The following conclusions can be drawn from the extensive testing in WP4.2:

- All grafting leads to less fouling, however, the anti-fouling effect depends on the grafted group and on the grafting method
- MGR membranes show unparalleled low fouling, and show no irreversible fouling at all for humic acids (with and without Ca), meat peptone and laminarin gum, all foulants representative for surface and ground waters. The same excellent anti-fouling effect was obtained in a model mixture for pulp and paper effluents, and in real olive oil waste waters (related to WP8, 9). In solutions containing a low

amount of aromatic rings (corresponding to a low UV/VIS adsorption at 254 nm), PGR membranes show the same low fouling as the MGR membranes. Results are summarized in Figure 5.

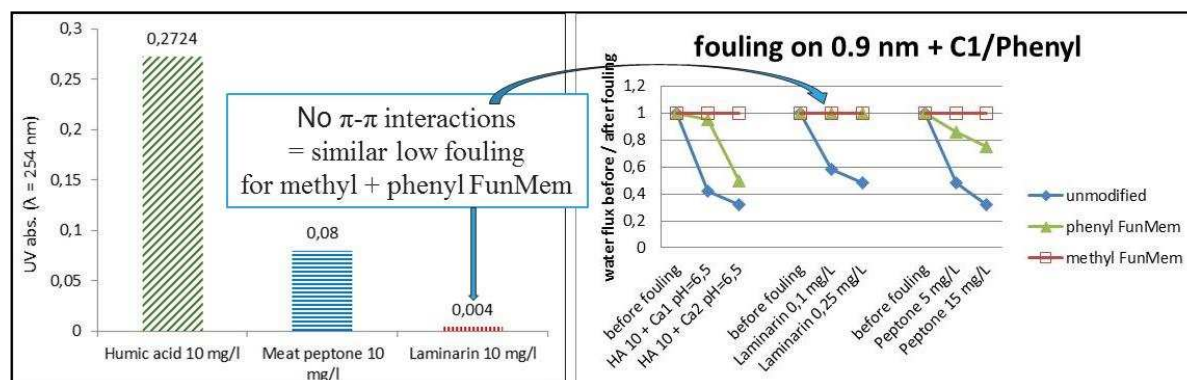


Figure 5: Irreversible flux decrease (normalised fluxes) of native and MGR and PGR membranes caused by different fouling solutions (right figure), correlated to the UV/VIS adsorption of the different foulant mixtures (in similar concentration).

- The anti-fouling effect of the grafting can be qualitatively explained by the physicochemical properties of the foulants and the membrane surfaces, and their possible interactions. The inert character (inert = no interaction with foulants) of the MGR membranes causes their extraordinary results.

Due to this very good results, and the knowledge how to steer the anti-fouling effect, it was decided to file a new patent application claiming grafting as a method to reduce fouling of ceramic membranes. The submission number and date was EP 14 156 401,3 at 24/02/14. The corresponding PCT application has the number PCT/EP2015/053772.

Task 4.3: Scale-up of the modification process in order to modify the NF honeycombs

During the project, successful steps were set to scale-up of the grafting:

- Batch reactors were exchanged for flow reactors, using a small trans membrane pressure in order to force the reaction liquid through the membrane pores.
- A new glove-box was designed and ordered to flexibly graft membranes of different size, up to 1.5 m length, and up to HCNF1 and HCNF2 design. In the new configuration, the standard filtration module of each membrane design, hanging now under the glove box, is utilised as flow reactor vessel.
- At first 50 cm and 120 cm long 19 channel elements were grafted in the new glove-box. Fouling measurements show that the grafting was successful (almost no irreversible fouling), reproducible and similar over the length of the membranes.
- In July 2014, the first HCNF1 membranes were grafted. The water flux ratio after humic acid fouling for the well-grafted membranes was about 0.9, similar to the one of the well-grafted 19 channel elements. End of January 2015 also one HCNF2a membrane was grafted. Fouling tests with humic acids showed that the quality of grafting was similar as the grafting on the HCNF1 elements.
- A variety of grafted membranes were handed over to different partners in WP6, WP8 and 9. Four grafted HCNF1's (CW support) were mounted in the pilot of partner VMW at the Blankaart, Belgium.

WP 5 Membrane characterisation

The developed HCNF1 and HCNF2 honeycombs, with and without anti-fouling layers, both in non-fouling and model fouling environment were intensely characterized. The filtrations used for this characterisation were done in cross-flow. Results were used to steer the developments in WP2, WP3 and WP4.

The results in the 3 task of WP5 are obtained by all partners involved.

Task 5.1: Determination of model foulant mixtures

In discussion with all partners involved, a list of model foulant mixtures was defined, relevant to the fouling situations studied in this project: surface/ground water for drinking water production, pulp and paper effluents, and olive oil waste water (in WP8 and 9).

Task 5.2: Characterization of the developed honeycombs in non-fouling conditions

Many different results have been obtained by different partners. We can summarize the results as follows:

- At the start of the project Partner UCA has characterized the standard 120 cm long 19 channel NF membrane of partner IKTS/RKV and has set as such a good reference performance for the HCNF1 and HCNF2 honeycombs in development.
- Partner IKTS used PEG retentions as a quality test of the HCNF1 and HCNF2 honeycomb membrane elements in development. This characterisation showed that the quality of the elements decreases with the increase of their surface area. This was also confirmed by measurements in non-fouling and fouling conditions by other partners.
- The first generation of HCNF1 elements showed MWCO values > 5000 g/mol. However, the last generation of honeycombs coated on supports of CW material, showed real nanofiltration performance: the HCNF1 elements show a MWCO of ~400 g/mol; the best HCNF2a elements show a MWCO of ~1100 à 1200 g/mol. Permeabilities were in both cases about 30 l/hm²bar.
- The reproducibility of the HCNF1 and HCNF2a coating was studied and proved to be very satisfactory.
- A variety of honeycomb membranes were delivered to different partners for tests in WP6, 8, 9. E.g. 3 of the last generation and 9 of the first generation of HCNF1 membranes were mounted in the surface water pilot from partner VMW, at the Blankaart (WP9).
- At partner UCA, a first generation HCNF1 membrane was installed on the pilot plant at “El Montañes” Metropolitan Drinking Water Treatment Plant (MDWTP). This membrane was characterised for its microsphere retention, and proved to be high (> 92%) if concentration polarization was low enough.
- Partner VITO has shown that also on large-scale membranes, up to HCNF1 and HCNF2a design, well-grafted membranes show a 50 % reduction in their water flux combined with a similar retention behaviour, as for smaller membranes (see also WP4, task 4.2).
- Partner LUT developed equipment and characterized streaming potential and surface charge of 50 cm long 19-channel nanofiltration membranes. Based on the preliminary measurements it seems that the zeta potentials of both native and grafted membranes are near neutral (less than -10 mV). Verification of these results is ongoing.

Task 5.3 : Characterization of the developed honeycombs in fouling conditions

Also in this subtask, many different results have been obtained by the different partners involved. We can summarize the results as follows:

- At the start of the project Partner UCA set a good reference performance for the HCNF1 in development in fouling conditions. For that they tested a 120 cm long 19 channel membrane of RKV with different model fouling mixtures mimicking surface or ground waters: humic acids, peptone, Aerosil colloid and microspheres. Influence of pH and the presence of Ca ions on flux and retentions of humic acid mixtures was studied as well.

- Similar tests using a first generation HCNF1 membrane were also performed by partner UCA. Retention results showed that the performance of this early HCNF1 is somewhat lower than the 19 channel tubes. This is logically attributed to the higher MWCO of this membrane (see task 5.2). However, the variation of the HCNF1 membrane fouling and performance with humic acid concentration, pH and Ca content, was similar as measured for the 19 channel membrane design (see Figure 2). With peptone used as organic foulant model, or Aerosil 200, used as inorganic foulant model, the membrane showed to be fouling resistant under the different operating conditions employed.

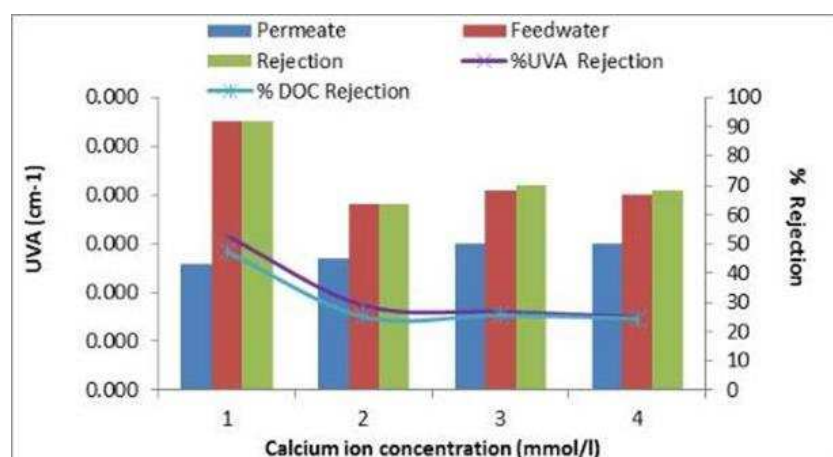
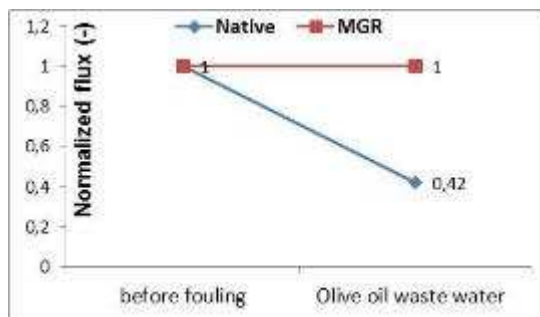


Figure 6: Influence of calcium concentration on humic acid rejection of a first generation HCNF1 membrane.

- Partner VITO showed that the cross-flow has an influence on the membrane performance during real surface water filtration: a higher cross-flow delivers a higher retention. This effect is smaller for grafted membranes. This effect was also not noticed in model fouling mixtures.
- Partner VITO proved that MGR grafting of membranes for anti-fouling action, spectacularly diminished the irreversible fouling in all fouling conditions tested. In the filtration of real olive oil waste waters it was shown that grafting cannot only lead to serious process flux increase, but also to increase of COD retentions (see Figure 3). In model fouling conditions using humic acids, meat peptone and laminarin gum, retentions of grafted and ungrafted membranes are similar (see also WP4.2).
- Partner UCA adapted the standard cleaning procedures for ceramic nanofiltration membranes to remove strong organic and/or inorganic fouling of first generation HCNF1 membranes. CaSO_4 scaling proved much more persistent than CaCO_3 scaling.
- Partner VITO studied cleaning of different grafted membranes, also on large-scale membranes up to HCNF1 and HCNF2a design. Organic fouling was easily (more easily than for native membranes) removed using pH=10 at 50 à 60 °C. Higher pH levels, and higher temperatures are not feasible (but also not necessary) due to the limited stability of the grafted groups (see WP4).



	pH	CE (mS/cm)	COD (mg/l)	Retention (%)
MGR	3.80	3.23	12,050	48
Native	3.58	4.96	20,820	11
Feed	4.74	4.53	23,280	-

Figure 7: Irreversible fouling (figure on the left) and retention results (table on the right) of native and grafted 50 cm long single tube membranes in real olive oil waste water supplied by partner Cyclus.

WP 6 Development of module and system design and an optimal treatment process

Major concerns for the application of membrane technology in water treatment processes are the energy demand, which is needed especially for pumping, and the control of membrane fouling. Factors influencing the energy demand are the pressure needed to drive the filtration process, to overcome the resistance of membrane, fouling layer and concentration polarisation. As the concentration polarisation and fouling is depending on the rejected water compounds and the flow field inside the channels one strategy to control fouling is by inducing turbulent flow conditions. Furthermore, pre-treatment processes are applied to prevent the module from foulants or damaging substances. As fouling cannot be avoided in real applications efficient cleaning strategies are needed. The module design is influencing the operation parameters, such as pressure drop along the channels, and needs to provide the mechanical and chemical properties suitable for the applications and cleaning methods. During the project a new module was developed and a treatment system adapted to the HCNF properties has been designed.

Task 6.1: Determination of an optimized process design in terms of energy and chemical demand

To assess the module properties and to develop an optimal treatment process tests using surface water from the river Ruhr (Germany) and effluent from a municipal waste water treatment plant (capacity for ~ 450,000 pe) have been performed in a semi technical scale. To study the influence of selected compounds in more detail, model solutions containing sodium sulphate, calcium chloride or humic acids have been tested, additionally. The module types 19 CT, HCNF1 and 19CT-grafted have been investigated under similar conditions.

The results of this application tests have shown:

- **Pre-filtration:** To prevent clogging of the module channels a micro-sieving with ~ 500 µm was applied
- **Anti-scalant dosing:** With the tested real raw waters only very little salt retention was observed (<10 %), whereas experiments with model solutions containing only Na₂SO₄ showed up to 80 % of ions retention This shows that an anti-scalant dosing might become necessary. Because the ion retention is strongly depending on the water matrix the assessment should be included into further pilot and laboratory experiments.
- **Cross flow velocity and permeate flux:** The module construction and material allow the operation of the HCNF modules at very low to very high crossflow velocities. The experiments showed that at a constant permeate flux of 40 L/m²h and laminar crossflow flow conditions (0.5 m/s) the permeability decreased slowly, but constantly (pressure increase between 2 to 7 bars within 5 to 10 h filtration). When the crossflow velocity was increased to reach turbulent flow (2 m/s) almost constant permeability could be maintained (~ 5 bar).



- **Hydraulic cleaning strategies:** To maintain the permeability on a constant level even at low crossflow velocities hydraulic backwash, forward flush and air flush was applied. A significant effect of these strategies was only observed during filtration of waters containing high amounts of colloids and particles, such as waste water or coagulated water (Figure 8).
- **Coagulant dosing at dead-end operation:** Experiments with constant coagulant dosing showed that the modules can be operated at dead-end filtration with regular backwashes (e.g. every 2 h for 2 - 5 min). Under this experimental conditions even higher permeate fluxes up to 80 L/m²h could be reached at stable low pressure conditions.
- **Chemically enhanced backwash:** The permeability decline caused by organic fouling could be partially removed by chemically enhanced backwash with NaOH at pH 11.5 (~ 20 °C) and 10 - 30 min of dwell time. CEBs have shown recoveries in permeability of 10 % for river water and even 70 % for humic acid solutions. The advantage of the CEB cleaning is the small demand of cleaning solution compared to the more intensive CIP.
- **Cleaning in place:** The cleaning in place (CIP) strategy which gave reliable good results was an alkaline cleaning at a crossflow velocity of 0.5 m/s for 10 min with NaOH and < 1 % EDTA (pH 11.5, ~30 °C) followed by an acidic cleaning with HCl (pH 2.5, ~30 °C). Figure 9 shows the effect of the different cleaning strategies which were performed one after the other after the membrane was fouled during filtration of surface water.
- **Further treatment steps:** It can be assumed that no pH-correction or other stabilisation technologies will be required resulting especially from the use of HCNF modules, as no significant change in pH-value and conductivity was observed. However, due to moderate removal of dissolved organic carbon (DOC) and low removal of trace organic substances, a post-treatment, such as activated carbon filtration, might be needed. Alternatively, powdered activated carbon dosing in front of the membrane could be used to increase the removal of organic substances if seasonal events occur.
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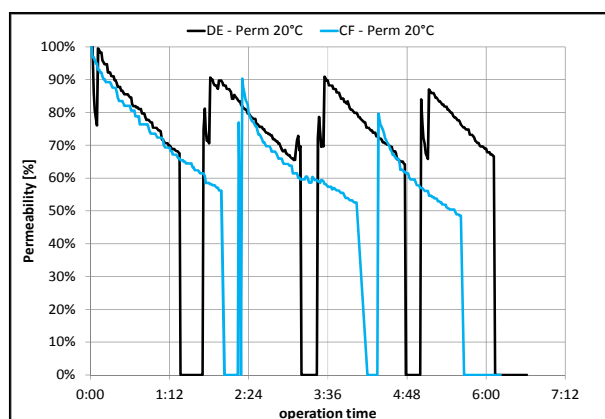


Figure 8:
Comparison of dead-end operation (plus coagulant 5 mg/L Al) and crossflow (0.5 m/s) at filtration of tertiary waste water using 19 CT with regular hydraulic backwashes

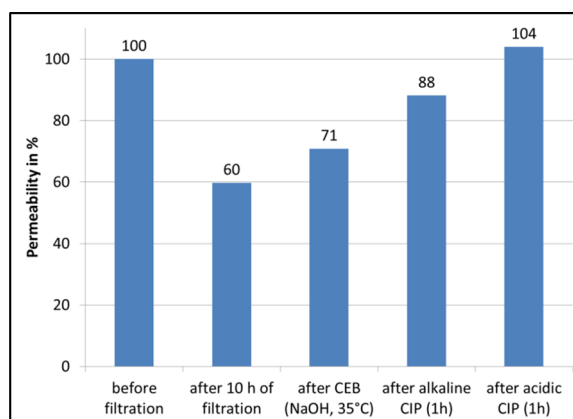


Figure 9:
Recovery of permeability (HCNF1) after river water filtration and subsequent chemical cleaning steps (starting permeability: 18 L/m²hbar $\pm$ 100 %)

In direct comparison 19CT and HCNF1 modules using corresponding process parameters showed similar results. Further results of pilot experiments carried out with surface water and highly polluted waters from industrial processes are reported in WP8 and WP9.



Task 6.2: Development of module (housing plus element) designs

The housing development is strongly linked with the development of the ceramic honeycombs, which is described in WP2. Different module and housing designs might be necessary with regard to the significantly different applications of interest. Furthermore, the possibilities for hydraulic cleanings should be regarded in the construction of the module housing. The different application tests showed that the crossflow operation is most likely to be applied and thus module and housing has been designed for crossflow.

In a first step the module type HCNF1 (136 channels; $\sim 1.3 \text{ m}^2$) and housing has been produced to be used for laboratory and pilot tests. For different sized pilot plants the modules can be installed either in single-element housings or in a multi-element housing. The module housing itself is made of stainless steel, however depending on the application a PVC-housing could be designed to reduce costs and weight. Further improvements are requested to facilitate assembly and installation of the modules.

In a second step the housing for the intermediate module type (HCNF2a – type; $\sim 4 \text{ m}^2$) has been developed on the basis of the quadrant-geometry of the ceramic support structures, which are assembled to form one module. The design of the HCNF2 housing provides the possibility to install larger membrane area with at the same time smaller footprint as the commercially available ceramic NF-module types. A prototype housing has been produced where the fixation of the single ceramic bodies and the separation between permeate and feed side are achieved by special shaped sealings. The design of these sealings turned out to be a key challenge for the prototype implementation and different options are still under investigation. A second housing was designed to hold just one quadrant in order to serve for multiple tests. (Figure 10)

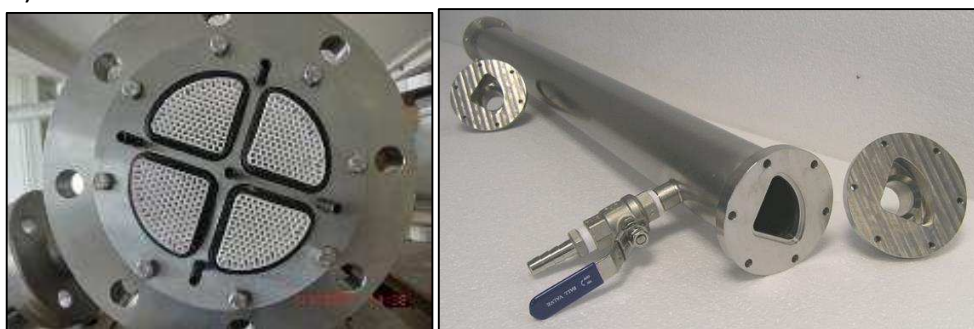


Figure 10: Prototype of HCNF-2a (left) and housing for tests on quadrant shaped ceramic support (right)

Task 6.3 : Development of system design

Experiments conducted during WP6 and WP8 have shown that different system designs were necessary depending on the treatment goals and raw water specifications.

- Heavily polluted waters require high pressure and high crossflow conditions, whereas the same module type can be operated at lower pressures and crossflow velocities with low polluted waters
- Aiming at high retention of small organic molecules or ions high cross flow and pressure will be needed which means that multi-stage systems are required to improve the recovery
- Aiming at the retention of larger organic molecules (like humic acids) moderate cross flow or even dead-end is possible, but cleaning frequency will be higher
- Aiming at particle retention or flocks dead-end filtration is possible, regular backwash and forward flush are recommended

- Depending on the raw water quality different pre-filtration steps will be needed, in particular for heavily polluted industrial waters even further pre-treatment steps must be regarded to prevent rapid fouling or membrane damage.
- Due to moderate DOC-removal and low removal of trace organic substances, further pre-or post-treatment-steps, such as activated carbon filtration, might be needed.

In view of the piloting in WP9, a process design for drinking water production has been developed. In drinking water treatment several treatment processes are available to achieve the main treatment goals of disinfection, removal of harmful substances, organoleptic acceptance and stabilisation for storage and transport. Depending on the raw water quality and the governmental and technical regulations a variety of treatment steps must be combined. The new HCNF-system can be used as substitute for single treatment steps or for a combination of several treatment steps. This could simplify the whole process chain resulting in less consumption of chemicals, lower energy demand and smaller footprint. In Figure 11 an example of a conventional drinking water treatment process is compared to a possible treatment process adapted to the new HCNF system.

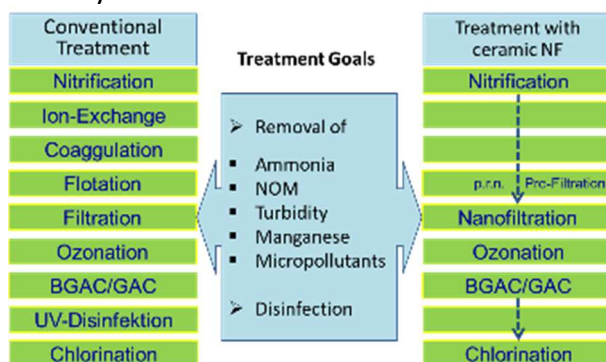


Figure 11: Comparison of the process steps of a conventional drinking water treatment system and a treatment system including the ceramic nanofiltration step for the same raw water type and treatment goals

The removal of organic matter by nanofiltration without the removal of salts bears some advantages; the system can be designed at higher fluxes and no post-treatment step to increase salt content for stabilisation is required. Another advantage of the HCNF process is that no additional chemicals must be added to the drinking water, such as coagulants or anti-scalants. The concentrate can be treated by coagulation and sedimentation. The cleared water can be discharged into receiving waters because the salt concentration is not increased. Depending on the choice of coagulant the remaining sludge can be reused in industry or agriculture (with regard to laws and local circumstances).

The NF will have a positive effect on the required ozone dose and the adsorption capacity of the granular activated carbon, because high removal rates for the organic load can be achieved. This can significantly reduce the needed amount of expensive activated carbon and increase the reactivation intervals and the risk that hazardous by-products are formed during ozonization is lower.

Task 6.4: Assessment of the removal capacity of the new HCNF in dependency on different process conditions

By adjusting the parameters permeate water flux, cross flow and recovery the concentration polarisation and the retention is being controlled. The results obtained during experiments described above (task 6.1) can be summarized as follows:

- Ions: Ion-retention depends strongly on the operation conditions and the feed water matrix. Experiments which have been performed with spiked de-ionised water at different crossflow



velocities, different membrane flux and mixed with tap water for different ionic strength (conductivity) showed that the retention of Na_2SO_4 changes between 10 % and 80 % depending on the concentration polarisation and water matrix. (Figure 12)

- **Particles:** Turbidity was removed to > 95 % resulting in turbidity values of < 0.2 FNU and most of the time < 0.1 FNU. The indicator organisms *E. coli* and coliforms could be removed completely from the waste water treatment effluent.
- **Natural organic matter (NOM):** For large organic molecules and colloids (like humic acids) only a slight influence of operation conditions on the retention was observed. The retentions indicated by UV-absorbance at λ 254 nm and λ 436 nm were constantly > 80 % and 90 %, respectively. The retentions for organic molecules from river water and treated waste water were significantly lower (10 to 60 %). The lower retentions are related to the partition of dissolved organic substances in the water which are usually smaller than humic acids molecules. In this case the operating conditions had significant influence as higher retention rates were achieved with increasing cross flow velocity, which can be explained by less concentration polarisation. Experiments at dead-end operation and inline coagulation have shown that this process combination leads to quite high and very stable NOM retentions.
- **Micropollutants:** Experiments with organic trace substances were conducted and only at crossflow-filtration with turbulent flow conditions (velocity of 2 m/s, 19 CT) a significant removal could be determined. The molar mass was not the essential reason of retention, but functional groups played a major role, interacting with the membrane or module material. On the one hand Iohexol with a high molar mass (820 g/mol) showed not the highest retention, on the other hand smaller molecules like diclofenac (296 g/mol) could be retained by at least 20 % (Figure 13). To get a better survey and understanding on the retention behaviour more sophisticated experiments are needed.

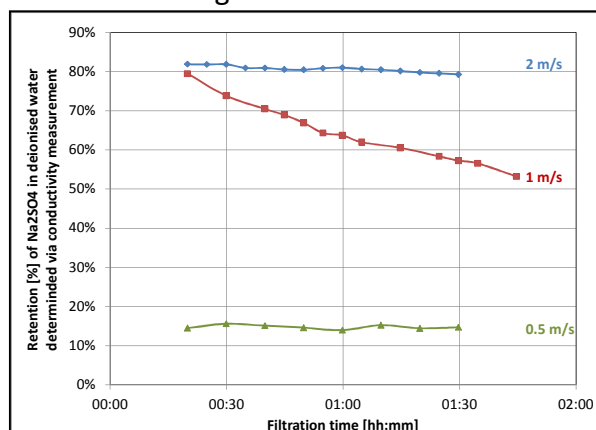


Figure 12:
Retention of ions from model waters: di-ionised water spiked with Na_2SO_4 at different crossflow velocities.

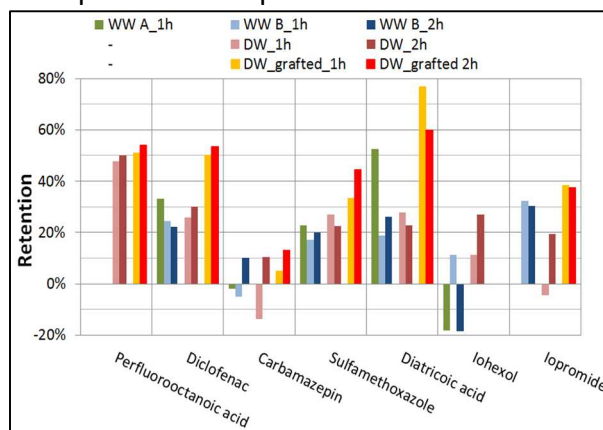


Figure 13:
Retention of micro-pollutants from experiments with waste water (WW) and drinking water (DW) matrix with the 19 CT native and modified (grafted)

Experiments conducted within WP 4, WP 8 and WP 9 provide further data on retention of ions, micro pollutants and humic acids as well as the optimisation of process and operating conditions.

Summary of results

Experiments conducted in WP 6, 8 and 9 with heavily polluted waters and low polluted waters have shown that the new HCNF-module type is suitable for very different application fields. Depending on the type of

raw water and the treatment goal the system set-up must be adapted. Despite a lot of experiments have been carried out to study the retention and fouling behaviour still many points remain only partially explored. Thus further pilot and laboratory tests should be directed to the interaction mechanisms of the ceramic NF-membrane and water components.

WP 7 Techno-economical and ecological benchmarking of the new HCNF

The new HCNF-modules offer a high flexibility in system design and can be adapted to different applications and treatment goals. In this project a techno-economic and ecological benchmark of the new treatment system and processes involving HCNF is provided for individual applications. A critical and comprehensive analysis demonstrates whether the application of HCNF for drinking water and industrial waste water treatment can be competitive against or even superior to alternative treatment options. The HCNF systems have been designed based on the hypothetical module type HCNF 2 with a membrane area of 25 m². The system design and data collection have been executed with the help of several project partners.

Task 7.1: Evaluation of the cost benefit of HCNF for drinking water treatment

For the evaluation of the new HCNF for drinking water treatment three options have been regarded: an enhanced conventional treatment system, a nanofiltration system using HCNF or a nanofiltration system using capillary polymeric membranes.

The treatment systems were designed on providing the same amount of drinking water (40,000 m³/d) of nearly equal quality and taken from the same raw surface water source. The LCA and cost analysis include the construction and the operation phase of each treatment plant, the demolition phase has not been included. In an inventory analysis the energy and material consumption were identified as well as the amount of different types of waste and their disposal routes.

The comparison of two drinking water treatment variants includes the following processes:

- Enhanced conventional treatment scheme: ion exchange, enhanced coagulation, flotation, deep bed filtration, ozonisation, activated carbon filtration, UV disinfection, chlorination (NaOCl), sludge treatment
- Treatment scheme using nanofiltration: nanofiltration, ozonization, activated carbon filtration, chlorination (NaOCl), sludge treatment

The nanofiltration process is replacing the processes ion exchange, flocculation, flotation and deep bed filtration of the conventional scheme. The nanofiltration process is designed twice: a) using HCNF membranes and b) using polymeric membranes (comparison). Ozonization, GAC filtration and disinfection with NaOCl are components of both treatment schemes but the consumables and energy demand may be different. Due to the different amounts of sludge in both treatment options the on-site sludge treatment has been included.

In Figure 14 the three different treatment systems are compared regarding the average specific treatment costs assuming a lifetime of the treatment plant of 20 years.

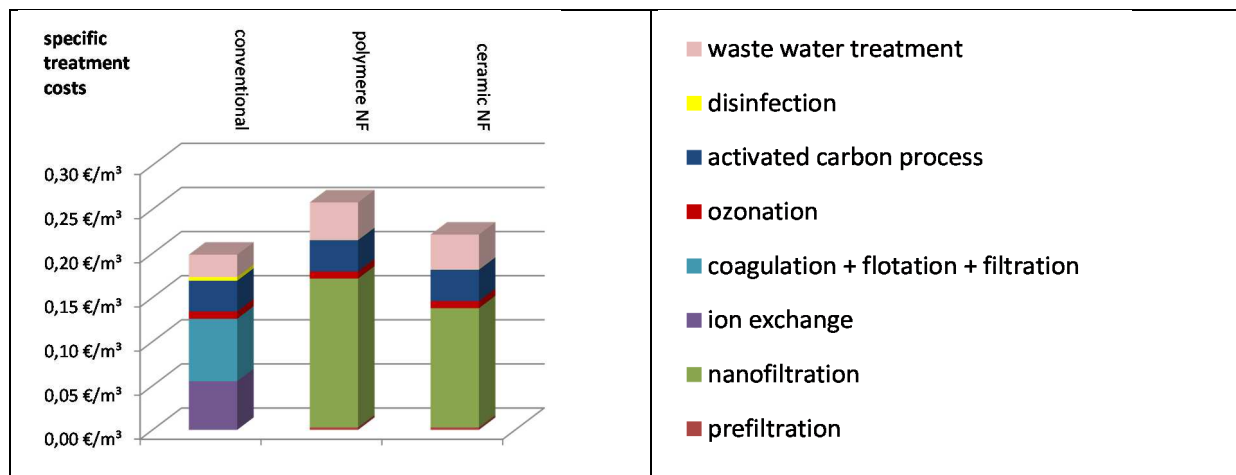


Figure 14: Comparison of costs of the drinking water treatment systems (basic design)

The average specific treatment costs, which include OPEX and depreciations, indicate that the conventional system is the most economical drinking water treatment option. Compared to this system ($\sim 0.20 \text{ €/m}^3$) the costs increased by about 10 % for the “ceramic NF”-option ($\sim 0.22 \text{ €/m}^3$) and by about 30 % for the “polymeric NF”-option ($\sim 0.26 \text{ €/m}^3$). However, the sensitivity analysis has shown, that the specific cost for the HCNF-treatment system can change up to >50 % and for the polymeric NF-system up to 20 %, depending on the input parameters used. The parameters with the highest impact have been: permeability, crossflow, pressure, recovery, waste disposal costs, module price and module lifetime, electricity price and discount rate. These results show that the HCNF system can be competitive to conventional or polymeric systems, but due to the drastic impact of certain process parameters reliable results of pilot experiments are crucial to get a firm statement on OPEX and CAPEX of the treatment system.

Task 7.2: Life Cycle Assessment of two rival processes

The objective of this task was to conduct a comparative life cycle assessment (LCA) of two options for drinking water treatment plants in the context of the case Blankaart in Belgium. LCA is a tool to generate information on the environmental impacts of products and processes.

The first treatment option is an enhanced conventional treatment system and the second a nanofiltration system using HCNF (details of both treatment plants see above, task 7.1).

The environmental impacts of both processes were assessed and compared in a critical and comprehensive analysis. Additional, a comparison was made with the polymeric membrane nanofiltration process. Furthermore the influence of an anti-fouling grafting of the ceramic membranes on the LCA result was investigated.

A comparison of the treatment options is shown in Figure 15. In the most important impact categories, the polymer NF treatment performs best. The conventional treatment has in four out of six categories the biggest share and scores slightly worse than HCNF treatment, which has the biggest impact on global warming and non-renewable fossil resources. An antifouling grafting of the HCNF membranes, however, does not have a significant impact.

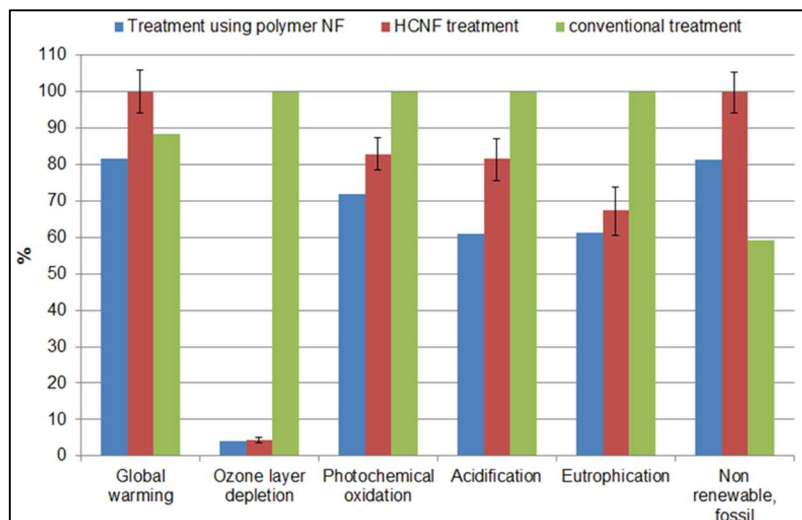


Figure 15: Comparison of the environmental impacts of conventional, HCNF and polymer NF treatment; uncertainties of the HCNF results

When looking at the shares of the sub-processes in more detail (not shown here) the largest contributions in the HCNF treatment scheme come from the HCNF operation and the membrane manufacturing in sum, followed by GAC filtration, sludge treatment and ozonization. The impact of HCNF operation and membrane manufacturing derived almost exclusively from the electricity consumption and the combustion of natural gas during the sintering of the ceramic support.

Task 7.3: Techno-economical evaluation of the developed membranes with bleaching effluents and waste waters from olive treatment

For the evaluation of the new HCNF system in heavily polluted waste water treatment systems the treatment of olive oil mill waste water has been chosen. The HCNF-system is compared to a conventional system including the following steps:

- Rotating screen filters to remove coarse matter from the waste streams
- Electrochemical system to destabilize and coagulate water impurities and oxidize phenolic compounds
- Flotation to remove the colloidal and particulate matter (mainly chemical oxygen demand (COD) and the dark colour are removed)
- Membrane Bioreactor (MBR) for further degradation of organic matter

The waste water from the flotation step and the surplus sludge of the membrane bioreactor are treated in a sludge tank for sludge thickening and finally the sludge is dewatered in a centrifuge and removed from the system. The sludge can be further processed in anaerobic digestion or reused as fertilizer. The filtrate from the MBR is the produced water, which can be reused or discharged.

The HCNF system should serve to substitute the electrochemical coagulation and the flotation step. The estimation of investment costs and operation costs for the conventional treatment system is summarized in

Table 3. The data for the first part of the system, which will be replaced by the ceramic NF, are reported in Table 4.

Table 3: Costs for conventional OMWW treatment system

	Conventional system, complete	First part of the system
Investment cost	900.000 €	300.000 € (for 64 m ³ /d, 4 m ³ /h)
Operation cost	1.5 - 4.5 €/m ³	1.5 – 2.5 €/m ³

The initial investment costs (CAPEX), the annualized operational costs (OPEX) and the average specific treatment costs for two different sized HCNF-systems, assuming an annual waste water treatment volume of 67 Tm³/a and 15 Tm³/a have been calculated for a plant lifetime of 10 years.

Table 4: Results of cost calculation for ceramic NF in OOMW treatment: CAPEX, OPEX, PV(c), specific costs

	large scale system	small scale system
CAPEX	325 k€	145 k€
OPEX	79 k€/a	33 k€/a
average specific treatment costs	1.2 €/m ³	2.2 €/m ³

Comparing the two systems designed for different treatment rates it turns out that the average specific treatment costs become significantly smaller for larger systems. Comparing the investment costs and the operational costs of the ceramic NF system to the estimated costs for the alternative conventional treatment process of electrocoagulation and flotation the average treatment costs are in about the same range. These results suggest that the ceramic NF could be feasible for this application. However, the sensitivity analysis has shown that, for example, a lower process permeability and higher crossflow velocity or booster pressure could increase the specific treatment costs for the HCNF-system to > 50 %.

Summary of results

The results of the techno-economic and ecological assessment show that large scale HCNF modules can be a very attractive technology, either as an alternative in potable water production processes or in special applications of waste water and industrial water treatment. By taking into account the advantages of the ceramic membranes, such as long life time, high flux and good cleaning behaviour, the costs for the overall process lifecycle can be kept at a competitive level. However, the energy demand during manufacturing and operation is still a major issue in terms of environmental impact and costs. Another important objective is the treatment of concentrate and cleaning solution. As the concept for concentrate handling is very much case dependent, this topic should be included in all further pilot and research studies. Looking at the current status of the module and system development it becomes clear that further optimizations and studies are still needed to create a more reliable and case sensitive process design of the HCNF system and to improve the techno-economic and ecological evaluation. However, the results give important indications on which topics further research should be focused on.

WP 8 Application tests and process fine tuning for different waters

PROCESS WATERS FROM CHEMICAL INDUSTRY AND OLIVE OIL PROCESSING

Cyclus ID carried out experiments with the new NF membrane elements in laboratory scale for the optimization of the working parameters. For the development of these experiments, housing for the small scale element and a laboratory scale treatment unit were constructed by IKTS and CYCLUS ID. The design

of the housing includes some modules in parallel in order to compare the new HCNF1 membrane with the 19-channels tube membrane in the same experiments. This treatment unit enabled CYCLUS ID to test all type of wastewaters in order to find the optimal process parameters and design.

Partner CYCLUS worked with real waste waters from different industries to assess the performance of the ceramic NF for different sample applications. Several process variants by variation of filtration parameters, cleaning strategy and pre-treatment were tested. In each experiment, the permeate and concentrate were collected and characterized to check the efficiency of the process.

The trials were done with wastewaters (WW) from:

- Brewery
- olive oil mill ("Orujera").
- Chemical industry manufacturing polymers and nitrogen derivatives
- Chemical industry manufacturing lactam and other products
- Olive oil WW ("Chorro de tolva").
 - o in pilot plant
 - o in industrial trials.
- Olive oil mill WW ("Aguas de centrifuga") (industrial trials)

The results showed that the ceramic membrane filtration technology provides high quality permeates for some types of industrial WW and new applications can be studied, for example the use of the membrane as a pretreatment for anaerobic digestion or the recovery of high added value compounds. However, each type of WW has to be tested with the pilot plant itself because the rejection of the different contaminants cannot be predicted theoretically due to the multiple effects that are affecting the process. Important differences, for example in ammonium or sulphate reduction, were detected in different samples. The comparative experiments between the standard module type (19 CT) and the HCNF1 module type showed similar results; however, the HCNF1 membrane permeability was lower in all the experiments, probably due to fouling in a smaller diameter tubes. Finally, interesting experiments at semi-industrial level were carried out in an industry of Spain with the aim of developing the most interesting application obtained in this project: the hydroxytyrosol recovery.

PULP AND PAPER INDUSTRY PROCESS WATERS

Process waters from the pulp and paper industry are often challenging to treat for various reasons. They may contain compounds that are harmful to the environment, that may interfere with the process if accumulated during recycling or that are valuable and need to be recovered as side products. Membrane filtration could be used to solve most of these challenges, but the properties of the process waters have been seen too demanding especially for the polymeric membranes: the extreme pH together with high temperatures may degrade polymeric membranes, while the compounds present in the waters may cause severe fouling of the membranes. Ceramic membranes, on the other hand, should be more stable in extreme conditions prevailing in the pulp and paper industry processes. Also, the development of an anti-fouling coating on top of a ceramic membrane makes them an appealing option for the treatment of different pulp and paper industry process waters.

The developed ceramic nanofiltration membranes (19-channel elements having a length of 50 cm), both with and without an anti-fouling coating, were tested in treating four different pulp and paper industry process waters. Two of the waters originated from a bleach plant of a kraft pulp mill, and the other two were wood extracts. The bleach plant process waters were of low pH (2.6) and high pH (11.5) and they were tested in temperatures of 50 – 60 °C. The wood extracts were also acidic (birch at pH 3.8 and spruce at pH 4.5) and they were filtered at 70 °C.

The results showed that due to a degradation of the membranes, the acidic bleach plant process water could not be treated with the ceramic membranes. However, the alkaline process water could be treated using the membrane without the anti-fouling coating, but when exposing the coated membrane to the same effluent the coating layer was seen to degrade. This was observed as an increase in the molecular weight cut-off of the membrane. The possibility to use the uncoated membrane without significant problems in the treatment of alkaline process water was considered to be positive, although the membrane tested was of a higher molecular weight cut-off (2,200 g/mol) than NF membranes (<1,000 g/mol) which was original goal of the projects. However, the tested ceramic membrane had a bit lower cut-off value than polymeric tubular PCI membrane (4000 g/mol) used to purify the bleaching plant effluents from the softwood line in Nymölla pulp mill in Sweden.

Based on the results, the treatment of wood extracts was considered to be the most promising application for the newly-developed membrane having anti-fouling properties. These waters are highly fouling by nature, and currently there are not many viable technologies available for their treatment. The wood extracts are rich of carbohydrates (hemicelluloses, oligomeric and monomeric carbohydrates), and a typical need is to recover, concentrate and purify carbohydrate fractions e.g. from lignin before they are refined further (for example to be used in packaging films). In these experiments it was shown that the anti-fouling coating layer prevented the membrane from severe fouling which occurred when the uncoated membrane was used (observed as a loss of pure water permeability by 30 – 55 %). The filtration capacity decreased with both membranes during the filtration, which was likely due to the changes in the osmotic pressure and viscosity. Comparison with the Desal-5 DL membrane (cut-off 300 g/mol) showed that the filtration capacity was significantly better with modified ceramic membrane (650 g/mol). The fouling of polymeric membrane measured by the reduction of pure water flux was 60 % compared to negligible fouling of coated ceramic membrane.

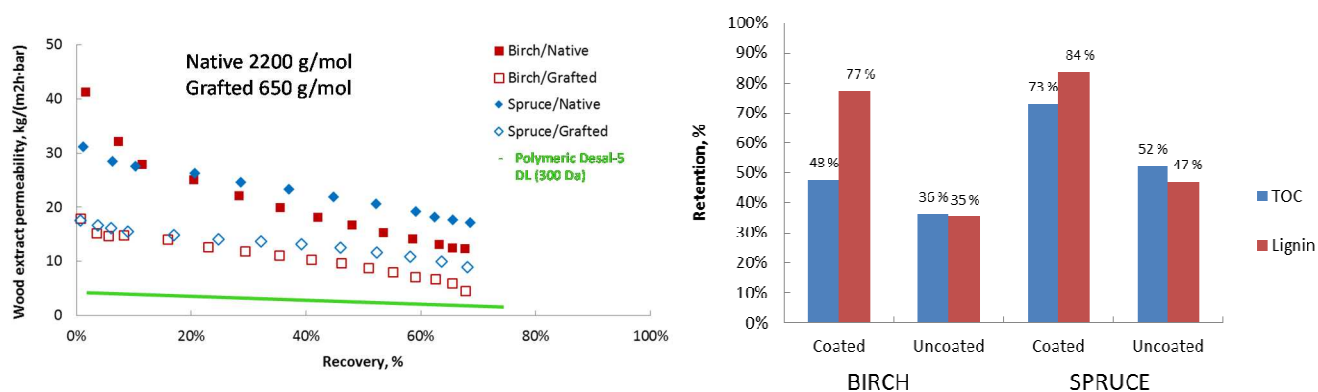


Figure 16: Filtration capacity for the wood extracts (70°C, 2.8 m/s, 5 bar) and retention of lignin and total organic carbon of the wood extracts (70°C, 2.8 m/s, 5 bar) (right)

As the separation efficiency of the anti-fouling coated membrane is on the NF range and seems to be able to separate lignin from carbohydrates (especially with the birch extract) it can be considered as a viable option in treating and fractionating this sort of a highly fouling wood-based process waters that fouls strongly polymeric membranes.



SURFACE WATER TREATMENT

ETAPERN pilot plant (50 m³/day) was originally designed to use commercial polymeric membranes for drinking water quality improvement. It was modified to use, successfully, Cerawater ceramic membranes. This pilot plant is located into “El Montañés” Metropolitan Drinking Water Treatment Plant at Bay of Cadiz (500.000 hab. served). It is necessary to highlight that this plant is powered exclusively by renewable energy.



Figure 17: Left, picture showing HCNF1 pressure vessel installed in ETAPERN plant substituting an original 4040 pressure vessel, right external view of the container of ETAPERN plant and PV and windmills units

The ETAPERN pilot plant tested first generation of HCNF1 membrane and worked in continuous operation with two kind of feed waters: reservoir water (surface untreated water) and with settled water (partially treated water). No chemicals were added during membrane treatment. Different operating conditions were tested, including dead and end filtration. Permeate water quality hardly changed regardless of working conditions and permeate flux kept constant during the studies, showing HCNF1 membrane excellent antifouling properties, so, comparing fouling resistance with polymeric membranes from previous ETAPERN plant studies, ceramic membrane performance was much better. No CIP (cleaning in place) was carried out. However, conductivity was reduced just a 10 % maximum, and most of the ions were rejected between 2 – 40 %. Color, turbidity, fluoride and the bacteria, were almost totally rejected. Aromatic components of NOM are preferentially rejected over hydrophilic components of NOM.

Besides of continuous operation studies, another study such as theoretical modelling; MWCO determination and humic acid removals were carried out in order to characterize HCNF1 membrane.

Although HCNF1 is fouling resistant with raw surface water, UCA developed an efficient and new cleaning procedure to recover the performance of the HCNF1. Membrane was forced to get fouled using peptone. During the fouling period the membrane permeability suffered a loss of 18 %. The new protocol (UCA protocol), optimized after several attempts, consisted of: NaOH (4 %) used with permeate valve closed (30 minutes) and with the same valve open (30 minutes). Then the system is drained and flushed. If flux is not entirely recovered, H₂SO₄ can be added (pH=2.0) for 30 minutes (15 minutes permeate valve closed and 15 minutes permeate valve open). With these conditions flux was totally recovered. Later, the system is drained and flushed again.

WP 9 Prototype application tests in process and drinking water purification

The nanofiltration membranes evaluated in the pilot test resulted in a very high permeate quality. The HCNF1 elements in module 2, with a PEG retention of 52 to 63 %, resulted in TOC removal efficiencies from 63 to 81 %, resulting in TOC concentrations between 2.6 and 3.9 mg C/L in the permeate. Thereby,



the nanofiltration outperforms the conventional drinking water treatment by means of enhanced coagulation. Besides excellent NOM removal, the nanofiltration membranes exhibited substantial removal of organic micropollutants, thereby lowering the load of organic micropollutants to be removed by the ozonization and activated carbon filtration steps. Finally, a small retention was observed for bivalent ions. Whereas the conventional treatment results in a large increase of the concentrations of sulphate, chloride and sodium due to the high chemicals usage in the enhanced coagulation step, nanofiltration has a positive effect on the concentrations of inorganic salts.

The anti-fouling coating applied by VITO was shown to have a significant effect on the membrane performance. When operated under the same conditions with respect to feed pressure and cleaning frequency, the flux through the membrane element with anti-fouling coating was a factor 1.5 higher than the flux through the non-coated membranes, despite the fact that a less aggressive CIP solution was applied on the coated membranes. The retentions of the modified membranes for micropollutants were higher than the retentions of the non-modified membranes.

Membrane prototypes were prepared by RKV and IKTS and delivered to the partners. The developed HCNF1 membranes (as is and anti-fouling coated) were tested in a pilot plant at the Blankaart from 19 September 2014 until 31 January 2015. The nanofiltration plant was equipped with 4 modules, each containing 3 HCNF1 elements (see Figure 18).



Figure 18: Nanofiltration pilot plant with HCNF1 membranes at VMW

The plant was operated at a constant flux in a “feed and bleed” mode. During filtration, a part of the concentrate was recycled to the feed side of the membranes to maintain a constant cross flow velocity. To keep fouling under control, a combination of forward flushes (every 10 t to 15 minutes) and CIPs (every day to every week) was applied.

Operation of the NF pilot plant.

The pilot plant was started up at a constant flux of 13 l/h, a cross flow velocity of 0.5 m/s and a recovery of 50 %. The flux was increased to 20 l/h on the 22nd of September, resulting in an increase of the TMP from 1.3 to 1.9 bar. The cross flow velocity was increased to 2.0 m/s on the 29th of September, resulting in a decrease of the TMP from 3.0 to 2.1 bar and an increase of dP from 0.1 to 0.9 bar. The first two CIPs had a limited effect on the membrane performance.

Throughout October, the pilot plant was operated at the following conditions:

- Constant flux of 20 l/h,
- Cross flow velocity of 2.0 m/s,

- Recovery of 50 %.

On the 22nd of October, an attempt was made to decrease the cross flow velocity again to 0.5 m/s, resulting in a very sharp increase of the TMP from 6 to more than 9 bar. Therefore, the cross flow velocity was reset to 2.0 m/s after a few hours. Throughout October, the TMP gradually increased from about 2.1 bar at the beginning of the month to 7.1 bar after the last CIP of the month. Although each CIP had a large impact on membrane performance, the weekly CIP did not suffice to maintain the TMP at a constant level. On the 29th of October, module F1, containing the membranes with the poorest removal efficiencies, was taken out of service. The first half of November was lost to failures of the electromechanical equipment, but from the 24th of November until the 18th of December, stable operation was obtained. Throughout this period, the recovery was gradually increased from 50 to 90 %:

- From 50 to 60 % on the 5th of November,
- From 60 to 70 % on the 5th of December,
- From 70 to 80 % on the 8th of December,
- From 80 to 90 % on the 15th of December.

Different techniques of membrane cleaning were tested (a combination of a caustic and an acidic CIP also NaOCl was applied in the caustic cleaning).

The anti fouling coating reduced the initial flux of the membranes down to about 50 % but in operation the permeate flux remained nearly stable over a period of several weeks. The overall flux over modules F2, F3 and F4 was kept constant at 20 l/mh by adjusting the speed of the feed pump. The flux over module F1 varied as a function of the pressure applied and was monitored on-line. The recovery and the cross flow velocity were maintained at 90 % and 2.0 m/s, respectively.

Caustic CIPs were performed separately for the membranes with and without anti-fouling coating. The membranes without coating were cleaned at a pH of 12 and NaOCl was added to the CIP solution. The coated membranes were cleaned at a pH of 10 without NaOCl. Acidic CIPs were performed on both membrane types simultaneously at a pH of 2.5.

The flux over the coated membranes was about 50 % higher than the flux over the non-coated membranes, indicating that the coating has a positive effect on the fouling behavior of the membranes.

Trials of reducing feed cross flow velocity down to 1.5 and 1.0 m/s showed a negative effect on membrane performance. Each time, the maximum feed pressure of 10 bars was obtained after less than 24 hours of operation, even after the recovery was decreased to 70 %.

Permeate quality. The results for TOC and UV₂₅₄ absorbance in the raw water, the NF permeate and as a reference the TOC concentration of the sand filtrate of the full scale treatment plant were compared. It was clearly shown that membranes show considerably higher NOM retention. The membrane process results in much lower TOC values than the conventional treatment.

From mid-September until mid-October, the NOM removal efficiency improved for all modules and reached a steady-state. However, the efficiency gradually decreased again in December. Two changes in the operating conditions are at the cause of this gradual decrease, being the gradual increase of the recovery in combination with the improved CIP procedure used from the 5th of December (addition of NaOCl to the caustic CIP solution). The decrease in the NOM retention was much more pronounced for the membrane elements in modules F3 and F4 than for the elements in module F2.



No significant difference was observed between the performance of the different membrane elements with respect to ions retention. For the bivalent ions, significant retentions were observed, whereas for monovalent ions, retentions were limited.

The removal efficiency of the treatment train with respect to organic micropollutants was monitored. For all of the remaining micropollutants except aminomethylphosphonic acid significant retentions were obtained in the nanofiltration step whereas the modified membrane elements showed higher removal efficiencies than the non modified membranes.

Task 9.4: Application test with real surface water for potable use at Metropolitan Drinking Water Treatment Facility of Bay of Cadiz (500.000 inhabitants)

Partner UCA: ETAPERN pilot plant worked in continuous operation with surface water using HCNF1 membrane. No chemicals were added. Four different operating conditions were tested, increasing the recovery up to dead-and-end conditions (the highest recovery: 100%). No fouling was observed during those periods of testing, despite of high recoveries, including dead and end filtration mode as it is mentioned above.

Removal of different heavy metals was also tested. Ceramic membranes have positive Z potential at low pH, and this is the case of HCNF1. This means that surface electrical charge is positive. Heavy metals have also positive electrical charge at low pH. So there should be potential electrostatic repulsion between membrane and heavy metals when they are close to membrane, working at low pH. So, it is interesting to study if this repulsion could lead to reject metals present in waters, taking in account that heavy metal have an atomic mass much lower then membrane MWCO. The influence of metal concentration as well as the variation of CFV was studied. The heavy metals studied were: iron, zinc, copper, cadmium, arsenic, manganese, cobalt, lead, aluminum and arsenic and two alkaline earth metals as typical indicators in nanofiltration: calcium, magnesium. The metal concentrations were 2, 10 and 100 mg/l, and the CFV were 2 m/s and 0.3 m/s (at high and a low CFV). Every metal was studied isolated and finally mixtures of all metals were studied with same conditions. The lowest rejections were recorded when the concentration is higher and the CFV minimum, that is when concentration polarization problems appeared. Despite of low atomic masses of heavy metals studied, there were rejections that are promising with this kind of membrane. Membrane performance must be related with Donnan and dielectric exclusions. Besides, existence of real nanopores in this membrane may affect to ion diffusion inside of these pores.

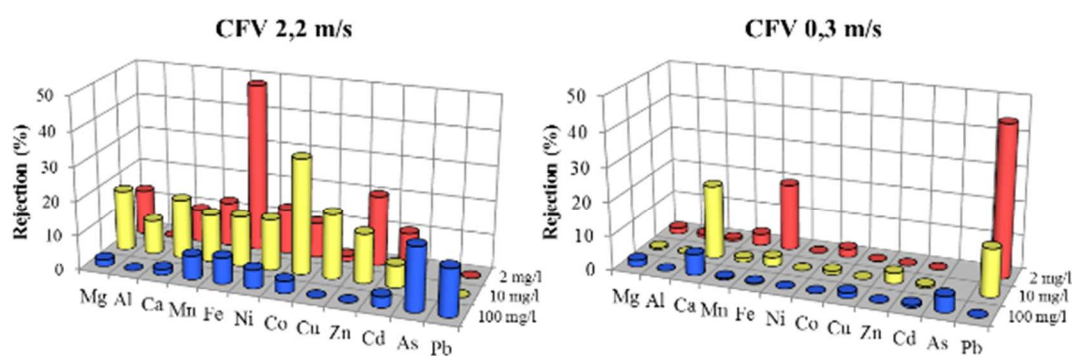


Figure 19: Influence of CFV and metal concentration on metal rejection

Removal of pesticides



Removal of charged compounds by nanofiltration is not difficult, however rejection of neutral compounds is a strong challenge. 19 pesticides and trihalomethanes were measured to study the influence of operating conditions: CFV (2.2 and 0.3 m/s) and HCNF1 rejection characteristics. These experiments were done at the labs of UCA, using known concentrations of different hazardous compounds and using the HCNF1 membrane in a close- loop circuit. Results show that it is clear the influence of the high CFV on rejection, reducing concentration polarization of those compounds onto the membrane surface, and so rejections are higher. With lower CFV rejections are lower.

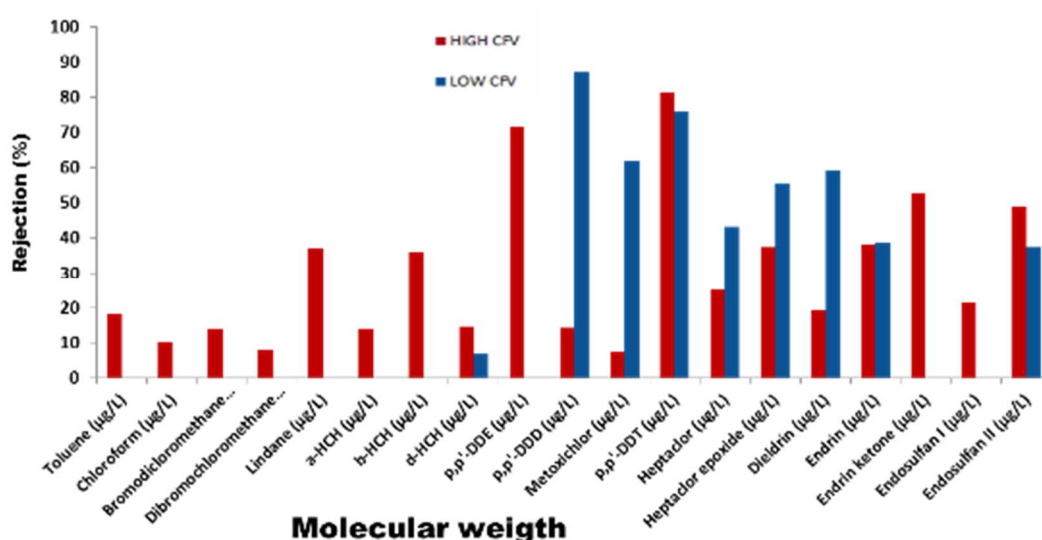


Figure 20: Rejection of 19 hazardous compounds (THMs and pesticides) ordered by molecular weights.

Rejections of studied compounds cannot be explained exclusively by mechanisms of size exclusion, as some of these compounds are really small, case of toluene (96 Da). There are another mechanisms taking part during filtration with this membrane. If these compound rejections are ordered according to its logP index, membrane hydrophilicity and compounds hydrophobicity could justify rejections even at very low CFV.

So, pesticides can be partially rejected, even having lower molecular weights than membrane MWCO. Rejections are improved at high CVF. Hydrophilic and hydrophobic characteristics of both membrane and solute play an important role in separation.

Highlighted significant results

HCNF1 membrane does not need any kind of pretreatment as it does not suffer any kind of fouling with surface water of Bay of Cadiz.

Metal rejections are promising; taking in account that low metal atomic weights and membrane MWCO are quite different.

This membrane can efficiently remove pesticides and THMs, even taking into account that compound molecular weights are much lower than membrane MWCO.

HCNF1 membrane shows filtration mechanisms more complex than only size exclusion; this means that Donnan and dielectric exclusions and hydrophobic and hydrophilic interactions have also a paramount importance. These characteristics make ceramic membrane rejection characteristics more complex than just size-exclusion phenomena.

4.1.4 The potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results

Due to the rising world population and industrial growth, water scarcity, catastrophes and the rising utilisation of process water, water has become an essential natural resource both in industrialised countries and in the developing countries. The need for the access to safe and pure water will create a further rising market for water treatment technologies. Several scientific studies state that this situation will be even intensified by climate change effects. As a consequence the water purification industry has become very important. The following gives some figures of the importance and growth of this market.

The European water industry takes a leading role in the World and is a major economic player (1 % of the EU15 GDP) that generates many positive impacts from social, economic and environmental perspective. The three largest water companies in the world are European. About 50,000 companies are active as service and technology providers of which the majority are SMEs. The sector represents an annual turnover of 80 billion € (worldwide 250 billion €) with an annual growth of 5 % and an even larger growth of employment (6 to 7 % per year).

In a publication of Global Water Intelligence the water reuse markets were assessed for the period 2005-2015. The global water reuse capacity is expected to increase by 181 % over this decade, rising from 19.4 million cubic metres a day in 2005 to 32.7 million cubic meters a day in 2010 and 54.5 million cubic meters a day in 2015. Expected 59 % of the additional capacity will involve so-called tertiary or quaternary treatment.

Currently the membrane market represents only a very small fraction of the global water purification market. However, as membranes have already proven their efficiency in many water purification processes, it is foreseen that the membrane market will grow at a higher rate than other water treatment technologies. According to a market study by Global Markets Direct the global membrane treatment market is supposed to have a compound annual growth rate of 13 % through 2015. Specifically for nanofiltration, the estimated global market was estimated in 2007 to be about \$ 97.5 million. It should reach \$ 310.5 million by 2012 with an annual growth rate of 26.1 % . This extra high growth rate reflects the extra benefits of this high-flux, high-selective, low-energy membrane process.

Expected impacts listed in the work programme

An improvement of the competitiveness of the European industry and the generation of knowledge to ensure its transformation from a resource-intensive to a knowledge-intensive base are challenging objectives of the NANOSCIENCES, NANOTECHNOLOGIES, MATERIALS AND NEW PRODUCTION TECHNOLOGIES theme.

Moreover the main and overall expected impact of projects funded under NMP.2011.1.2-3 is a positive contribution to one of the main global societal issues – the access to safe and pure water. By focusing of this aim the improvement of a number of important water purification processes is addressed.

Contribution to the expected impacts

CeraWater has a direct impact to the main global societal issue of access to safe and pure water, and to some specific aspects that are not well assessed/solved in current water purification technologies, and are specifically addressed in the call.

Table 5: Impact of CeraWater in the water treatment sector

Expected impact by the call	CeraWater project
- Overall positive contribution to the main global societal issue of access to safe and pure water - Increased performance for the removal of toxins, pesticides, fertilizers and bacteria. Robust on-site treatment in developing countries. - Improvement in energy efficiency and high performance water treatment - Improvement of the competitiveness of the European environmental technologies industry	- Honeycomb like nanofiltration membranes for various applications of enlarged membrane were developed - The developed membranes were also tested for the removal of the targeted compounds and showed good retention properties - Various process conditions were evaluated, also crossflow velocities were evaluated from dead-end to higher velocities. Results of the different process parameters are known - The project will strengthened the position of the European ceramic membrane manufacturers, developers, testers and appliers. The developed membranes will help to increase membrane production and market share. Partner RKV will soon start offering the membranes as products.

Together with the impacts named above the results of the CeraWater project may influence in many other industrial sectors besides the water treatment sector as detailed below:

Table 6: Impact of CeraWater in other industrial sectors

Results	Potential applications
Advanced grafting techniques for tuneable ceramic membrane surfaces	- Membranes with anti-fouling coatings fit to be used in chemical product purifications as e.g. direct bio-ethanol extraction from fermenters. - Membranes fit for affinity separations to recuperate/purify high value products in water and solvents. - Membranes fit for filtrations in very aggressive media (e.g. strong acids).
Optimised material processing techniques	High quality support architecture for gas separating coatings
New membrane design and process	For gas and vapor separation with gas selective coatings

Increasing competitiveness of European research

CeraWater gathered key R&D players in (inorganic) membrane technology within Europe to promote development and technology of the membranes and processes to be developed. The CeraWater partners moreover are very complementary, assuring the development of new break-through results. The key scientific results and new knowledge that were obtained within the CeraWater project are:

Table 7: Key scientific results and new knowledge of CeraWater

	Scientific results	New knowledge
Support development	- New support material and geometry for NF application - Improved composition of membrane layers	Parameters for choice of material and material processing/extrusion
Modelling of mass transfer through support	New support material with an optimised mass transfer	Generic and fundamental knowledge how to design membrane supports
Membrane coating development	New ceramic NF membranes with very high surface to volume ratio	Understanding of the coating parameters allowing defect free NF coatings on high-surface membrane supports
Antifouling coating development	New ceramic membranes with optimized antifouling coating for drinking water production and specific waste water filtration	Structured knowledge how to choose the right grafting (grafted molecule and coverage) for a specific fouling situation.
Application process	New highly-efficient process for water filtration	Expertise in the use and process technology of honeycomb NF membranes

Competitiveness and economic impacts

The successful development, production and use of the filter element developed in CeraWater will lead to a strong growth of European water purification industry in a variety of products and services.

Basing on the project results the following three sectors can be named that are/will be influenced by the project results, starting with the application of highest potential:

1. Treatment of specific process water (high temperature, extreme pH-values, presence of aggressive chemicals, extreme fouling behaviour).
2. Emergency water supply and local water treatment
3. Large scale drinking water production by the filtration of surface water

In all sectors a significant impact of exploiting the technology developed to commercial benefit of industrial partners and end users can be analysed.

At first the ceramic filter module has to be mentioned because it is well understood that the membrane is the heart of the cleaning technique. The ceramic honeycombs will be produced by company Rauschert. In the pilot and pre industrial scale the coating of the supports will be done by IKTS. Later the technology can be transferred to Rauschert. Similar technology transfer from the research organisations to industry – here Rauschert or its subsidiary inopor – was done a couple times before. For example the coating technologies of the tubular membranes down to the UF range from the IKTS or rather its predecessors to Rauschert/Inopor.

As fouling is a serious problem in many different applications, the unparalleled anti-fouling effect of methyl Grignard grafting (developed by partner VITO in WP4) was noticed by different membrane

suppliers and appliers (consequence of a series of dissemination actions, see section A, table A1 and A2). In the meantime it is also clear, following results at VITO outside CeraWater, that the anti-fouling effect not only works in case of nanofiltration membranes and relatively low molecular weight foulants, but also for very open microfiltration membranes used for e.g. the treatment of oil/water emulsions. Moreover, the low fouling properties of Grignard grafted membranes proved very positive for direct filtration of fermentation broths. As a consequence, application in e.g. oil produced water treatment and in the numerous separation tasks in the upcoming bio-technology can be very lucrative. Discussions are ongoing with Rauschert, and other European ceramic membrane suppliers for a possible technology transfer. Furthermore, besides membrane manufacturers, also European plant manufacturers will and already do strongly benefit from the ceramic module. Since the membrane will financially not dominate the plant price, producers of other components will participate from the development as well. Furthermore, all end users of membrane equipment and the society will benefit strongly due to an increase of plant economics and ecology.

The CeraWater consortium itself includes besides the manufacturer of the developed membranes, also two other industrial partners: VMW and CYCLUS end user and technology provider of the designed modules. Thereby VMW has a strong focus on the end user application in the drinking water sector. This sector is characterised by large applications. CYCLUS is a representative of plant and technology providers in the waste and process water sector. This is a sector with a variety of different applications and requirements. The project is expected to impact competitiveness of these industries and to promote the technology via their exploitation plans of the results. The expected application of the ceramic membrane (HCNF1) for industrial waste water was achieved. The results showed that, for some type of waste waters, the technology has got clear advantages in front of the typical treatments, especially physico-chemical treatments and ponds. In the first case, the filtration process provides a reduction of chemicals added to the waste stream (coagulants and flocculants) and the consequent elimination of production, transport, storage and handling, also allows 100% reduction of their associated economic costs. In the second case, the treatment of high contaminant waste waters from olive oil mills and “orujeiras” avoids the installation of ponds in the field and the consequent elimination of unhygienic conditions around the ponds and the high management costs of them. For this kind of waste waters there are no other appropriate technologies. Similarly, the expected energy reduction associated with these membrane techniques would suppose a significant economic saving with regard to conventional practices.

On the other hand, considering polyphenols or other interesting compounds recovery, the targeted industry will be able to internally use it or apply it for different uses (animal food, cosmetic). This will provide them a significant economic advantage.

Additionally, as a consequence of reusing, there is a water input reduction -with regard to the end-user consumption-, a proportional cost reduction is expected.

Another important aspect that is to be considered is the CERAWATER operational costs, 35 – 50 % operational cost reduction is achieved when compared to conventional plants. In some types of waste waters, ceramic membrane filtration has lower management costs than coagulation-flocculation and aerobic treatment.

The dissemination activities about the results of the Project by Cyclus were carried out through:

- a publication in a specialized national journal, “Tecnología del Agua” (not published yet).
- a presentation of the results in a technical meeting organized by Cyclus the February 26, 2015.

Dissemination activities of Cyclus were compatible with the protection of intellectual property rights, confidentiality obligations and the legitimate interest of the owners of the foreground.

Cyclus ID has contacted a number of agro-food companies in Spain, both to obtain samples and to promote CERAWATER solution. In addition, other contacts were done in other industries –belonging to different sectors- that also produce large amounts of waste water. Cyclus ID has also carried out testing and trials in a number of these areas.

IWW is a research institute with a strong branch in consulting where results from research projects are transferred into the sector of drinking water treatment and advanced waste water treatment. The project content and results have been distributed on branch-specific conferences and through the IWW-network (e.g. by the contribution in IWW Journal and poster presentations). The results of CERAWATER will be concerned in further research activities and application cases. Due to the intense connections of IWW in the German and international water sector and specific committees IWW will act as a multiplier of the new gained knowledge on HCNF.

University of Cadiz has developed a program to bring knowledge developed by its researchers to society by performing comics. In them projects show their objectives to mass public. Only selected projects were chosen and this was the case with CERAWATER project.



ES UN PROYECTO PARA EL USO DE MEMBRANAS CERÁMICAS DE NANOFILTRACIÓN, CON ESTRUCTURA DE PANEL DE ABEJA, PARA EL TRATAMIENTO EFICIENTE DEL AGUA.



DESPUÉS DE ANALIZAR LOS PRIMEROS RESULTADOS, INVESTIGADORES DE ALEMANIA, BÉLGICA Y FINLANDIA VIAJAN A CÁDIZ PARA VISITAR LA...

ESTACIÓN DE TRATAMIENTO DE AGUAS POTABLES DE EL MONTAÑÉS

es una planta piloto única, diseñada por el Grupo de Investigación de Tecnologías del Medio Ambiente de la UCA para mejorar la calidad del agua potable



y completamente automatizada, de manera que se puede controlar incluso mediante un móvil

funciona únicamente con energías renovables

EL AGUA SE FILTRA A TRAVÉS DE ESTOS TUBOS

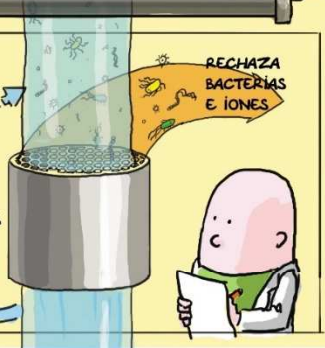
¿CÓMO FUNCIONA?

agua llena de bacterias e iones

ESTOS SON FILTROS QUE POR SU ESTRUCTURA IMPIDEN EL PASO DE BACTERIA E IONES. ADEMÁS SON MUY RESISTENTES A LAS SUSTANCIAS QUÍMICAS Y FÁCILES DE LIMPIAR.

agua limpia

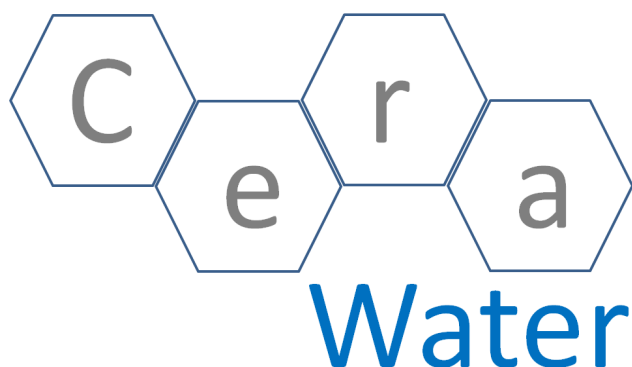
RECHAZA BACTERIAS E IONES



ESTA INVESTIGACIÓN ES SOSTENIBLE Y AYUDARÁ A MEJORAR LA CALIDAD DEL AGUA POTABLE EN CÁDIZ

More information on the project can be found here:

www.cerawater.eu



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4.2 Use and dissemination of foreground

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES

NO.	Title	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Year of publication	Relevant pages	Permanent identifiers ⁴ (if available)	Is/Will open access ⁵ provided to this publication?
1	<i>Novel grafting method efficiently decreases irreversible fouling of ceramic nanofiltration membranes</i>	<i>Ghulam Mustafa</i>	<i>Journal of Membrane Science</i>	<i>No 470</i>	<i>Elsevier</i>	<i>Amsterdam</i>	<i>2014</i>	<i>pp. 369 - 377</i>		no
2	<i>Rejection and permeability comparative studies between polyamide and ceramic nanofiltration membranes</i>	<i>N. García-Vaquero</i>	<i>Desalination</i>	<i>Submitted</i>						no
3	<i>Tbd</i>	<i>Francisca Olmo</i>	<i>Tecnología del Agua</i>	<i>Not yet submitted</i>						no

⁴ A permanent identifier should be a persistent link to the published version full text if open access or abstract if article is pay per view) or to the final manuscript accepted for publication (link to article in repository).

⁵ Open Access is defined as free of charge access for anyone via Internet. Please answer "yes" if the open access to the publication is already established and also if the embargo period for open access is not yet over but you intend to establish open access afterwards.



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TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES

NO.	Type of activities ⁶	Main leader	Title	Date/Period	Place	Type of audience ⁷	Size of audience	Countries addressed
1	Conference	FRAUNHOFER	Nano4water workshop	24-25 April 2012	Thessaloniki	Scientific Community, Industry	70	European
2	Conference/Fair	FRAUNHOFER	Ceramitec	24 May 2012	Munich	Scientific Community, Industry	Hundreds	European
3	Conference	VITO	NMG-BMG posterday	6 June 2012	Amsterdam	Scientific Community, Industry	Approx.. 100	European
4	Conference/Fair	FRAUNHOFER	ACHEMA	18-22 June 2012	Frankfurt	Scientific Community, Industry	Thousands	Worldwide
5	Conference	IWW	Aachener Membrankolloquium	7-8 November 2012	Aachen	Scientific Community, Industry	Hundreds	European
6	Conference	CYCLUS, VITO, FRAUNHOFER, IWW, RKV, VMW, LUT, UCA	Nano4water workshop	17-18 April 2013	Dresden	Scientific Community, Industry	85	European

⁶ A drop down list allows choosing the dissemination activity: publications, conferences, workshops, web, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters, Other.

⁷ A drop down list allows choosing the type of public: Scientific Community (higher education, Research), Industry, Civil Society, Policy makers, Medias, Other ('multiple choices' is possible).



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7	Conference	FRAUNHOFER	Euronanoforum	18-20 June 2013	Dublin	Scientific Community, Industry, policy makers	1200	European
8	Conference	FRAUNHOFER	Engineering with membranes	3-7 September 2013	Saint-Pierre d'Oleron	Scientific Community, Industry	80	European
9	Conference	FRAUNHOFER	Russian Membrane Conference	1-4 October 2013	Vladimir	Scientific	70	Russian
10	Conference	FRAUNHOFER, VITO, IWW, UCA	Nano4water workshop	23-24 April 2014	Stockholm	Scientific Community, Industry	90	European
11	Conference	VITO	CITEM	25-28 May 2014	Santander	Scientific Community, Industry	Approx.. 100	European
12	Project introduction in IWW Journal (No. 41)	IWW	Project introduction in IWW Journal (No. 41)	May 2014	Mülheim	Scientific Community, Industry, policy makers	➤ 1000	Mainly Germany
13	Conference	VITO	Invited oral presentation at the ICIM conference	6-9 July 2014	Brisbane	Scientific Community, Industry	Approx.. 200	Worldwide
14	Conference	FRAUNHOFER	CEI industrial workshop	15 July 2014	Storrs	Scientific Community, Industry	Approx.. 100	USA
15	Conference	VITO	ICOM	20-25 July 2014	Suzhou	Scientific Community, Industry	Thousands	Worldwide
16	Conference	VITO	Posterday of membrane societies of Belgium, the Netherlands and Germany	8 September 2014	Aachen	Scientific Community, Industry	Approx.. 100	European



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17	Conference	VITO	EMS Summer School	28 September – 3 October 2014	Cetraro	Scientific Community, (Industry)	Approx.. 100	European
18	Fair	IWW	Poster and Flyer at exhibition "Innovations for Europe based in NRW"	30-31 October 2014	Düsseldorf	Scientific Community, Industry	Approx.. 200	German
19	Conference	VITO	NPS14	3-5 November 2014	Utrecht	Scientific Community, Industry	Approx.. 300	European
20	Press report in WssTP newsletter	IWW, FRAUNHOFER	WssTP newsletter	November 2014		Scientific Community, Industry	Thousands	European
21	Interview with project coordinator	FRAUNHOFER, IWW	Interview with project coordinator	March 2015		Scientific Community, Industry	Thousands	European

Section B

Part B1

TEMPLATE B1: LIST OF APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS, ETC.					
Type of IP Rights ⁸ :	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant (s) (as on the application)
Patent	NO		EP 14 156 401,3	Filtration membranes	Buekenhoudt, K. Wyns, V. Meynen, G. Mustafa

Part B2

⁸ A drop down list allows choosing the type of IP rights: Patents, Trademarks, Registered designs, Utility models, Others.



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Type of Exploitable Foreground ⁹	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application ¹⁰	Timetable, commercial or any other use	Patents or other exploitation (licences) or IPR	Owner & Other Beneficiary(s) involved
Commercial exploitation of R&D results	Large scale honeycomb ceramic NF modules (incl. housing)	NO		Large scale stable housing and membrane elements for nanofiltration	Filtration of aqueous mixtures (waste water, drinking water)	2017		RKV, IKTS, CYCLUS, VMW, IWW
Commercial exploitation of R&D results	Anti-fouling layer on commercial ceramic NF elements			Anti-fouling layer on commercial ceramic NF elements	Filtration of aqueous mixtures (waste water, drinking water)	2017		VITO, IWW, VMW, LUT, UCA, CYCLUS, IKTS
General advancement of knowledge	Application of ceramic NF for drinking water production			Application of ceramic NF for drinking water production	Drinking water production by using stable ceramic nanofiltration membranes with large specific membrane area	Small systems: 206, large systems: 2019 – 2024		CYCLUS, VMW, RKV, IWW, IKTS, LUT, UCA, VITO
General advancement of knowledge	Application of ceramic NF for treatment of waste water and process water			Application of ceramic NF for treatment of waste water and process water	Cleaning/treatment/re-use of waste and process waters	Small systems: 2015 – 2016, large systems: 2019 – 20124		Depending on prroces and application (for example CYCLUS, LUT, RKV, IKTS)

¹⁹ A drop down list allows choosing the type of foreground: General advancement of knowledge, Commercial exploitation of R&D results, Exploitation of R&D results via standards, exploitation of results through EU policies, exploitation of results through (social) innovation.

¹⁰ A drop down list allows choosing the type sector (NACE nomenclature) : http://ec.europa.eu/competition/mergers/cases/index/nace_all.html

The consortium of the CeraWater project generated important quantity of knowledge. Thanks to the wide networks of contacts of the project partners, collaborations with national or international organizations and expertise in R&D projects all partners were successfully active in the exploitation of project results. Fraunhofer IKTS as institute of Fraunhofer Society, Europe's largest application-oriented research organization has a strong interest of the exploitation of project results. Since its existence (1991) VITO has been active in the valorization of in-house developed technology by adequate patenting, licensing to existing companies or by creating spin-offs. A further strong exploitation potential was given especially by IWW as leading organization active in the water research sector. Furthermore academic partners like UCA and LUT have strongly disseminated results from the field they focus on in particular: LCA, waste/waste water process design, system development.

Four key exploitable results were gained in CeraWater. Two of the results can be described as precursors of technical products and two results are knowledge-based technologies that use the precursors of the technical products.

The first key exploitable result are “large scale honeycomb ceramic NF modules (incl.

housing)”. The uniqueness of the membranes is the combination of ceramic nanofiltration and large specific membrane area. The membranes can be used for drinking water treatment and for waste water treatment as well. In pilot scale the membrane supports can be produced by RKV and the active layers can be applied by IKTS. After prove of membranes in technical processes and rising demand for membranes, IKTS will transfer the coating technology to RKV (this was also done with other membrane types before). The time for this technology transfer depends on further development of membranes and demand. It is supposed to be in the following 2 – 5 years. Further demand for development is seen in further increase of specific membrane area, to further decrease foot print and area specific membrane costs and decreasing pore diameter further increasing selectivity for small molecules. It was decided not to patent the technology of membrane preparation and coating due to the necessary disclosure of detailed information. The policy of membrane preparation is the nondisclosure of detailed information and processing steps of the nanofiltration coating procedure.

By this technology RKV will be the counter weight to honeycomb producers from the USA and Japan. So this project could improve or even establish the competitiveness of ceramic European membrane producers in this sector. As mentioned before, for nanofiltration, the estimated global market was estimated in 2007 with about \$ 97.5 million. It was estimated to reach \$ 310.5 million by 2012 with an annual growth rate of 26.1 %. Assuming a market share of ceramic NF membranes (tubular) of the project consortium of 0.5 % in 2006 and an annual rise of market share of 0.3 % (a clearly higher rise is expected when the development and application of the ceramic NF honeycomb succeeds) consortiums ceramic NF membranes will have a market share of 4.7 % in 2020 resulting in a global market of more than 93 \$ million with a strongly rising tendency.

The second key exploitable result “Anti-fouling layer on commercial ceramic NF elements”.

As fouling is a serious problem in many different applications, the unparalleled anti-fouling effect of methyl Grignard grafting (developed by partner VITO in WP4) was noticed by different membrane suppliers and appliers (consequence of a series of dissemination actions, see section A, table A1 and A2). In the meantime it is also clear, following the results of extra tests at VITO outside CeraWater, that the anti-fouling effect not only works in case of nanofiltration membranes and relatively low molecular weight foulants, but also for very open microfiltration membranes used for e.g. the treatment of oil/water emulsions. Particularly the potential use of the grafted membranes in oil produced water, proved attracting a lot of interest. In this specific growing separation problem (currently, due to end-of life of

many oil wells, up to 4 barrels of oil contaminated water if produced for 1 barrel of oil), ceramic membranes are typically used due to their lower fouling capacity, which is however still substantial. As a consequence, discussions are ongoing with Rauschert and other European ceramic membrane suppliers. Moreover, VITO is involved in a small project, partnering different European oil producing companies, looking at testing Grignard grafted membranes in model oil/water emulsions, and real oil produced water. In contract research at VITO, grafted membranes proved also capable of direct filtration of a fermentation broth, with economically viable flux without any serious flux decline during filtration. A native membrane, on the contrary, showed a much lower flux, and a continuous flux decline during filtration. As a consequence pretreatment such as centrifugation might be avoided. This shows the potential of Grignard grafted membranes in the numerous separation tasks in the upcoming bio-technology. Possibility to sterilize these membranes adds to their potential in this specific application. Exploitation of these results is possible in further bilateral projects of VITO.

As shown in WP8, Grignard grafted membranes have also interesting advantages in pulp and paper effluents, and in olive oil waste waters. As a consequence, extra collaboration between VITO and partners LUT and Cyclus is planned for the near future, to further explore this potential.

In drinking water production from surface water (WP9), the Grignard grafted membranes proved interesting too. The pilot results from partner VMW, at the Blankart, Belgium clearly showed the systematic higher fluxes of the grafted membranes (even after milder cleaning), allowing maybe processing at lower cross-flows and therefore at lower energy demand and thus lower price. However, due to the limited piloting period, it is not clear that the price of the membranes is not too high to make this application economically viable.

The **third key exploitable result “Application of ceramic NF for drinking water production”** and the **forth key exploitable result “Application of ceramic NF for treatment of waste water and process water”** base on the knowledge of membrane and process performance of the developed membranes in drinking and waste and process water treatment. The CeraWater consortium itself includes besides the manufacturer of the developed membranes, also two other industrial partners in water treatment, VMW and CYCLUS end user and technology provider of the designed modules. Thereby VMW has a strong focus on the end user application in the drinking water sector. This sector is characterized by large applications. CYCLUS is a representative of plant and technology providers in the waste and process water sector. This is a sector with a variety of different applications and requirements. The project is expected to impact competitiveness of these industries and to promote the technology via their exploitation plans of the results. Furthermore the academic partners and Fraunhofer IKTS act as multipliers of membrane process technology. Especially at IKTS manifold technologies exist to perform lab- and pilot scale membrane application tests and piloting of processes. So IKTS acts as development partner for processes using the developed membrane technology leading to wider experiences in the use of the membrane and market entrance of the membrane process in further fields of application.

As mentioned before, in drinking water production from surface water (WP9), the anti-fouling effect of Grignard grafted membranes proved interesting too, allowing maybe processing at lower cross-flows and therefore at lower energy demand and thus lower price. However, due to the limited piloting period, it is not clear that the price of the membranes is not too high to make this application economically viable.