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Nowelties
European Joint Doctorate

NOWELTIES – Joint PhD Laboratory for New Materials and Inventive Water Treatment Technologies. Harnessing resources effectively through innovation

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D1.1 Establishment of an evaluation concept to be used to compare advanced wastewater treatment processes for their efficiency of eliminating OMPs.

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D1.1. Establishment of an evaluation concept to be used to compare advanced water treatment processes for their efficiency of eliminating OMPs.

1. Purpose of the present deliverable:

The present document aims to set guidelines for the different ESR projects on how to evaluate the treatment technologies they research. Specifically, we aim to design “standard experiments” with as many common parameters (organic and inorganic background matrix, target contaminants) to be shared among different ESR projects. Thereby, analytical approaches can be shared, and related technologies can be better compared among each other. The recommended protocols also include the comparative assessment with an appropriate benchmark technology, that is a technology that is considered mature and either commercially common practice or at least close to commercial implementation, in the eventual case that a commercial solution does not exist for the specific treatment problem.

However, it is important to mention is that this evaluation concept should be considered as a dynamic concept and initial definition and selection of protocols for comparative assessment will be modified and updated if needed along the realization of the project.

2. Overview on technologies researched, contamination removal mechanisms and preliminary grouping of the 14 ESR projects

One challenge for finding a common approach to experimentation and analysis is that NOWELTIES embraces a wide variety of matrices and treatment strategies. Even the common nexus of micropollutant control is by itself a highly heterogeneous research topic, mainly because of the wide variety of chemical structures of the universe of organic substances included under the umbrella of the term micropollutants. An apparent consequence of the structural diversity of micropollutants is that each pollutant may be considered refractory against certain mechanisms, whereas it may be amenable to transformation and eventually subsequent mineralization via other mechanisms.

Table 1 lists the different ESR projects and their title by research block (corresponding to WP2 – WP5). An overview over the different transformation mechanisms involved in each researched technology is given in Table 2. Table 2 also shows in which part of the treatment train the invested technology is most likely to be used, i.e. during secondary wastewater treatment or as a polishing treatment before discharge or beneficial reuse.

In the coordination meeting in Santiago de Compostela (October 2019), the project members decided to establish the following sub-groups:

- ESR group 1: Biological wastewater treatment: ESR1, ESR2, ESR11, ESR12
- ESR group 2: Advanced treatment: all others

Consideration shall also be given to the fact that ESR4, ESR5 and ESR12, all three included in either ESR group 1 or 2, aim to employ chemical reduction mechanisms that could be employed specific contaminants groups that may require e.g. dehalogenation.

Table 1. Overview of ESR projects: Titles of PhD theses and institutions involved

ESR	Title of PhD thesis	Institutions
Block 1 (WP2): Enhancing biological processes and their understanding		
1	Understanding biotransformation mechanisms of OMPs during anoxic biological wastewater treatment	USC-RWTH
2	Studying the bioavailability and biodegradability of OMPs during treatment	RWTH-USC
3	Coupling the new concept of sequential biofiltration with in situ electron acceptor delivery for enhanced OMP removal and effective attenuation of disinfection by-product precursors	TUM-ICRA
Block 2 (WP3): Advancing physico-chemical processes		
4	Design, development and characterization of atmospheric plasma system for wastewater treatment	IPB-ICRA-TMF
5	Understanding transformation of OMPs during plasma treatment and its ecotoxicological implications	ICRA-UNIFE-IPB
6	Application of UV LEDs AOPs for the efficient removal of OMPs from wastewater	FKIT-ICRA
Block 3 (WP4): Exploring the potential of new materials		
7	Surface modification and functionalisation of adsorbent materials	TMF-IPB-FSB
8	A green microwave - assisted synthesis of Au/TiO_2/graphene oxide nano-hybrids for visible light-induced photocatalysis	FSB-ICRA
9	Removal of OMPs by nanophotocatalysts and nanobiocatalysts immobilized into magnetic supports	USC-RWTH
10	Novel TiO_2 - SnS_2 based composite co-catalysts for solar driven water purification	FKIT-ICRA
Block 4 (WP5): Innovation in hybrid processes		
11	Studying the enhancement of the removal of OMPs from wastewater by adding powder activated carbon in an MBR	UNIFE-FKIT
12	Design of hybrid nano-engineered reductive bioprocesses for wastewater treatment and biogas generation	ICRA-TUM
13	Development of hybrid treatment system by integrating nanocatalyst and adsorptive composites *in situ* in sequential biofiltration systems	TUM-USC
14	Hybrid ozone-ceramic membrane process: increasing hydroxyl radical yield and OMP reduction while reducing membrane fouling	ICRA-FSB

Table 2. Overview of contaminant removal mechanisms involved in different ESR projects

ESR	**T: Technology development or** **M: mechanistic investigation** **Application in secondary WW treatment or in** **advanced (tertiary or quaternary) treatment *** ● : primary treatment mechanism ○ : secondary treatment mechanism	**Oxidative biodegradation**	**Reductive biodegradation**	**Chemical oxidation**	**Chemical reduction**	**Photolysis**	**Adsorption**	**Sieving**
1	**T:** Anoxic biological WWTP	●	●				○	
2	**M:** Bioavailability and biodegradability	●	●				○	
3	**T:** Biofiltration	●	●				○	
4	**T:** Atmospheric plasma			●	●			
5	**M:** Atmospheric plasma			●	●			
6	**T:** UV LEDs - photocatalysis, AOP			●		●		
7	**T:** Nano-engineered adsorbents						●	
8	**T:** Photocatalysis			●		●	○	
9	**T:** Magnetic adsorbents						●	
10	**T:** Photocatalysis			●		●	○	
11	**T:** activated carbon in MBR	●					●	
12	**T:** RGO adsorbents in anaerobic treatment		●		●		●	
13	**T:** Combined biofiltration and adsorption	●	●	●			●	
14	**T:** Integrated ozonation and membrane filtration			●				○

* could also be applied in advanced drinking water treatment

3. Suggested evaluation approach

The presented evaluation approach shall serve as a guidance for a final technology evaluation after technology optimization has concluded within the scope of the ESR project. Each ESR project must decide by its own, which contaminants need to be employed during the technology development and optimization phase. Where appropriate it is recommended that the overlap in the analytical approach between development and evaluation phase is maximised.

After the conclusion of the technology optimization phase each ESR project shall carry out a technology evaluation approach described in the following. The technology evaluation can also be carried out multiple times during the ESR project if feasible. This way the improvement during the project can be effectively monitored.

A summary of the suggested evaluation approach includes the following four steps, which will be described in detail afterwards.

- Step 1: Selecting a benchmark technology
- Step 2: Select target contaminants
- Step 3: Establish treatment performance experimentally

- Step 4: Comparative analysis including complementary engineering and economic aspects

3.1. Step 1: Selecting a benchmark technology

As a first crude approach that will have to be validated at a later stage for each ESR the benchmark technologies listed below have been selected:

- Conventional activated sludge treatment: ESR1 (&ESR2), ESR11
- Upflow anaerobic stream blanket: ESR12
- Biological activated carbon adsorption: ESR3, ESR13
- Granular activated carbon adsorption: ESR7, ESR9
- Ozonation: ESR4 (&ESR5), ESR6, ESR8, ESR10, ESR14

ESR2 and ESR5 do not per se develop technologies but rather work on detailed mechanistic studies about individual processes. Hence, instead of developing their own performance assessments these ESRs are to contribute to the performance assessments of ESR1 and ESR4, respectively.

As stated above, these are the currently suggested benchmark technologies. They are based on a very simplified approach based on the information provided in Table 2, e.g. ozonation is a treatment technology that exclusively uses chemical oxidation mainly through direct reaction with ozone or the hydroxyl radicals that are generated as secondary oxidant. It is also commercially employed with very good data availability regarding its performance for water quality amendment and engineering aspects relating to cost, energy and material requirements. As such it seems a suitable benchmark for several of the novel technologies developed based e.g. on plasma chemistry or photocatalysis even though these technologies include several pathways that can lead to contaminant abatement including reductive pathways and adsorption. During the execution of the project the set of benchmark technologies may be expanded if deemed reasonable due to research findings of the NOWELTIES project.

3.2. Step 2: Select target contaminants

As described in section 2, the different treatment projects were grouped into

- ESR group 1: Biological wastewater treatment: ESR1, ESR2, ESR11, ESR12
- ESR group 2: Advanced treatment: all others

In summary, these are the suggested factors to be considered for contaminant selection:

- Environmental relevance (e.g. inclusion in relevant European or national policies)
- Biodegradability
- Stability against chemical oxidation (O_3, $^{\bullet}OH$) and reduction ($^{\bullet}H$, e^-)
- Solubility and sorption behaviour (logP, K_{OC}, logD)
- Practical considerations regarding ease of analytical quantification and handling of contaminant in the laboratory (e.g. avoid use of carcinogens for health and safety reasons)

A starting point for the selection of target OMPs was previous experience of group members in on process performance assessments using the concept of indicator chemicals. As suggested by Alvariño et al., Journal of Hazardous Materials 308 (2016) 29-36 and Dickenson et al., Environ. Sci. Technol. 43 (2009)6242–6247 indicator chemicals (Tables 3 and 4) have been selected to assess treatment performance and to properly describe the underlying removal mechanisms for trace organic chemicals (e.g., non-biodegradable, moderately degradable, well degradable for biological transformation; different secondary rate constants for ozonation; different adsorbabilities for activated carbon, etc.).

However, it is important to mention that not all compounds will be monitored in specific individual research project, but the selection will be adapted to the specific needs of each process studied and also to the analytical capabilities of the participating groups.

Table 3. Indicator substances for biological systems

NSAIDs	**Hormones**	**Antibiotics**	**Other OMPs**
Ibuprofen	Estrone E1	Amoxicilin	Bisphenol A
Diclofenac	Ethynil estradiol EE2	Clarithromycin	
		Azithromycin	
		Erythromycin	
		Roxithromycin	
		Cefalexin (1G)	
		Sulfamethoxazole	
		Ciprofloxacin	
		Trimethoprim	

Table 4. Indicator substances for Systems Using Ozone or other AOPs

Pharmaceuticals	**Personal care products**	**Other**
Acetaminophen	Triclosan	NDMA
Salycilic acid	Triclocarban	Bisphenol A
Naproxen	Caffeine	
Codein	DEET	
Atorvastatin		
Sulfamethoxazole		
Carbamazepine		
Atenolol		
Diclofenac		
Fluoxetine		
Erytromicyn-H2O		
Trimethoprim		
Ciprofloxacin		
Iopromide		

Additionally, ESR4, ESR5 and ESR12 utilize chemical reduction mechanisms that shall be addressed specifically during the process of target contaminant selection.

The initial proposal is to test elimination of perfluorinated compounds (PFC) in ESR5, ESR12 and ESR13 and the following compounds are selected as shown in Table 5.

Table 5. Selected perfluorinated compounds to be used as indicator substances

Perfluorinated compounds
GenX: 2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid HFPO-DA
Perfluorooctanic acid (PFOA)
Heptadecafluorooctanesulfonic acid potassium salt (PFOS)
Undecafluorohexanoic acid (PFHxA)
Tridecafluorohexane-1-sulfonic acid potassium salt (PFHxS)
Perfluorobutyric acid (PFBA)
Nonafluorobutane-1 -sulfonic acid (PFBS)

3.3. Step 3: Establish treatment performance experimentally

Step 3.1. Establish water quality amendment regarding micropollutants

Treatment performance shall be established by a set of experiments described in Table 6, whereby each ESR must choose which experiments are useful in the context of his project, e.g. biological wastewater treatment in a distilled water matrix will not make much sense.

Table 6. Overview on standard experiments. Compositions for model freshwater, wastewater and secondary effluent inorganic and organic matter are given in the appendix of the present document.

Exp*	Water	Inorganic model composition	Organic model composition	Spiked target contaminants
1	demineralized	no	no	yes
2	demineralized	yes	no	yes
3	demineralized	no	yes	yes
4	demineralized	yes	yes	yes
5	Tap water	yes	yes	yes
5	real	no	no	yes

* The same experimental design can be applied for blank experiments, i.e. without spiked target contaminants.

As mentioned at the beginning of this section, this experimental design may be too comprehensive to be carried out on a routine basis, when developing a technology and varying other experimental parameters such as e.g. the transferred ozone dose, hydraulic residence time etc. But it is recommended that the ESR projects adhere as closely as reasonable to these protocols during the technology development and optimization phase.

Step 3.2. Complementary data collection including surrogates

For each sample the following data shall be recorded:

- Datalogging, Engineering, and experimental conditions:
  - Systematic experiment name and sample name / number
  - Date, time, operator names
  - Link to a short experiment description
  - Link to a full description of the experimental system
  - ESR project specific experimental conditions (to be established by ESR)
  - Temperature, pH, electrical conductivity

- Bulk organic matter
  - Dissolved organic carbon (DOC) after filtration through 0.45 µm.
  - As an alternative to DOC: Chemical oxygen demand (COD), filtered and UV absorbance at 254 nm.
  - COD unfiltered, where applicable

Other routine water quality measurements to be considered to further characterize the water matrix:

- Dissolved inorganic nutrients (N-NH_4^+, N-NO_3^-, N-NO_2^-, P-PO_4^{3-})
- Further detail on inorganic composition (e.g. Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, Br^-, SO_4^{2-})
- Turbidity (report as NTU)
- Inorganic carbon or alternatively total alkalinity, as for most waters one can be converted into the other knowing the pH

Surrogates

- UV-Vis absorption spectrum from 200-800 nm, 1 nm step, expressed as [1/m], measured in a 1cm cuvette. Potentially, dilutions need to be applied to measure short wavelengths correctly.
- The acquisition of fluorescence excitation-emission matrices (EEM) shall be discussed further onwards in the project as the complexity of the measurement, or rather its evaluation, requires further information exchange among partners. If going ahead, at this stage, normalization to Raman units would be recommended.

3.4. Step 4: Comparative analysis including complementary engineering and economic aspects

Step 4.1. Economic and resource use performance data

Due to the innovative nature, most ESR technologies are being researched at laboratory-scale. The consortium hence decided that a full life-cycle assessment for environmental performance and life-cycle cost study are not warranted as for most technologies full-scale technology design and volumetric reactor throughput will not be easily estimated.

However, the following key figures for operation shall at least be estimated

Operational cost - material:

- Electricity usage (kWh/m^3)
- Reagent use during operation (mass per m^3 treated)
- Foreseeable replacement parts (e.g. UV lamps)
- Aggregate the above to generate an estimate of operational cost

Operational cost – human resources:

- Develop a short verbal narrative of the envisioned operation scheme, i.e. the human resources aspect for supervision, control and maintenance requirements.

Infrastructure cost:

- Estimate the range of infrastructure cost and land use per 1000 m^3 daily treatment capacity. Discuss the uncertainties.

Summary of cost structure:

- As the cost assessment will be very rough, under this heading the ESR should briefly discuss the cost structure: What are the biggest contributions to overall cost and where are the biggest uncertainties in this assessment, i.e. opportunities for improvement.

Step 4.2. Establish treatment performance of benchmark technologies

The approach for this must be assessed on a case-by-case basis. The objective would be to acquire data that is as comparable as possible to the dataset obtained for the technology under development. Where different ESRs benchmarks their technology against the same technology they shall come to a joint conclusion on how to generate this data. The data should allow comparison for water quality amendment (i.e. to be compared to the data generated by the ESRs in step 3.1) and economic performance (step 4.1).

Where possible the benchmark data can also be generated experimentally, which is certainly the preferable solution, i.e. the one that allows for the most accurate comparisons.

Step 4.3. Analyse downstream impacts when embedded in a treatment train

ESRs should list upstream demands and downstream impacts of implementing their newly developed technology and compare this to the benchmark technology.

As an example, an UV/H_2O_2 advanced oxidation process will require that upstream process remove solids.