FINAL REPORT

Circular economy of water in industrial processes – CEIWA

CEIWA

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Preface

Water systems intersect with all sections of society and industry and opportunities exist in these interfaces to create additional value by application of Circular Economy principles. There is enough water to meet the world's growing needs, but it will not be achievable without dramatically changing the way water is used, managed, and shared. Global demand for freshwater will exceed viable resources by 40% by 2030, if the consumption trend does not change. Climate change and increase in pollutants will further deplete the quality and amount of available freshwater resources.

Industry is paving its way to sustainability, which includes improving carbon neutrality and resource efficiency. In addition, industrial emissions are facing more stringent regulations that concern especially water intensive industry, such as pulp and paper industry, and biorefineries. To respond to these ascending challenges CEIWA developed solutions for digitalization, technology development, methods for detect, analyse, and manage of different pollutants – especially micro- and nano plastics (MNP), and understanding how regulations and legislation and technology development affects each other. In addition to providing solutions to the water intensive industry, the results of the project are also exploitable for technology and service providers.

Regulation affects the development of new technologies, thus the technology suppliers desire to understand and to be prepares for regulation. Also, in development of novel technologies—based on AI, Big Data, or on-site and on-line measurements—it is pivotal to know regulation's impact to the commercial potential of the technology. In the optimal situation, the regulatory environment will impact the choices already during the innovation and development work and does not hinder the application at later stages.

Also, the development of the regulation depends on the technology development. It is important for technology developers to understand what the processes, actors, and dynamics are related to regulation development. For players on global markets, it is also important to know the differences in these processes in the different markets. The dynamics, the speed how the regulation is evolving, depends heavily on the processes, but also on the development of technologies, and the activity of the developers. Regulation and the related processes are an important and very interesting part of the CEIWA project.

The main research questions of CEIWA project are: How the new prospective methods and technologies can help in improving efficiency, water recycling and reuse, recovery of substances and energy, and avoiding environmental waste and pollution; and how these technologies can be utilized in creating new products and services that will obey the current and future regulations in the main global markets.

The CEIWA consortium is multidisciplinary, including biologists, chemists, material scientists, data scientists, control engineers, and legal scholars. Therefore, a vast among of scientific knowledge and a huge number of research approaches and methods have been applied to creating the results. For example, the technology and law interface of the regulation of industrial water pollution are analysed for comparing the operating environments. Data analysis, domain expertise and different modelling approaches are combined in developing solutions for monitoring, controlling and optimization. The methods were developed for sampling, separation, and measurement of MNP, and prototypes are developed for in situ monitoring of micro plastics by integrating and combining different optical methods to effectively detect semi-transparent particles in water flow.

The results presented in this Final Report of CEIWA project cover the most important and the most interesting topics that were selected in collaboration of researchers and company partners. The partner companies of CEIWA have provided their know-how, continuous collaboration, access to the process data, and provided samples to the researchers, which have enabled focused research actions and provided novel findings for the scientific community and immediate results for the partners.
The project has provided regular meeting forum, despite the challenges induced by COVID, and both the research and industry partners have bee unusually active in these meetings. Similarly, companies have been very active in the work of Work Packages. The companies have mentioned that CEIWA project provides a platform to look beyond business as usual, to test and develop tools to monitor and remove detrimental substances from processes, to ensuring the sustainable value proposals of products and operation and to understand future changes in regulation. Also, companies have found that collaboration on digitalization and new purification technologies has generated new ideas and concepts across the industry to help achieve customers' targets, and the project's public part has strengthened companies' own development work in industrial and process water treatment.

Prof. Matti Vilkko, Scientific Director
Tampere University

Anu Kettunen, Chairman of the Steering Committee
Teollisuuden Vesi

CEIWA project in brief

CEIWA in numbers

Duration	1 March 2021–30 September 2023
Budget	€6.32 million
Company budget	€3.36 million
Research institution budget	€2.96 million
People involved	89
Publications	31

Consortium

The Circular Economy of Water in Industrial Processes (CEIWA) project aimed to advance safe, sustainable and resource efficient water treatment. In the two-and-a-half-year project, the CEIWA partners developed solutions for digitalisation, technology development, management of different pollutants, and legislative aspects.

CEIWA brought together a wide consortium of actors in the industrial water ecosystem. The consortium consisted of five industry core partners with their own parallel projects, and six research institutes responsible for high-level scientific research. In addition, two collaborative partners supported the project implementation.

Figure 1: CEIWA project consortium

Industry core partners

- Andritz
- Kemira
- Teollisuuden Vesi
- UPM
- Valmet

Research institutes

- LUT University
- Tampere University (TUNI)
- University of Helsinki (UH)
- University of Eastern Finland (UEF)
- University of Oulu (UOulu)
- VTT Technical Research Centre of Finland (VTT)

Collaborative partners

- Fortum
- Gasum

Project management

The coordination of the project was organised by a steering group and four thematic working groups (Work Packages). The steering group consisted of the project partners' representatives and expert members. Its main function was to oversee the overall management of the project.

The research activities were organised around four main themes that spanned across the whole ecosystem: 1. Technology and law interface of the regulation of industrial water pollution, 2. Control of closed industrial water circles based on analyses, 3. Sustainable treatment processes, and 4. Micro- and nanoplastics.

Thematic group 1 focused on understanding how the regulatory environment does not hinder the application of innovations at later stages but will impact the choices already during the innovation and development work. In theme 2, the focus was on the dynamic properties in closed water circuits and operating conditions, depending strongly on the operation of production processes. Theme 3, Sustainable treatment processes, focused on improving current wastewater and sludge treatment technologies and developing new ones. Micro- and nanoplastics are emerging pollutants that may cause concerns for the public and industry. Theme 4 provided valuable information on the effects of microplastics in industrial waters.

The scientific director of the project was Professor Matti Vilkko from Tampere University. The chairman of the Steering Committee was Mikko Haapalainen, Valmet, until April 2023, and from then on, Anu Kettunen, Teollisuuden Vesi.

The four themes were managed by WP leaders from research institutes. The companies took an active part in the activities of the theme groups and in guiding the project. The collaboration between the companies and researchers was very close and successful.

WP leaders

WP1: Tiina Paloniitty, University of Helsinki
WP2: Jani Tomperi, University of Oulu
WP3: Marika Kokko, Tampere University
WP4: Arto Koistinen, University of Eastern Finland

The project coordination was contracted for CLIC Innovation Oy, and Pirjo Kaivos was appointed as the project coordinator.

Work Package Structure

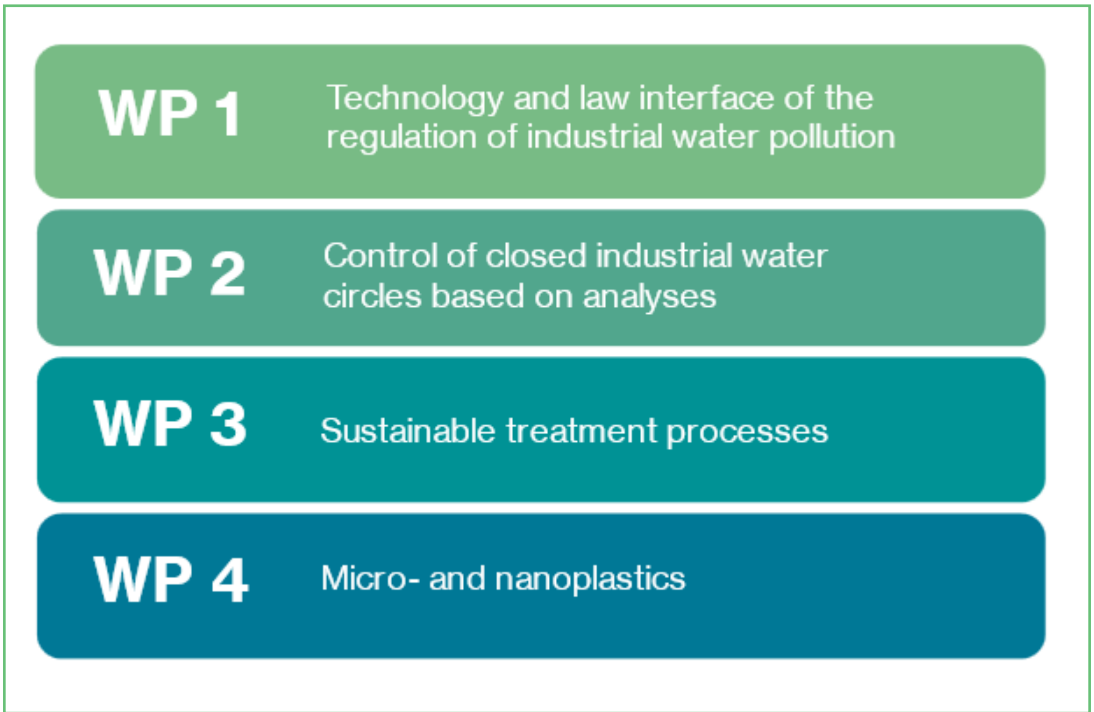

Figure 2: The project structure

CEIWA

Steering Committee

Anu Kettunen, Chairman (Mikko Haapalainen, Valmet, until April 2023)	Teollisuuden Vesi
Naveen Chenna	Andritz
Outi Grönfors	Kemira
Viljami Kinnunen	Gasum
Heikki Korhonen	Valmet
Corinne Le Ny Heinonen	UPM
Marja-Liisa Ripatti	Fortum
Lauri Kujanpää	VTT
Prof. Matti Vilkko, Scientific Director	Tampere University
Adj.prof. Arto Koistinen	University of Eastern Finland
Prof. Mika Mänttäri	LUT University
Dr. Tiina Paloniitty	University of Helsinki
Prof. Mika Ruusunen	University of Oulu

Expert members

Tuomas Lehtinen	Business Finland
Markku Lämsä	Business Finland
Pirjo Kaivos, Coordinator and Secretary	CLIC Innovation
Tiina Witikkala	CLIC Innovation
Taina Kujanpää	CLIC Innovation

International collaboration and networking

University of Oulu collaborated with the University of Modena (Italy), Mälardalen University (Sweden), and Oslo Metropolitan University (Norway). During the project, the Control Engineering research group (UOulu) had close ongoing research collaboration with Oslo Metropolitan University related to wastewater treatment, data analysis and modelling topics. The collaboration included information exchange regarding, among other things, the best available research methods and the achieved results related to the above-mentioned topics, preparing a joint scientific journal article and planning future collaboration after CEIWA. The collaboration between the Fibre and Particle Engineering research unit (UOulu) and the University of Modena included a two-month research visit, joint research work and preparing joint scientific publications.

LUT University collaborated with Universidad de Cádiz (Spain) in the implementation of Task 4.2. PhD student Ana Franco del Pino visited LUT University during between 23 January and 31 March 2023. The main objective of the research visit was to learn about the utilisation of the Raman imaging microscope for microplastic analyses and to exchange experiences with the purification of environmental samples and the identification of microplastics. During the visit, Ana Franco del Pino also developed an analysis method for microplastics with a Raman imaging microscope by assessing the suitability of different filters. After her visit, Ana Franco del Pino continued as a project researcher from 3 April to 30 September 2023. She focused on the development of concentration and purification methods for pulp and paper effluents, as well as the analysis of microplastics from purified samples. The collaboration with Universidad de Cádiz targeted to a joint publication focusing on the development of a purification method for concentrated aqueous samples.

Tampere University (TAU) has done international collaboration in terms of research visits. The experimental work on the development and implementation of anaerobic wastewater treatment (Task 4.1) was taken forward in 2023 via collaboration with Asst. Prof. Emre Köroglu from Kahramanmaras Sutcu Imam University, Turkey, who visited TAU for one year with his own funding. This collaboration will result in a joint publication. In the spring of 2022, the degradation of microplastics in anaerobic digestion (Task 4.4) was experimentally studied with the help of researcher Dries Brosens (Krale de Grote Hogeschool, Belgium), who visited TAU for five months in 2022. A manuscript on the results from this study has been submitted.

At the University of Eastern Finland (UEF), this funding has initiated several international research collaboration actions. Based on the work partially conducted in CEIWA, UEF/Photonics participates in a HORIZON-RIA EU project (2022–2026): IBAIA - Innovative environmental multisensing for waterbody quality monitoring and remediation assessment. Further, UEF/Photonics collaborates with CEDRE (France) in view of testing the prototype also in a natural environment for accidental pollution of water. Advances in photonics solutions for the detection of microplastics in water raised the interest of another European consortium for the preparation of a new HORIZON-IA project (DanubeSens). Together with UEF/SIB Labs and TAU, collaboration with Indian Institutes of Technology has been elaborated with the aim of joint activities regarding microplastics detection, degradation and ecotoxicological research. These actions include researcher visits within the partners.

The University of Helsinki has had a ‘senior advisers’ body, comprising of research leaders in the field of EU innovations law (Professor Dr. Leonie Reins, Erasmus University Rotterdam), water governance (University Lecturer Henrik Josefsson, Uppsala University), industrial pollution regulation (Professor Dr. Wolfgang Köck, Helmhulz Centre for Environmental Research) and plastics governance (Professor Elizabeth Kirk, University of Lincoln and Assistant Professor Naporn Popattanachai, Thammasat University). The UH team has had active communication with the senior advisers, guiding the research. Of the UH team, Tellervo Ala-Lahti also paid a research visit to Professor Reins in spring 2022; they also wrote a research article together. Collaboration has produced a book chapter on EU plastics governance, by Paloniitty and Ala-Lahti, to a research handbook edited by Kirk and Popattanachai. Reins and the UH team also created a special session on innovations and environmental law for the IUCN Academy of Environmental Law annual colloquium in 2023, and one of the articles Ala-Lahti has written in the project is submitted to a special edition of RECIEL journal where Prof. Reins visits as co-editor.

CEIWA

EU Green and Digital Transition Policy Meeting the Realities of Industrial Water Pollution Regulation

Summary

The EU Green Deal desires to be two things, green and digital, so the EU is seeing high potential in securing a sustainability transition and greening the industry with help of digitalisation and innovations. The need to ascertain a rapid transition to sustainable EU is not, however, taking place in a void but in a legal space filled with pre-existing regulation impacting the daily lives of a water-intense industry. On the one hand, this regulation restricting industrial sites' environmental and water impact can result in better innovations, as better technologies are needed to meet the environmental quality norms that in contemporary EU environmental law emerge from various pieces of legislation. On the other, the dense web of environmental, chemical, and water regulations may obstruct the use of novel and disruptive innovations as in the eyes of the precautionary principle, prominent in environmental regulation, risks stemming from innovations may appear too high to be accepted. Our research in the CEIWA project was set to map out these interactions and dynamics they create.

The landscape of EU regulation on water quality was known to have become stricter in past years. The practice started from the Court of Justice of the European Union (CJEU) case law when the Weser ruling clarified the normativity of rules and principles enshrined in the EU Water Framework Directive (WFD). As the legal instrument is a directive, implemented in the Member States (MS), we set out to explore any variation in the MSs, visible in their legislation and court practice on industrial sites with water impacts. There turned out to be even more variation than we anticipated, and the legal ambiguity the variety causes makes the operational environment more difficult to navigate for practitioners. On a general level, all MSs examined have kept their distance from the strict interpretations the CJEU has promulgated. Bringing together this and the diversity of legal approaches means that each MS has found its own avenue of adaptivity to negotiate the strict norms the Weser ruling created and the realities of needing to allow activities with impacts on waters.

We also explored the legal status outside of Europe to gain perspectives on how regulation of water management and closed water circuits are done elsewhere. The Chinese legal system illustrated the indirect legal ways to reach CE goals. China has an abundance of CE policies and guidelines, steering the nation's path towards circularity, but the strict norms that drive the water technology innovations come from a Chinese legal innovation on water governance, the River Chief System (RCS). The RCS has advanced participatory rights and added accountability, but also made water quality norms stricter to an extent that it has even forced sites to close. Contrary to the European WFD, the Chinese RCS is relatively clear, making the legal landscape more predictable for operators.

Contact person

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The awkward relations between EU innovations and environmental law

Description

The constantly growing stringency of water pollution regulation serves as an incentive for developing circular water economy technologies. Regulation affects the choice over technologies, thus the technology suppliers are keen to understand and prepare for regulation. Also, in the development of novel technologies—based on AI, Big Data or on-site and on-line measurements—it is pivotal to know the impact of regulation on the commercial viability of the technology. In the optimal situation, regulatory environment will impact the choices already during the innovation and development work, without hindering the application at later stages. We study, on the one hand, the regulative bottlenecks that obstruct or disincentive the use of novel technologies and on the other hand how the administrative and legal systems and substantial regulation could better serve these novel technologies. We also examine the role of AI-based technologies, whether their role differs from other technological innovations, discussing the technologies from the uncertainty perspective, probing whether legal and judicial decision-makers have properly understood the technological solutions impacting their decisions.

On top of these themes of disruptive innovations, uncertainties and environmental impact, one specific environmental concern is also probed: microplastics pollution. The upcoming EU regulation on microplastics is analysed in detail, as it is currently in the regulator's focus. In the best possible scenario, the ongoing regulatory activity could impact the current technological development and innovation, and result in an outcome where regulation would not obstruct the utilisation of novel technologies.

Results

Environmental permit systems disincentive the use of disruptive innovations. Uncertainties in innovations are hardly ever considered in courts – ”technological” uncertainties are treated differently from ”scientific” ones. Consequently, if technological development does not influence assessment of a site's environmental impact, it is ignored by the legal system.The legal system is in this sense “technology blind” and does not pay attention to the type of technology in question (for example, whether it is based on AI technology or not). But if the innovation can influence the environmental impact, its risks are often evaluated very carefully. Case analysis from Finnish administrative courts shows how legal decision-makers dealing with environmental issues are not necessarily always using the possibilities at their disposal to alleviate the challenges that emerging technologies face when they are a part of proposed industrial plans. A very high level of knowledge is required if novel technologies are introduced. There are limited scientific indicators for assessing the sufficient performance of novel technologies without references to the best available techniques (BAT) conclusions. There is also lack of official methodology to assess the twelve conditions in Annex III of Industrial Emissions Directive (implemented in Finnish EPA 53§) in relation to technologies outside of BAT conclusions. One of the answers for the non-incentivising permit procedures could be more dynamic regulations in which conditions for granting a permit would become more stringent by means of continuous revisions. The system would build on continuous learning but may require legislative changes to be realised.

Legal protection of existing environmental permits and revision requirements based on updated BAT conclusions provide incentive only to incremental, not disruptive innovations. Within industrial emissions regulation, the BAT range has been an important tool for flexibility. However, in revising existing regulation in the name of harmonisation, flexibility is probably lost. Awareness needs to improve among EU Green Deal policy drafters on how the Industrial Emissions Directive (IED) and best available techniques (BATs) operate at the grassroots level.

The EU legal system is both requiring and restricting innovations. EU environmental regulation is not in line with EU green and digital transition policies but may in fact cause barriers to the use of emerging technologies, contrary to the aims of the EU Green Deal. EU Green Deal contains conflicting policy aims, while regulatory silos make the setting even more complex. This fragmentation of EU's legal system – to environmental and innovation silos – can cause inefficiency inimplementing the policy goals.

Strict environmental norms incentivise the development of technological innovations but, simultaneously, environmental regulation may obstruct their use. Industrial environmental regulation may result in high implementation costs and heavy burden of proof to operators wishing to use disruptive technologies. Especially disruptive innovations may not reach the required technological readiness level (TRL) to be evaluated under experimental regulations like INCITE or regulatory sandboxes,probably needed to solve the situation. Regulatory sandboxes are spaces where environmental regulation is temporarily not applied. Because of the awkward relations between EU innovations and environmental law, these may be needed for testing innovations in practice.

On the other hand, at times the regulator seems to pose excessive hopes on the role of technological development to solve environmental problems. The EU Commission has defined 'microplastic' (MP) in its decision-making when it comes to intentionally added MPs, and is planning to regulate on so-called secondary MPs, for example found in wastewater. Decision-makers in the EU and Member States must be cautious not to use the definition created for intentionally added MPs analogically for secondary MPs too, as technologies detecting microplastics from wastewater are not yet matured enough.

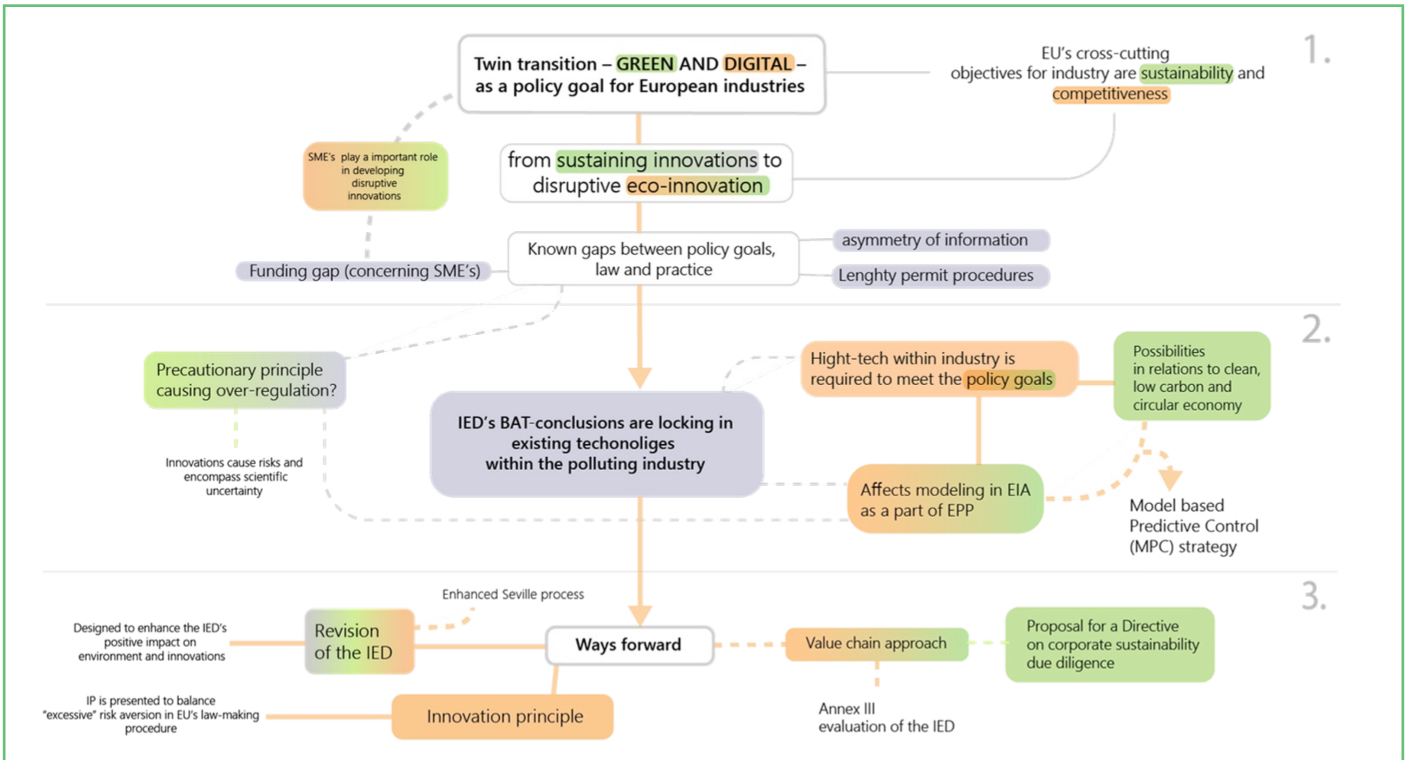

Figure 3: The EU Innovations and environmental law create a dynamic system with various components and interactions.

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Publications

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BENEFITS FOR PARTICIPATING COMPANIES

Teollisuuden Vesi

Efficient management of water usage using data-driven control

Teollisuuden Vesi (TeVe Water), as an independent expert company for water treatment solutions, frequently faces circular economy questions in its core business. TeVe Water clients, operating in water-intensive industrial sections, aim at efficient water utilisation and consequently, at closed water circles.

In this context, CEIWA project "Circular Economy of Water in Industrial Processes" addresses the essential aspects of TeVe Water business already today, but even more so in the future. CEIWA allowed TeVe Water to a gain deeper insight into the regulation of environmental issues where WP1 assessed the contradiction between precautionary principle and innovation principle in relation to uncertainty as well as

sustainability. Work carried out in WP4 serves TeVe Water by revealing the state-of-the art in analysis of microplastics and by presenting the challenges to be solved to monitor microplastic concentrations in industrial systems. WP3 pilot systems studying anaerobic processes strengthen TeVe Water by providing a view on the degradability of wastewater streams in anoxic conditions. The multi-metal analysis of interesting industrial process waters in WP2 helps to understand the capability of different purification techniques to remove metals from the waters.

Furthermore, the lively discussion within the CEIWA network has been inspiring and provided TeVe Water with a profound insight into the core questions of circular economy.

Teollisuuden Vesi
Anu Kettunen, CSO
CEIWA Steering Committee chair person

Avenues of adaptivity in EU Member States' water governance

Description

In EU environmental law mainly operating with directives, differences in national implementation may mean significant variation in the regulatory context in which companies operate and in which the legitimacy of their novel innovations is adjudged. For this reason, we have zoomed in and explored the variations of legislation in certain EU Member States. How does regulation in various European countries differ when it comes to implementation of the EU Water Framework Directive, especially regarding industrial sites?

Though the EU regulation must be effectively implemented through the Member States, the variations in implementation may cause significant risks for industry. For this reason, regulation in some Member States has been examined, with an aim of identifying points where national variations in implementation, administrative-legal systems and/or case law cause significant differences to the regulatory environment.

Results

As EU environmental law mainly operates with directives, differences in national implementation may mean significant variation in the regulatory context in which companies operate. The variations of implementation may cause significant risks for industry, warranting closer research. In CEIWA we have conducted comparative legal analysis on the ways Member States (MSs) have added adaptivity to the Water Framework Directive (WFD). Various aspects have been relevant in the MSs when implementing the WFD, making the legal landscape even more diverse than anticipated. Some MSs govern with exemptions; others consider large parts of their waters to be too small to belong to the scope of the WFD. Some have found WFD norms on 'public interest' relevant, when others' courts tiptoe around the normativity of the WFD, unable to decide how to react to it. Then again, in some MSs the aims of EU green energy transition have been found to be conflicting with the EU water quality norms, illustrating the tension there is between addressing climate change and biodiversity degradation. To summarise, MSs have found various ways to add adaptivity to the rigid system of the WFD – but while doing so, they have added further variation to the reality of water governance in the EU. As the Member States all have found their own ways to negotiate the realities around EU WFD, it means that there is no single EU water governance regime but many. To certain extent this is also what a Directive as a regulatory instrument calls for but on the other, the extent of variation makes one question whether uniform application of EU law is secured with regards the EU WFD.

	Sweden	Germany	Austria	England & Wales	Finland
Art 4(1) WFD	-Originally chemical status more binding than other environmental objectives -Situation corrected 2019	-Transposed into national law -All environmental objectives and the deterioration ban are legally binding	Transposed into national law -All environmental objectives and the deterioration ban are legally binding	Transposed into national law -All environmental objectives and the deterioration ban are legally binding	-In Water Law and Environmental Protection Law, obligation to "take into account" what is taken in the river basin management plans -Good status objective and non-deterioration rule not part of Finnish law
Art 4(7) WFD Exemption for new developments	-Originally transposed in a way that exemption could not be used -Changed 2019 -Law now requires considering all possibilities to apply the exemption	-Transposed into national law -Case law interpreting the "public interest" requirement	-Transposed using the wording of the WFD -The exemption is used often, especially regarding hydropower -Is the exemption becoming a rule	-Originally not transposed at all into national law -Use of the exemption not clearly reported	- Law drafting on ongoing (due August 2023) - the rules would be taken into Finnish law, as would the exemptions too
Other exemptions		-Extensive use of Art 4(4) & 4(5) relating to lignite mining		-Extensive use of Art 4(4) and 4(5) -Justifications for use of exemptions have been unclear	N/A
Diverse approaches & interpretations	-Encouraging to make full use of exemptions	-Excluding small water bodies -Transposition and case law in line with the ECJ interpretations -Lack of ambition in the implementation	-Transposition in line with the WFD -Flexibility in legal interpretations	-Best effort approach -Reliance on voluntary measures	- Approach an anomaly in Europe as is not the "best effort" nor the "objective" approach -Focus on seeing the WFD in its managerial role

Table 1: "Avenues of Adaptivity"

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Publications

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BENEFITS FOR PARTICIPATING COMPANIES

Valmet

CEIWA targeted the megatrends that affect Valmet’s business environment

Valmet is a leading global developer and supplier of process technologies, automation and services for the pulp, paper and energy industries. Valmet joined the CEIWA consortium because of the focus on the megatrends that are the most important for Valmet’s business: resource efficiency, digitalisation, and urbanisation. The need for more efficient use of water, natural resources, and chemicals is increasing in all areas of industry, including pulp mills, which are key customers for Valmet. This requires new technologies and operational solutions, which can only be developed through cooperation between research institutes and companies.

The key topics for Valmet were:

- Changing business environment due to legislation and regulation
- Measurement and control technologies in closed water cycles
- New methods for solid waste treatment and nutrient recovery in pulp mills
- Microplastics knowledge and measurement possibilities
- Reducing freshwater usage and the environmental impact of effluents

In addition to increasing the knowledge of these topics within Valmet, the CEIWA project has brought more skills and knowledge to research and business partners, which can initiate even more fruitful cooperation in the future.

Valmet
Aino Vettenranta,
Chemical modelling specialist in Pulp & Energy
CEIWA Steering Committee deputy member

Re-imagining EU water governance with a Chinese example

Description

Compatibility with multiple markets is at the heart of the technology providers' R&D actions. They need to know the regulatory environment and its prospective changes in different markets. That is why regulatory variations at global level are discussed here, and regional variation was covered in the previous section. The relevant regulatory environment in China is examined and the dynamics between the Chinese and the EU regulators are analysed. China's actions on circular water economy are studied, as are the dynamics between the Chinese and the EU regulators. We have examined the ways China has adopted to curb industrial water pollution – which regulatory instrument has been most influential in the task, when was it adopted, and so on. We also consider how the EU's response to the development in China, the regulatory dynamics of the two superpowers and whether we could see similar stringency also in the EU. According to the so-called Brussels Effect, EU has regulatory power beyond its geographical boundaries when businesses voluntarily adopt the strict EU standards in their actions (due to economics of scale in globalised economy). Does the Brussels Effect work in this regulatory context—or is it rather a Beijing Effect, where Chinese regulators take the lead?

Results

It is known that China has been active in pursuing water quality regulation and thus driving innovative water technologies. We have zoomed in the details of this activity, with the aim of finding out how this is advanced in practice. Although circular economy policies are in place, legally impactful regulation comes from elsewhere, constituting an indirect driver of the circular economy. Regarding waters, China was unsatisfied with its integrated water management system (which the EU WFD also exemplifies) and created a River Chief System (RSC) instead. The RSC has proved to be effective – interestingly, not through revising the environmental or water quality norms but through collaborative governance. The RCS has succeeded in bringing together the various institutional actors responsible for waters and created accountability for local government. When the EU has left the implementation of the WFD to the hands of the Member States (MSs), the variation that ensues means that the same level of effectiveness cannot be reached. Whether the EU could learn from the Chinese example remains to be seen. It may be that the constitutional differences between the two systems are too significant for a successful legal transplant. However, the Chinese example shows that the regulator must not consider integrated and holistic management as the last stage of regulatory development – there are avenues beyond it, should the regulator wish to use them.

In the EU it seems that the Union regulator has no desire to move beyond integrated and holistic water management. The EU legal system on environment and water is going through significant changes when the Nature Restoration Law's (NRL) impact reaches all environmental law sectors, water governance included. Should the Commission's ideas of the NRL's impact materialise, some of the ways the Member States have used to add adaptivity and flexibility to the strict WFD would no longer be available. Though barely discussed in public, this would be part of the proposed NRL in action. The EU seems thus to be faithful to the regulatory solutions it has taken, and the regulatory path-dependancy is not considered an issue, even when following the chosen path has proved difficult in the Member States, as shown in our comparative research.

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Publications

Paloniitty, T., Yuan, L., Kaavi, S. 2023. Regulating Emissions, Management, or Biodiversity? Navigating the Evolving European Legal Landscape around Waters. Submitted.

Yuan, L., Paloniitty, T. Re-imagining Water Management and Law: Can the Chinese River Chief System Inspire Change in the EU Water Governance? in Amanda Kennedy, Brian J. Preston, Rowena Macquire and Tiina Paloniitty (eds) Re-imagining Environmental Law (Edward Elgar 2024 upcoming). To be submitted.

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BENEFITS FOR PARTICIPATING COMPANIES

Kemira

Increasing industrial water treatment competencies and creating networks

Kemira is a global leader in sustainable chemical solutions for water-intensive industries. We provide the best-suited products and expertise to improve our customers' product quality, process and resource efficiency. Our focus is on the pulp & paper, water treatment and energy industries. In 2022, Kemira had annual revenue of around EUR 3.6 billion and around 5,000 employees.

Kemira joined the CEIWA project as we believed that, through collaboration, more can be achieved than working alone, and we wanted to create new networks with the academia and companies. CEIWA brought together experts in the field. A consortium like CEIWA helps to develop new scalable solutions for industrial water treatment. A unique feature of CEIWA was how it combined regulatory thinking with the development of technologies.

We considered all the research important in CEIWA and joined in all the work packages actively, providing also our expertise for the project.

CEIWA has given all participants an opportunity to develop competences. Our future research for sustainable chemical solutions will benefit from this and the overall level of competences that has increased within all the organisations.

Kemira Oyj
Outi Grönfors
Application Development Manager
Water treatment, CEIWA Steering
Committee member

Solutions for monitoring, controlling, and optimising the management of industrial process water and wastewater

Summary

The purpose of water-intensive industrial processes is to improve the water circulation for environmental and economic reasons. Nevertheless, a considerable amount of water that cannot be internally recirculated is discharged to wastewater treatment. To promote internal water circulation, there is a need for enhanced monitoring and adequate purification to prevent the accumulation of contaminants. In closed water processes, a big challenge is to control the dissolved elements not actively contributing to the actual processes, as the accumulation and precipitation of these elements may be detrimental to the process. There is a need to understand and predict the effect of these detrimental elements in plant-wide perspective and further to track the accumulation of these elements in an aqueous phase, to locate the process stage of precipitates and scaling, as well to find out the optimal stages to remove these harmful components. For multi-metal analysis of industrial waters, a new measurement protocol was developed and tested, based on *in-situ/on-line* precipitation of the dissolved metal on solid filter and the subsequent/direct X-ray fluorescence analysis. The work aimed to develop a methodology to realise the metal analysis of water matrix for *on-line and real-time* use.

The operation of upstream industrial processes, of which there may be many, cause varying quality and quantity of influent discharged to wastewater treatment, making the operation of the treatment process challenging. To optimise the wastewater treatment and to achieve better effluent quality and enhanced resource efficiency in varying operating conditions, full situational awareness, the early detection of the changes and anomalies, and model-based feedforward control actions are required. Here, data-based methodologies form the core. Advanced data analysis and modelling approaches were utilised in developing intelligent solutions for monitoring, controlling, and optimising a wastewater treatment process. Situational awareness was built by utilising advanced methods and expertise of the data from several sources. The research focused on data quality, uncertainty assessment, nonlinear effects and temporal behaviour. State-of-the-art time series analysis tools were used in big-data analytics for extracting multidimensional dynamical information (to identify patterns and complex interdependencies) for automatic control and modelling. Virtual sensors were developed for indicating the process state and predictive models for estimating the upcoming situation. With developed simulators, process behaviour was simulated as it would appear on site without affecting the actual process.

Artificial and computational intelligence were used in order to find interactions and presenting solutions for the assessment domain experts. AI-based data estimation methods were applied to bring practical value in thermodynamic simulation of multicomponent industrial aqueous solutions. Thermodynamic models predicted the interdependencies of various process parameters, also in conditions and locations where experimental data were extremely difficult or even impossible to obtain.

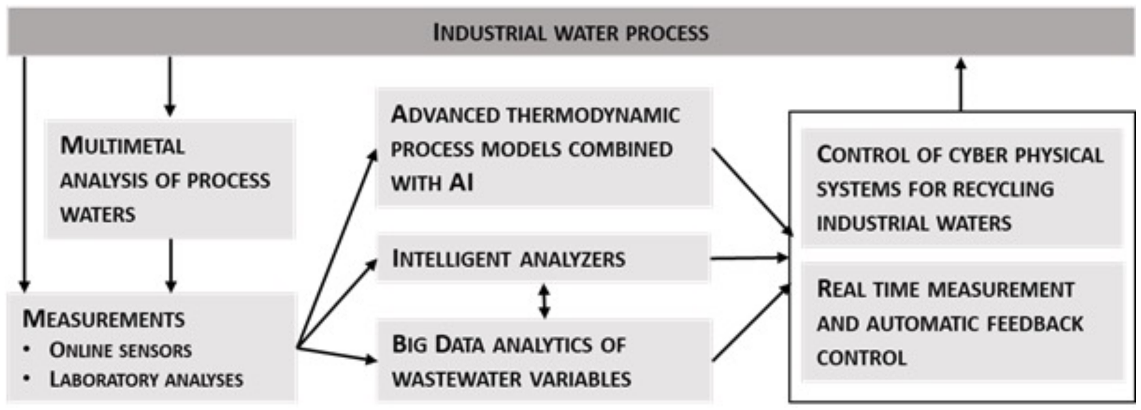

Figure 4: Monitoring, controlling and optimizing industrial water process.

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BENEFITS FOR PARTICIPATING COMPANIES

Fortum

FORTUM RECYCLING & WASTE

We are rethinking recycling and leading the way towards a revolution of materials. Our mission is to transform waste streams back to essential raw materials. Our role is to find solutions for our customers' environmental and waste challenges to enable the circulation of materials.

Recycling & Waste participated in the CEIWA project as a funding company partner, and was also included in the steering group. We were able to collaborate with universities as well as other companies. Following the public research part in the CEIWA project, we gained valuable insight into the latest results from all the CEIWA research subjects and gained further know-how to wastewater treatment technologies and microplastic analysis. The research work in the project's public part has strengthened our own development work in industrial and process water treatment. Our core business is waste management and supply of overall services to our customers. Wastewater is involved in many processes, and we need to follow changes in regulation as well as the latest innovations. CEIWA has been an excellent opportunity to follow extensive development in many industrial wastewater issues.

Fortum Waste Solutions Oy
Marja-Liisa Ripatti
Project Manager
CEIWA Steering Committee member

Advanced thermodynamic process modelling

Description

Added circularity and biomass-based replacements for fossil energy are some of the reasons for increasing the need to model the behaviour of various non-process elements in pulp and paper mills. In task 2.1, thermodynamics-based chemical aqueous solution models were enhanced with several approaches: Existing thermodynamic modelling framework was extended with property calculators for solution density and estimated boiling point, using modelled activity coefficients' molar volumes in multicomponent, multiphase systems. A mixed hydroxide-carbonate model was implemented to amend simulation results for aqueous solution compositions typically present in pulp mills. To enable better models in systems with insufficient experimental data, methods based on machine learning were studied for acquiring estimates and simplified correlations for missing interaction parameters in aqueous solutions.

New dynamic unit operation models for aqueous processes were developed that support dissolution and precipitation reactions. The calculation of transient mass and energy balances is based on solving the local thermodynamic equilibrium in combination with kinetic equations. A commercial ChemApp library is used for all thermodynamic routines (equilibrium composition and stream enthalpies). The thermodynamic system used contains relevant chemical species in gaseous, aqueous (using Pitzer activity model) and condensed phases that are compiled from elements C + H + O + N + S + Cl + Ca + Na + (Al + Mg + K + P + Si). The new unit operation models have been integrated with the inhouse simulator CROM developed at VTT. It is a tool for dynamic simulation of chemical processes in high-temperature and aqueous systems. A new interface has been developed for it that allows its use as a digital twin in the future. The new dynamic unit operation models include models for green liquor and burned lime handling, and slaker and causticisers where green liquor and burned lime are mixed to produce white liquor and lime mud.

The studies supplement the more experimental and data analytical parts of the work package. New analytical methods can add to the input data for the thermochemical models, while the models can be used to estimate the state of parts of the processes that are not experimentally measurable due to factors such as temperature, mechanical wear, clogging or corrosion.

Results

Property calculator modules have been implemented to work with thermodynamic modelling software used by VTT, enabling an accurate modelling of density and boiling point of aqueous process solutions. The boiling point predictions have good accuracy for temperatures up to 5 °C above the active simulation temperature and fair accuracy above it.

The estimates to supplement missing thermodynamic parameters provided useful accuracy and an improvement over older methods. While estimated parameters cannot truly replace the need for experimental data, they can be used for systems where this experimental data does not exist. Comparison of various estimation methods with calculations done without them is shown in the figure below, illustrating the reduction in model inaccuracy when using estimates. Data processing routines that enable amending existing datafiles with new data have been implemented. Further work would be useful for improving estimates especially regarding interactions and very complex systems.

The dynamic simulation tool was used for calculating the recausticising process in Kraft pulp mill including unit operations for lime kiln (using a model developed in an earlier project), lime silo and its screw feeder, green liquor clarifier and storage tank, slaker and three causticisers consisting of three compartments each. In slaker and causticisers, the formation of calcium carbonate was controlled by using the constrained-free energy (CFE) method to take into account its time-dependent reaction rate. The example results show the calculated causticity efficiency in the slaker and nine compartments of the causticisers as function of total residence time.

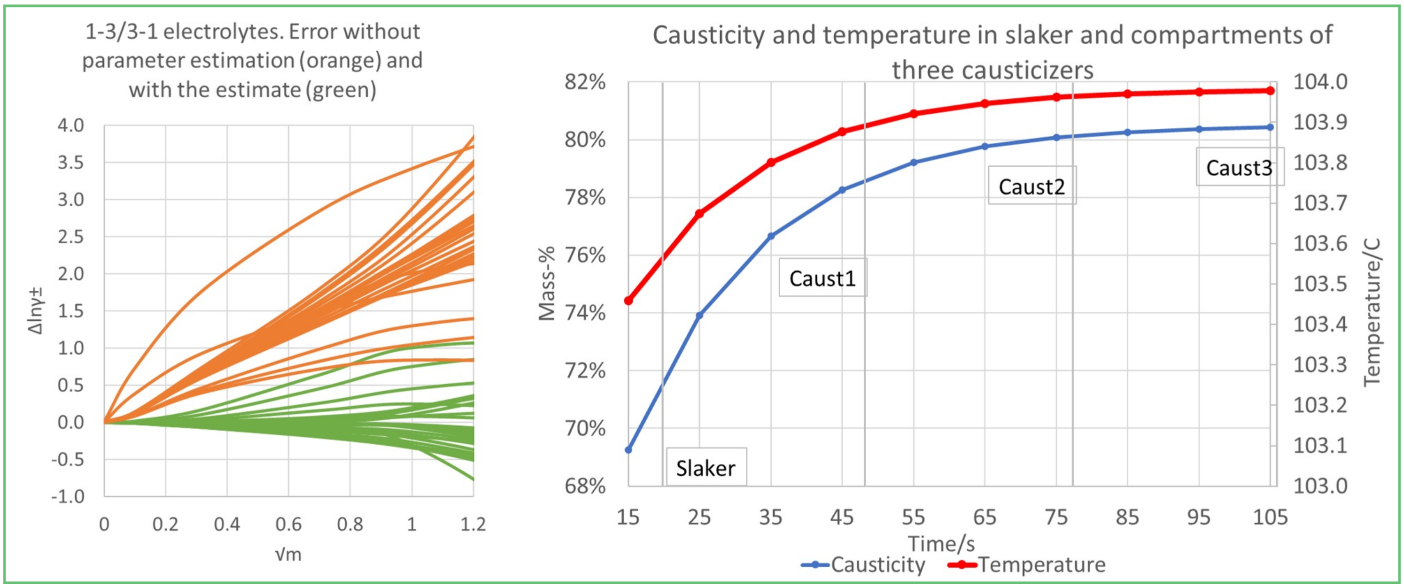

Figure 5:
Left: Error with estimate-based activity coefficient values when compared to experimental ones for groups of various electrolytes in VTT database. Square root of molarity on X-axis, error in logarithmic mean activity coefficient on Y-axis. Right: Causticity and temperature in slaker and causticiser compartments. Temperature of the green liquor feed from the GL cooler to the slaker 80 °C, temperature of the burned lime feed from the lime silo 150 °C.

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Publications

Dynamic Simulation of a Recausticizing Plant, Karri Penttilä, GTT Users' meeting 2023

CEIWA

Data-based solutions to improve the monitoring, controlling, and optimising a wastewater treatment process

Description

Despite the effort to increase internal closed-water loops, the fact is that water-intensive pulp and paper processes produce vast amounts of wastewater that need to be treated before discharged to environment. Influent wastewater originates from several sources and the widely varying quality and quantity of wastewater are dependent on the operation of the upstream processes. The changes can be drastic and occur fast, but the adaptation of biological wastewater treatment is slow. To avoid causing harm to the vital biomass and breaches of emission limits while minimising the usage of resources, efficient treatment process operation requires for instance the early detection of changes and anomalies and feedforward model-based control actions that are adaptive for varying operating conditions.

This research provided data-based solutions to improve monitoring, controlling, and optimising the operation of a Finnish paper mill's wastewater treatment plant in varying operating conditions. The online measurements and laboratory analysis data were combined and brought to the same level. Enhanced situational awareness was achieved combining expertise, and advanced data analysis and modelling approaches. Indirect measurements were developed for indicating the process state, and predictive models were developed to estimate the upcoming situation. Soft sensors can be used redundantly for monitoring the functionality of the hardware sensors or for estimating the process variables that are difficult, unsafe, costly, or impossible to measure reliably with the hardware sensors. Here, soft sensors were data-based models that combine the outputs of hardware sensors to estimate the targeted variable. Non-linear effects and temporal behaviour were important aspects in the work, and data quality and uncertainty assessment were carried out to develop truly usable solutions.

The research work included three main targets: 1) to develop a soft sensor for estimating the influent wastewater quality, namely chemical oxygen demand (COD), an important variable in assessing the wastewater quality that indicates the amount of oxygen that is needed to oxidise the organic matter present in a quantity of wastewater; 2) to develop a predictive model for effluent wastewater COD; and 3) to develop and test a dynamic simulator to simulate the process conditions and control actions as they would appear on site. The simulator enabled the experimentation of extreme phenomena and control actions without affecting the real treatment process. The developed soft sensor for influent COD was utilised as one of the inputs of the prediction model for the effluent COD. As the changes in inspected data can be either changes in process or changes in measurement due to, for example, fouling or sensor malfunction, the research work also included a data-based inspection for the need of maintenance and a recalibration of an online sensor.

Relevant data treatment tasks were performed to process the available data into the most complete form so that the data could be used for analysis and modelling. These tasks included combining data from different sources, removing non-informative variables, detecting and removing outliers, replacing the missing values with interpolated values, normalising data to the same common scale, resampling the data, and scaling data using a non-linear scaling method. Data resampling method using a moving median, where the median value represents all the values in a moving window, decreased the number of data points in each variable drastically without losing any critical information, and thus reduced the computational load on analysis and modelling stages. The use of the non-linear scaling method made the linear methodologies applicable to the non-linear wastewater treatment case.

Developing the best possible practicable models for influent and effluent COD was done by testing several model structures on both cases to see which model structure would fit the data best, and by tuning optimal model parameters utilising an exhaustive algorithm. The suitable model structure was systematically ested for different attributes (time delays, training windows, input variable combinations, model order) on the chosen dataset by utilising full factorial design. As the purpose was to develop models that are easy to interpret, the linear regression model structure was prioritised.

Results

Figure 6 presents the functionality of the soft sensor for influent COD and the predictive model for effluent COD during the independent testing periods. The study showed that practical and accurate data-based models for predicting the effluent wastewater quality and assessing the quality of influent wastewater via soft sensor approach can be developed by combining data from various datasets and utilising expertise and advanced data analysis and modelling methods. Even though some phenomena cannot be modelled with high accuracy due to absent measurement data, the developed models are usable for the purpose. With in-depth data analysis, and the indirect measurements and prediction models developed, the situational awareness and predictability are increased. The developed solutions enable the enhanced monitoring and controlling of the challenging nonlinear wastewater treatment process in varying operation conditions.

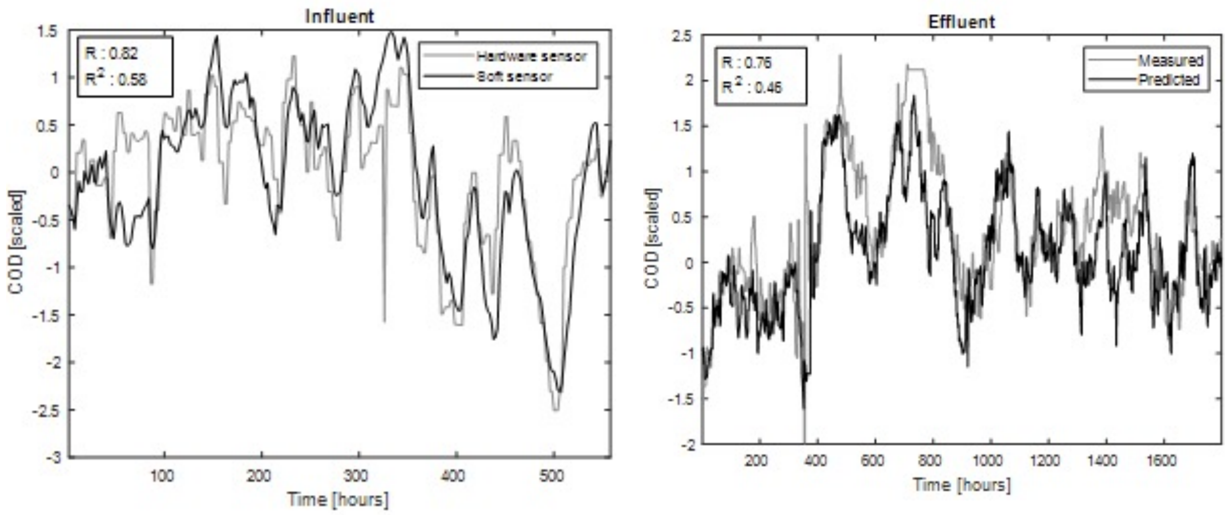

Figure 6: The independent 23-day testing period of the developed soft sensor for influent COD and the independent 75-day testing period of the predictive model for effluent COD.

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Publications

Komulainen, T.M., Baqeria, A.M., Pörhö, H., Juuso, E., Tomperi, J. Comparison of effluent estimation methods for municipal and industrial WRRFs. To be submitted.

Pörhö, H., Tomperi, J., Sorsa, A., Juuso, E., Ruuska, J., Ruusunen, M. (2023) Data-based tools for wastewater treatment optimization. Automation Days 2023, Helsinki, Finland, March 28-29, 2023.

Pörhö, H. Tomperi, J., Sorsa, A., Juuso, E., Ruuska, J., Ruusunen, M. 2023. Data-Based Modelling of Chemical Oxygen Demand for Industrial Wastewater Treatment. Applied Sciences 13, no. 13: 7848. https://doi.org/10.3390/app13137848.

CEIWA

Real time measurement and automatic feedback control

Description

The generation of wastewater with high levels of Chemical Oxygen Demand (COD) by paper mills poses a significant environmental concern, necessitating its removal before discharge into water basins. However, the process of removing COD from wastewater is complex and energy-intensive, especially with globally rising energy costs. Therefore, there is a need for designing cost-effective and efficient COD removal solutions for wastewater treatment plants (WWTPs). Additionally, the variability in wastewater sources and environmental regulations requires innovative tools to understand and optimise COD removal processes in WWTP operations.

COD in wastewater is generally classified into two categories: biodegradable and non-biodegradable. In typical paper-mill wastewater, non-biodegradable COD is present in small quantities and can typically be removed using physical techniques. However, biodegradable COD constitutes the primary component of total COD and is a major contributor to the complexity of the process operation and cost of COD removal in WWTPs. Aeration treatment is a common method used to remove biodegradable COD from wastewater. This process involves multiple complex biological processes that operate simultaneously to remove various COD biodegradable components from the influent. Hence, a thorough understanding of the aeration process is necessary to comprehend the factors which affect effluent COD levels.

In Task 2.4, we utilised Activated Sludge Model No.1 (ASM1) to investigate the COD removal process in WWTP and estimate the effluent's COD. This model describes in detail the biological processes in the aeration treatment and gives an insight into the factors that affect the aeration treatment. Such in-depth analysis of the aeration process can potentially help the process operators make more accurate decisions that could increase the effluent quality and reduce the energy requirement, thus reducing the economic and environmental footprint.

Results

Task 2.4 is focused on the aeration process and provides a valuable platform for process operators to analyse the influent COD and identify the factors that affect the effluent COD. Effective operation of the aeration process is essential for optimising the cost-efficient operation of WWTPs. The overall objective of this task is to analyse the influent COD in the aeration process and determine the factors that affect the effluent COD under varying operational conditions.

To achieve this objective, Task 2.4 requires detailed sampling data from the industry, laboratory, and other sources to identify the most effective model-tuning parameters for the ASM1 model.

The first goal for this task involved tuning the ASM1 model using limited wastewater sampling data collected during the measurement campaign in Task 3.1 (Figure 7). Using this data, the ASM1 model provided a brief insight into the aeration process and identified opportunities for improving process operations, such as optimising urea loading. The second goal was to improve the applicability of the ASM1 model, which requires a large amount of wastewater sampling data. Utilising the wastewater sampling data from Task 3.1 and industrial online and laboratory data, artificial data is generated to determine the optimal tuning parameters for the ASM1 model. The third goal involves the ongoing process of ASM1 model tuning for the artificial data. Using the hit and trial method, the optimal model parameters will be calculated to enhance the accuracy of the ASM1 model (Figure 8).

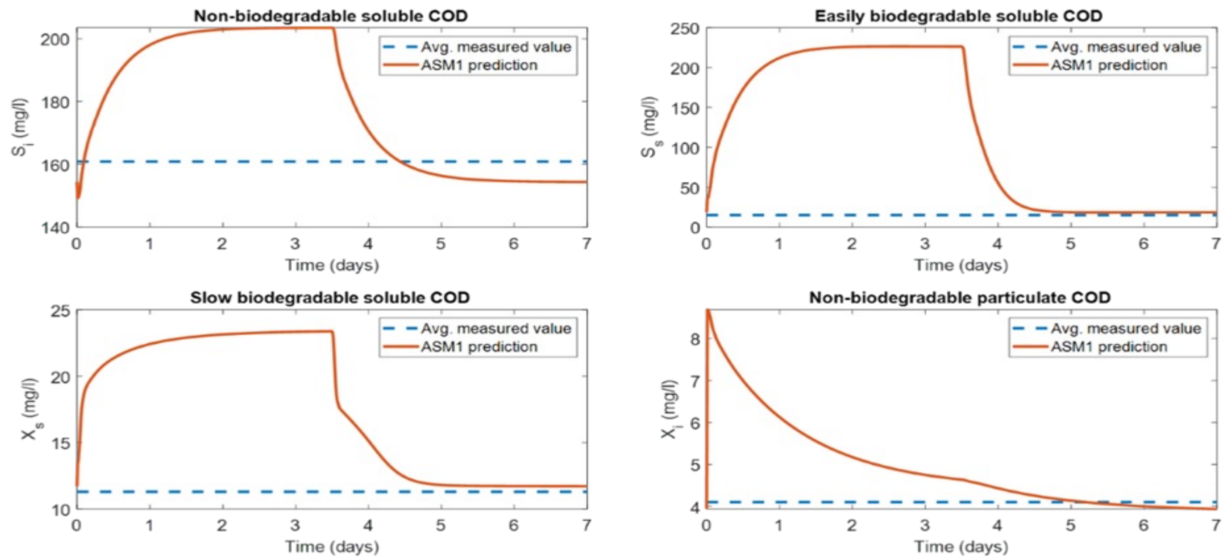

Figure 7: Calibration of the ASM1 model using collected COD samples.

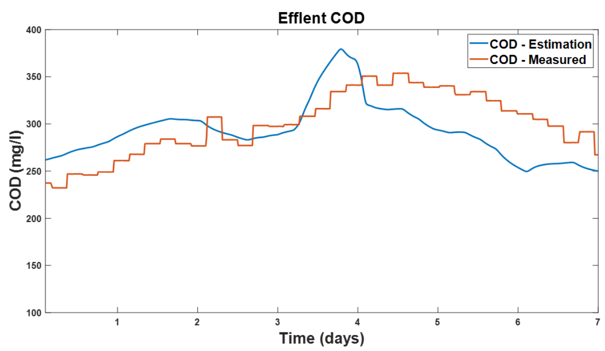

Figure 8: Comparison of the estimated effluent COD generated by the ASM1 model with the effluent COD measurements obtained through the online monitoring system in the WWTP.

Publications

Ahmed, H., Pörhö, H., Toivonen, E., Räsänen, E., Tomperi, J., Vilkko, M. 2023. Activated Sludge Model No.1 Calibration and Data Analysis for a Paper Mill Wastewater Treatment Plant, IWA ecoSTP conference.

Ahmed H., Vilkko, M. 2023. Activated Sludge Model No. 1 Calibration for a Paper Mill Wastewater Treatment Plant. Poster session presented at 10th IWA Microbial Ecology and Water Engineering Specialist Conference, Brisbane, Australia.

Ahmed H., Vilkko, M. 2023. Activated Sludge Model No. 1 Calibration for a Paper Mill Wastewater Treatment Plant. To be submitted.

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CEIWA

Big Data analytics of industrial water variables

Description

Modern wastewater treatment plants (WWTPs) produce large amounts of data, which can be analysed to produce valuable information about the treatment process. This data is collected both continuously and by performing laboratory measurements. As the regulations concerning wastewater discharges become more stringent and energy costs rise, the wastewater treatment process needs to be optimised, and for this purpose, the large amounts of data collected from the process can be utilised. However, the data is often non-stationary and the dependencies between different variables can be complicated, which makes analysis with conventional methods difficult. Also, the relevant timescales are different. Hence, advanced data analysis methods are needed to (i) obtain a detailed understanding of the system dynamics and correlations with respect to the underlying WWTP processes, and to (ii) analyse nonlinear and non-stationary data which poses a significant methodological challenge to conventional time-series analysis.

In Task 2.5, the data provided by the company was analysed with advanced time-series analysis methods stemming from computational physics. We introduced the Potts model for effective pre-processing of chemical oxygen demand (COD) and phosphorous data. This was followed by detrended fluctuation analysis (DFA), dynamical DFA (DDFA) and empirical mode decomposition (EMD) to analyse the dynamical correlations and frequency contents in the real-time COD data. Further, we established time-lagged windowed cross correlation (TLWCC) as a powerful tool to capture the real-time cross-correlations and time delays between relevant measured parameters such as the influent and effluent COD or effluent COD and biological oxygen demand (BOD). The time delays can be further optimised by employing simulated annealing. These methods were shown with our case example to be valid additions to the present ensemble of methods used in water treatment processes. The analysis was performed in close collaboration with Tasks 2.2 and 2.3.

Results

The relevant data was received from the WWTP and analysed with a variety of methods that are described in detail in our publications (Toivonen 2023, Toivonen and Räsänen 2023). Here we summarise our main results on (i) data extraction and preprocessing, (ii) empirical mode decomposition, and (iii) cross-correlation between different variables.

In the preprocessing, the obvious artifacts or outliers in the WWTP data were removed with a median-based scheme. Secondly, we noted that COD and phosphorous contained spurious step-wise segments due to the fact that the sampling frequency was not directly compatible with the data update frequency. These piecewise-constant functions were extracted from a noisy signal by minimizing the Potts functional with an efficient algorithm – a problem present in various signal processing applications. This approach was shown to be successful in the context of WWTP data.

Empirical mode decomposition (EMD) was proven to suit well to the nonlinear and nonstationary WWTP data to process the frequency content. In particular, we applied an extension of the conventional EMD, i.e., complete ensemble EMD with adaptive noise implemented in the libeemd library to obtain the intrinsic mode functions of several wastewater-related variables. This supported the interpretation of, e.g., the COD data.

Our results for the cross-correlations between WWTP variables provided important insights into the dynamical dependencies between the relevant measured values, especially the influent and effluent COD, effluent BOD, phosphorous and oxygen concentration. Figure 9 summarises some of our TLWCC results for COD and BOD. We found that – as expected – the influent and effluent COD have a strong correlation. However, we were also able to extract the relevant time lag (23 hours) for the maximum correlation, which gives us the relevant time delay in the wastewater treatment. Further, we found a strong correlation between the effluent COD and BOD with relevant information about the time-delays at different phases of the WWTP operation. With these results we were also able to show that the BOD can be predicted by the automatically measured COD with a reasonable accuracy (Toivonen, 2023). Further information about our TLWCC results is available in the publications listed below.

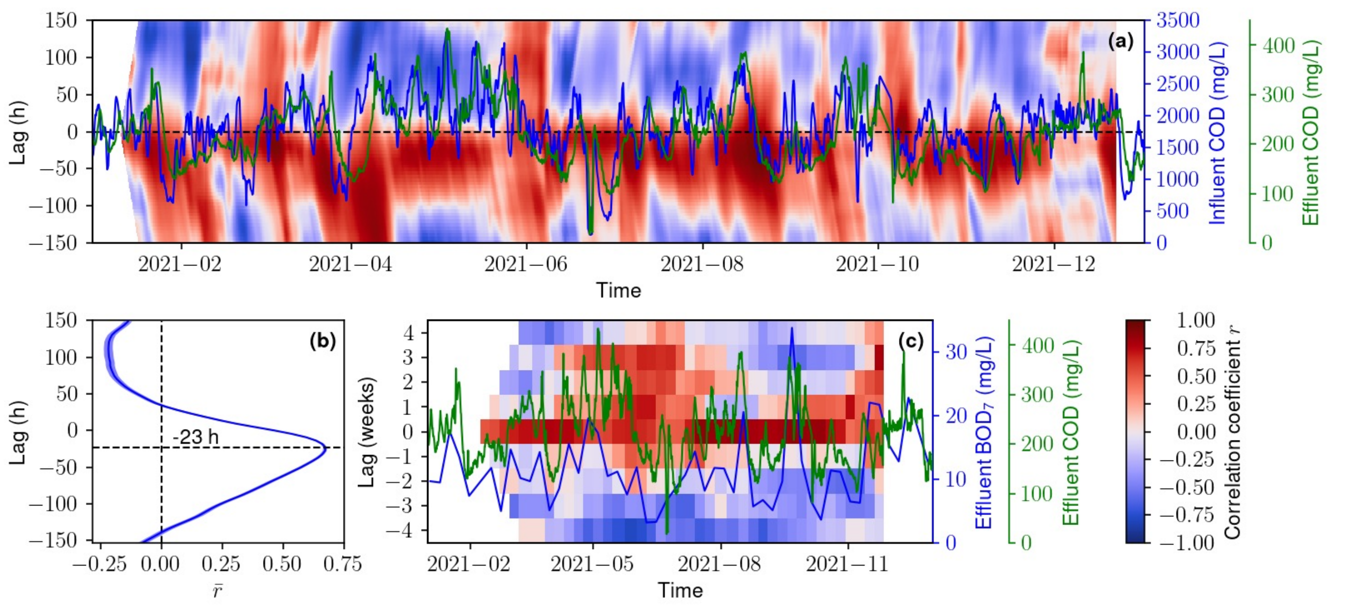

Figure 9. (a) Time-dependent cross correlation (colour map) between the influent and effluent COD for different lags. (b) Average cross correlation for each lag. (c) As in (a) but for effluent COD and BOD.

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Publications

Toivonen E. 2023. Paperitehtaan jätevesien aikasarja-analyysi ja vedenkäsittelyprosessien optimointi, Master's thesis. Tampere University.

Toivonen E., Räsänen E. 2023. Advanced Time-Series Analysis of Wastewater Variables Measured in Paper Industry. Submitted to Water Research.

CEIWA

Multimetal analysis of process waters

Description

The industrial processes are aiming to be more and more closed for minimising effluents and emissions, and thus to improve their sustainability and to reduce their footprint. When the aqueous medium is circulating in the process for a prolonged time, the undesired components (non-process elements, NPEs) may become enriched and cause errors and malfunctions in the process. Also, when waters need to be discharged to the environment, their quality must be known to prevent contamination and to follow the regulations. Thus, it is important to be able to monitor the state of the process and discharged waters, also regarding the metal concentrations. Accordingly, the purpose of task 2.6 was to develop a methodology to realise the multimetal analysis of process waters provided by the partner companies. Task 2.6 aimed to develop a system that 1) collects a suitable/representative water sample from the process water stream, 2) makes the appropriate conditioning of the sample, 3) concentrates the metals into a solid filter, 4) quantifies the metals from the filters utilising X-ray fluorescence (XRF), and finally 5) produces analytical data for the feedback control of the process. The idea was to apply the commercialised system for environmental waters (https://www.3awater.com/) with more complicated waters from industrial processes. In the commercial system, the collection of dissolved metals is based on adsorption which turned out to be non-efficient with the waters provided by the partner companies. Thus, a new type of metal-collecting filter based on in-situ precipitation was developed and tested with real process water samples.

Results

Basic analyses were made of the water samples obtained from several partner companies, and the reports were sent to the companies. Typically, the concentrations of certain metals were too high, and the adsorbent filters were saturated, preventing XRF to quantify the metals reliably. Instead of adsorption, the metal collecting filter was designed to be based on in-situ precipitation of the metals while the water sample is pumped through the filter. The development of this type of metal collection filter was tested in a laboratory setting with several waters from the partner companies (Figure 10). The developed metal analysis system is working with the site-specific calibrations from metal concentrations of sub-ppm level up to hundreds of ppm.

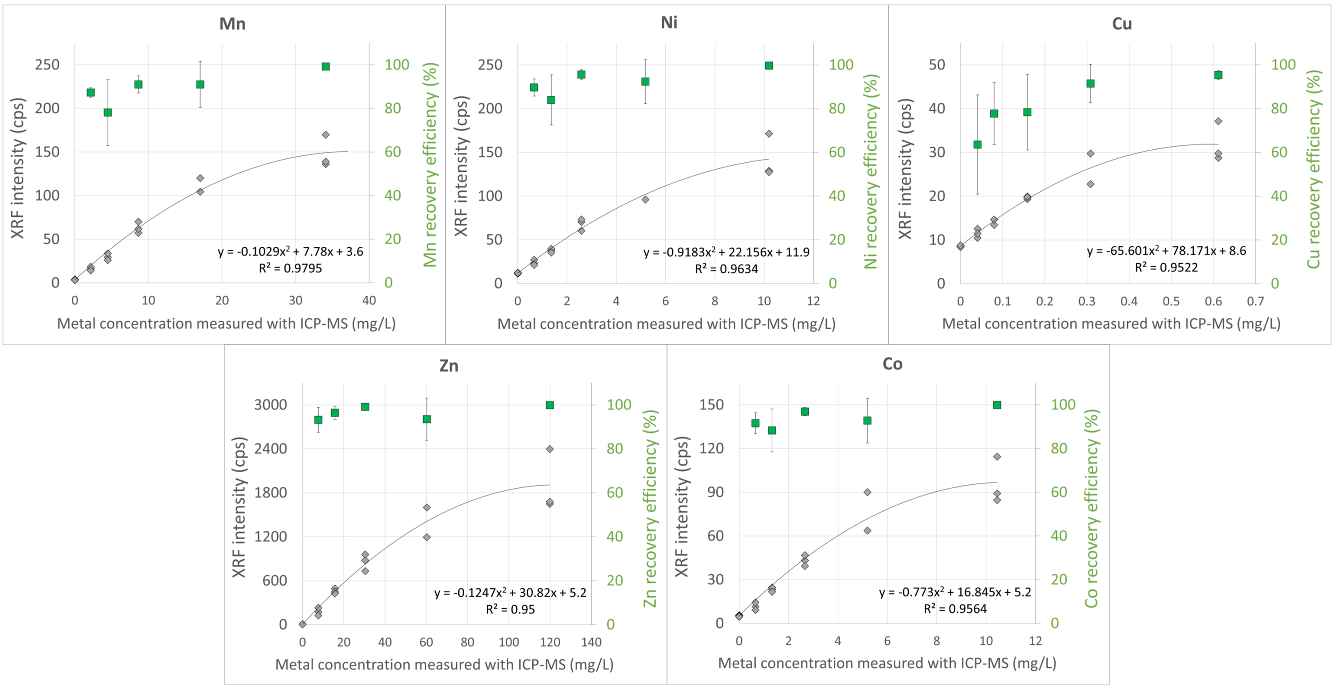

Figure 10: The metals were precipitated in-situ on/in the metal collecting filter and analysed directly from the filter with a portable XRF device. X-axis is the real metal concentration obtained with inductively coupled plasma mass spectrometry (ICP-MS) and the Y-axis is the fluorescence intensity measured with XRF. The data is used for the site-specific calibration of the system.

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Sustainable treatment processes

Summary

The targets of wastewater treatment are affected by tightening legislation and e.g., a company's own carbon neutrality and/or sustainability targets, which will require the improvement of current and the development of new wastewater treatment processes and concepts. Thus, industrial wastewater treatment requires various improvements in the near future, which may result in more demanding best available technique (BAT) requirements. In addition, e.g., new industrial production and implementation of new wastewater treatment unit processes result in new types of wastewaters and wastewater treatment systems. Thus, new processes for water and sludge treatment are required. For example, to enhance the use of membrane technologies in wastewater treatment, the lifetime of the membrane modules has to be increased, the efficiency of the commercial membranes can be improved, and the treatment of highly saline retentates has to be improved. In addition, biological processes should be developed towards more sustainable and energy-efficient systems, and alternative sludge treatment technologies are needed to replace combustion. For example, considering the current wastewater treatment systems in the pulp and paper industry, aerobic wastewater treatment processes are designed according to BAT. However, changes in industrial production, e.g., increasing or decreasing wastewater loading or tightening discharge limits create situations, where the designed processes and parameters are no longer optimal. In these situations, the adjustment of, for example, the activated sludge process in terms of the altered wastewater volumes and characteristics may be challenging and require novel practices on how to operate the wastewater treatment plants. In addition, anaerobic wastewater treatment processes, although designed according to BAT, are still facing challenges with, for example, seasonally changing wastewater characteristics that may result in an increase in inhibitory compound concentrations in certain wastewaters. To conclude, there is a need to develop and implement wastewater systems that consume less energy and able to recover at least part of the energy, carbon, and nutrients.

The aim of this work package was to develop new wastewater and sludge treatment systems and to improve existing ones. Improvement of the current treatment processes included adjustment of biological wastewater treatment processes to changes in industrial production and sustainability targets, and integration of anaerobic treatment to current wastewater systems (Task 3.1). In addition, sustainability and feasibility of membrane treatment processes was developed through the reuse of end-of-life membranes, modification of commercial membranes (Task 3.3), and utilisation of membrane concentrates for production of geopolymers (Task 3.2). Furthermore, strategies for sludge valorisation were determined (Task 3.1).

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CEIWA

Chemical oxygen demand (COD) fractionation of pulp and paper mill wastewater

Description

The activated sludge process (ASP) and its various modifications have been used for wastewater treatment in the pulp and paper industry (PPI) for decades, for example in Finland since the 1980s. During the years, ASP has remained the main process to ensure the final effluent quality even though for example anaerobic processes have largely been implemented as pre-treatment to remove organic load. The removal of organic load in the ASP depends on the wastewater quality, which in turn in PPI is affected by the biomass source and the specific industrial processes, and biological oxygen demand (BOD) and chemical oxygen demand (COD) removals up to 90–95% and 60–70% can be considered typical (e.g., Leiviskä et al. 2008).

Wastewater regulations and restrictions have been tightened in different countries in the past decades and the discharge limits may become more stringent also in the future. To meet the new discharge limits, the operation and performance of the current treatment processes may need to be improved or alternatively the treatment plants may be supplemented by other techniques (Hreiz et al. 2015; Toczyłowska-Mamińska 2017). In the ASP, the removal of organic matter (COD, BOD) is based mainly on the biodegradation of organic material by micro-organisms and thus we need to understand the biodegradability of compounds in wastewater. Wastewater components may greatly vary from mill to mill and even up to more than 250 different organic compounds have been identified in PPI wastewaters. The effect of ASP on wastewater COD can be assessed separately on the biodegradable (bCOD) and non-biodegradable COD (nbCOD), which can be further assessed for soluble readily biodegradable (rbCOD), particulate slowly biodegradable COD (sbCOD), soluble non-biodegradable (nbsCOD), and particulate non-biodegradable COD (nbpCOD). In ASP, rbCOD is readily removed as it can be transported immediately to cells and oxidised into biomass, while sbCOD requires hydrolysis into readily biodegradable form before being used by microorganisms. Besides bCOD, the amount of nbpCOD is also decreased during the ASP as it may accumulate in the activated sludge and is removed from the plant through the excess sludge. In PPI wastewater, the rbCOD consists of, for example, volatile fatty acids, alcohols, amino acids, and simple carbohydrates, while the nbsCOD consists of lignin and its derivatives as well as aromatic compounds, originating, for example, from chemical dyes with aromatic or heterocyclic ring structures. In addition, additives used during papermaking can contain non-biodegradable compounds that cause the nbCOD load on effluent. The PPI wastewaters often contain a high amount of nbCOD, specifically nbsCOD (El-Fadel et al. 2012, Choi et al. 2017).

Currently as part of routine operation, wastewater treatment plants apply online monitoring of parameters, such as pH, COD, and temperature, as well as manual sampling to analyse more parameters and provide performance information for authorities. More detailed and recent studies on wastewater treatment plants' performance concerning, for example, concentrations of different COD fractions before and after wastewater treatment plant are rare and not available. However, they could be critical in decision-making for the future of wastewater treatment plant development, and the information could be used to assess the plant operation factors on the process plant performance through computational and kinetic modelling approaches. Thus, the aim of this study was to assess the feasibility of wastewater COD fractionation in assessing the performance of a full-scale ASP treating PPI integrate wastewater in order to provide information of the potential to improve the performance of the current process. For that purpose, the COD fractions of wastewaters from debarking and thermomechanical pulping (TMP) wastewaters and from the influent and effluent of the ASP of the studied pulp and paper mill were studied. One of the aims was to provide information for the evaluation on which wastewater fractions and activated sludge process parameters affect the removal of different COD fractions.

Results

The COD fractions were determined from wastewaters collected during intensive manual or composite sampling done in three consecutive weeks in June 2022 and characterised with COD and respirometric BOD analyses. Debarking and TMP wastewaters led to the ASP were characterised.

The largest fraction of the debarking wastewaters was nbsCOD (35–46%), followed by rbCOD (21–28%), sbCOD (16–20%) and nbpCOD (16–20%). TMP wastewaters also contained mainly nbsCOD (45–59%) followed by rbCOD (26–30%), sbCOD (12–19%) and nbpCOD (0–8%). The COD/BOD5 ratio in the debarking and TMP wastewaters were 4.7–4.9 and 3.5–4.6, respectively, indicating that the wastewaters are slowly biodegradable (Pluciennic-Koropczuk and Myszograj, 2019). Examination of the wastewater flows revealed that debarking wastewaters accounted for 28% of the nbCOD entering the ASP, while TMP wastewater accounted for up to 57–79% of the ASP influent nbCOD. From the COD loads to the ASP, debarking and TMP wastewaters accounted for ca. 8% and 20%, respectively.

The influent to the ASP consisted mainly (59–70%) of readily and slowly biodegradable COD and smaller amounts of nbpCOD (13–28%) and nbsCOD (13–18%). The COD/BOD5 ratio in the ASP influent was 2.6–2.9, indicating that it is more prone to biodegradation than the debarking and TMP wastewaters. The total removal of COD in the activated sludge process was in the range of 89.8–91.1%. The removal of rbCOD (98.6–99.3%), sbCOD (97.1–97.9%), and nbpCOD (97.8–100%) was high, while the removal of nbsCOD (35.7–50.5%) remained low. Thus, the effluent included mostly nbsCOD (86–87%), originating mainly from debarking and TMP wastewaters, while there was variation in the rbCOD (3–6%), sbCOD (4–7%) and nbpCOD (0–4%).

Based on the results, the ASP was mostly able to remove biodegradable COD efficiently. The removal of biodegradable COD could likely be further improved by adjusting the operation of the ASP. As the ASP effluent still contained nbCOD, its removal could be enhanced by utilising tertiary treatments (e.g., chemical precipitation, advanced oxidation processes or electrochemical technologies) or by treating the debarking or TMP wastewaters before leading them to the ASP. More efficient removal of nbCOD may become more important in the future if the COD removal regulations are tightened.

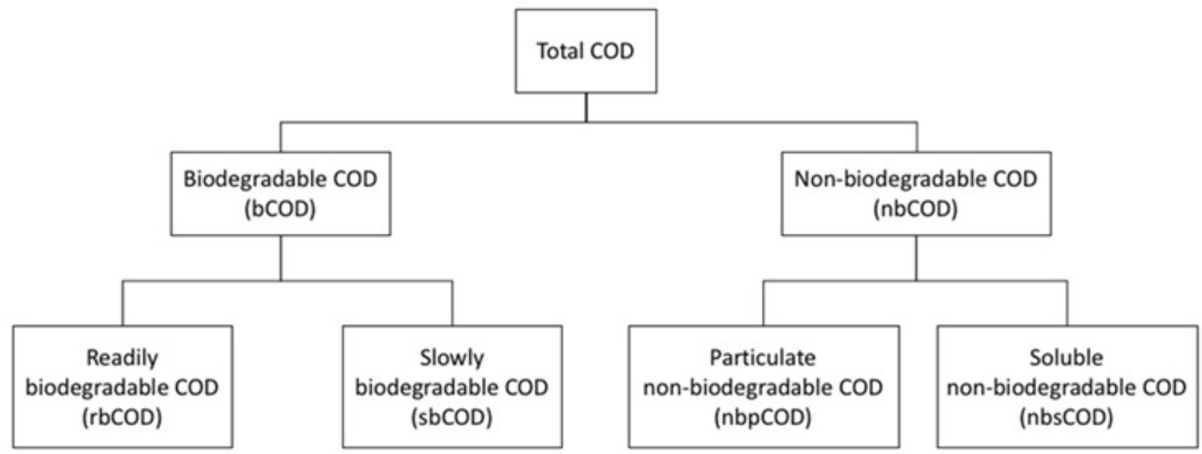

Figure 11: The different COD fractions characterised in this study

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BENEFITS FOR PARTICIPATING COMPANIES

Andritz

Working towards a more sustainable industry and biorefinery of the future

International technology group ANDRITZ offers a broad portfolio of innovative plants, equipment, systems, services, and digital solutions for a wide range of industries and end markets. With its extensive portfolio of sustainable products and solutions, ANDRITZ aims to make the greatest possible contribution to a sustainable future and help its customers achieve their sustainability goals. ANDRITZ is a global market leader in all four of its business areas – Pulp & Paper, Metals, Hydro and Separation.

CEIWA had provided valuable information from wide-ranging phenomena: the global trends direct the industry into more sustainable and efficient water utilisation. ANDRITZ aims to be the forerunner in resource efficiency and effluent flow minimisation, and this consortium has provided the framework for creating a sustainable future. Collaborating on various topics and research areas, such as digitalisation and new purification technologies, has generated new ideas and concepts across the industry to help achieve our customers’ targets. The mill-wide research projects have been performed together with various universities and companies to create a concept for a water-efficient biorefinery of the future.

ANDRITZ Oy
Aino Pesola
Development engineer

CEIWA

High-rate anaerobic treatment of novel wood-based bioethanol production pilot-plant wastewater in an expanded granular sludge bed reactor

Description

Biorefining has become an emerging industry to promote bioeconomy, meaning the use of renewable biomass resources to replace fossil ones. New bioproducts and biorefining processes using different feedstocks are being developed to reduce environmental impacts and decrease the use of fossil fuels in the manufacturing industry. However, refining processes produce large amounts of wastewater, containing high concentrations of organic matter and potentially compounds inhibiting biological processes.

High-strength biorefinery wastewaters can be treated with high-rate anaerobic reactors to remove organic matter with simultaneous biogas production. Anaerobic treatment is considered as a sustainable wastewater treatment method and it has several advantages, e.g., no energy is needed for aeration, secondary waste (excess sludge) is not produced, and renewable energy is produced during the treatment process. However, high-rate anaerobic treatment is sensitive for inhibiting compounds such as sulphur compounds and wood extractives, which are commonly present in different wood-based biorefinery wastewaters. Thus, to ensure and improve the feasibility of high-rate anaerobic reactors for novel wood-based biorefinery wastewaters, research and development is required.

Inhibition can be controlled in anaerobic reactors, for example by diluting the wastewater to decrease the concentration of inhibiting compounds. One option is to use the anaerobic reactor effluent to dilute the high-strength wastewater fed to the anaerobic reactor, although inhibition caused by residual compounds present in the effluent is possible. In this study, the anaerobic treatability, process inhibition, methane production and organic loading rate (OLR) potential of a novel wood-based bioethanol production process wastewater was studied in an expanded granular sludge bed reactor (EGSB).

Results

Three parallel EGSB reactors (Figure 12) were run for 90 days, during which OLR was increased stepwise by diluting the wastewater in different ratios and using a hydraulic retention time (HRT) of 22 hours. Granular sludge from a sludge storage tank of a high-rate anaerobic reactor treating biorefinery wastewater was used as inoculum. The reactor effluent was used for diluting the wastewater in two of the reactors: in the other one as such, and in the other one the effluent was treated with sulphide removal. Sulphide removal was done to study the potential inhibiting effects of additional sulphide on the process performance. In the control reactor, tap water was used to dilute the wastewater. Soluble organic matter removal, volume of biogas, methane content, sulphate, sulphide and volatile fatty acid concentrations and pH were analysed several times a week.

The wastewater from the piloted wood-based bioethanol production process was acidic (pH 4.2–4.6) and contained high concentrations of soluble organic matter (soluble chemical oxygen demand (sCOD) 22-51 g/L) and sulphate (1–2.5 g SO_4^{2-}/L). Wastewater was treated successfully with OLRs up to 22 kg COD_{ww} (COD in wastewater)/m^3d with HRT of 22 hours, and average $sCOD_{ww}$ removals of 74–77 % were achieved.

The reactor effluent was found to be feasible for diluting the high-strength wastewater to adjust the OLR, although it contained mostly non-biodegradable organic matter. Inhibition of granular sludge was not detected in any of the reactors. At OLR of 14 kg COD_{ww}/m^3d, the average methane yield ranged from 279 to 308 L-CH_4/kg-$sCOD_{ww,fed}$ with methane concentration of 62–67%. Sulphate was reduced by up to 99% and biogas contained 1–1.5% hydrogen sulphide, while sulphide in the reactor effluent was partially precipitated as elemental sulphur.

The results provide information for the implementation of an anaerobic treatment plant for the new industrial-scale process processing wood-based feedstocks. Extrapolating the process to larger scale with simple calculations showed that 201 GWh of methane could be produced annually from 4800 m3/d wastewater flow. Additionally, sulphide could be recovered as elemental sulphur and be further utilised, e.g. as recycled fertiliser. Overall, by applying anaerobic wastewater treatment, circular economy in the biorefinery can be promoted.

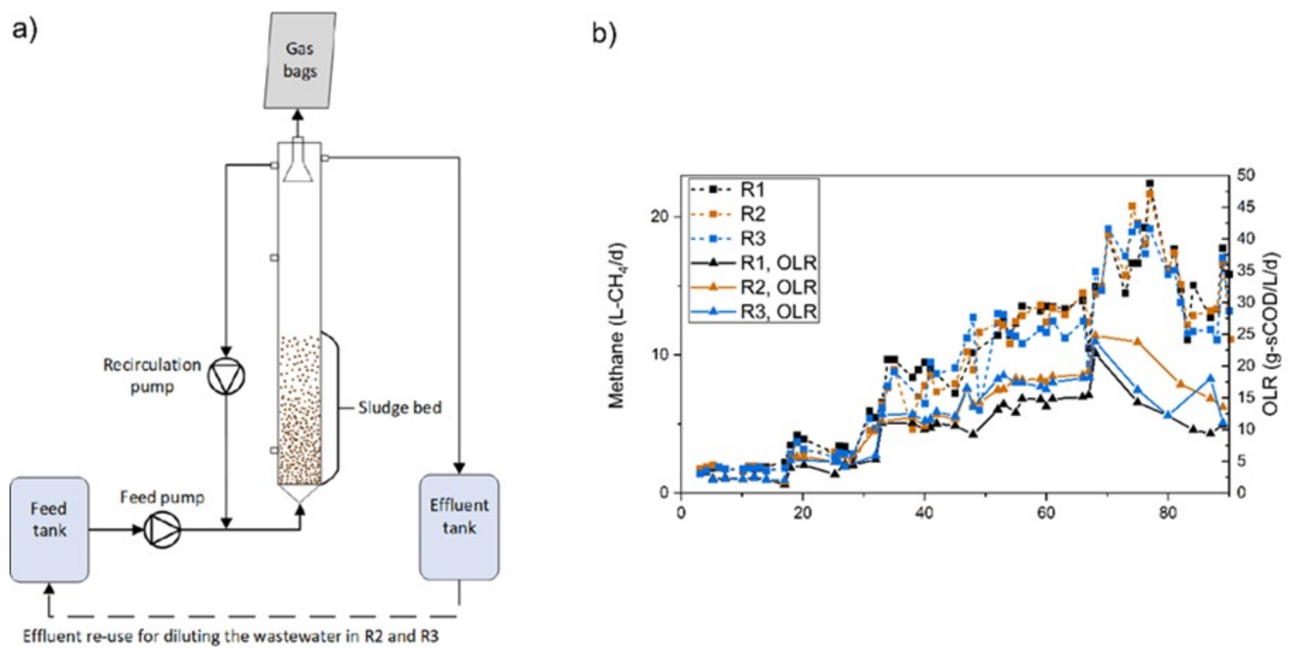

Figure 12: Process scheme (a) and methane production at different OLRs (b).

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Stabilisation/solidification of membrane concentrates using alkali-activation technology

Description

Water and wastewater treatment processes, such as membrane separation, produce concentrates. Currently used disposal methods for these concentrates, such as deep wells or evaporation ponds, may not be feasible in all cases. In this project, a novel concept for managing high-salinity wastewaters was studied: stabilising/solidifying into alkali-activated materials (AAMs), which have a lower CO_2 footprint than Portland cement-based concrete. The concept studied here would be applied to wastewaters without feasible recovery or reuse potential. AAMs are made by mixing an aluminosilicate precursor with an alkali-activator solution and allowing it to harden at room temperature. One interesting prospect for utilising AAM-based, high-salinity wastewater management could be in the mining industry: certain types of mine tailings can be utilised as an aluminosilicate precursor after pre-treatment, which could be combined with high-salinity mine effluents and NaOH. The mixture could be used as mine back-filling material.

The main objectives were to (1) optimise the mix design to obtain binders with suitable physical, chemical, and mechanical properties with low leaching of salts, and (2) evaluate material long-term performance. Additionally, techno-economic feasibility of the developed materials was considered by avoiding high-cost and high-carbon footprint chemicals.

Results

Metakaolin, blast furnace slag, or their mixture (they represent typical low, high, and medium Ca-content raw materials) were compared as an aluminosilicate precursor, and NaOH solution prepared with deionised water was used as an activator. Samples were characterised for their 7 d compressive strength and setting time. The purpose of this work phase was to find out the optimum NaOH content in a reference system not containing high salt content. It was found that for metakaolin, the optimum NaOH dose was 33 weight-% (of precursor) in the range of 13–33%. For blast furnace slag, the same value was 3.9 weight-% in the range of 0.6–3.9%. For the mixture, an average value 14 weight-% was selected.

The next stage of the experiments were conducted using the optimised system but replacing water with synthetic seawater (according to the ASTM D1141–98 standard) or reverse osmosis reject waters from the pulp and paper or mining industry. The samples were comprehensively characterised for compressive strength (at 1, 7, and 28 d), setting time, calorimetry, leaching of salts from crushed or un-crushed samples, efflorescence formation, pore solution composition, identification of crystalline phases (by XRD), and elemental mapping (by EPMA or SEM-EDS). The main results were that strength of the samples increased as salinity of the water increased. The samples prepared with blast furnace slag were the most stable when submerged in water. Thus, in the future work, high-Ca precursors are the preferred ones. Leaching of salt from uncrushed samples (blocks of 50 × 50 × 50 mm^3) was low, while leaching from crushed samples (< 4 mm pieces) indicated higher leaching for chloride or sulphate (i.e., anions) than is allowed for "inert waste" as per European Council Decision 2003/33/EC. The results indicated that the salts were mainly immobilised via physical encapsulation and not by formation of new phases.

During the experiments, it was observed that when using high–salinity wastewaters, it was possible to further decrease the NaOH content while the strength of the samples remained constant. This observation can aid in developing yet more cost-efficient binder systems.

Finally, biomass ashes were also studied as precursors for AAMs. In the mix design involving metakaolin and blast furnace slag, it was possible to replace approx. 70% of these precursors with ash. It was also noticed that no NaOH is required, likely due to the free lime content of the ash. However, the compressive strength of the samples was rather modest (approx. 1 MPa). Green liquor dregs had low Al, Si, and Na content, making them unfeasible as aluminosilicate precursors or activator. They were able to harden when mixed with water but were not stable if submerged in water.

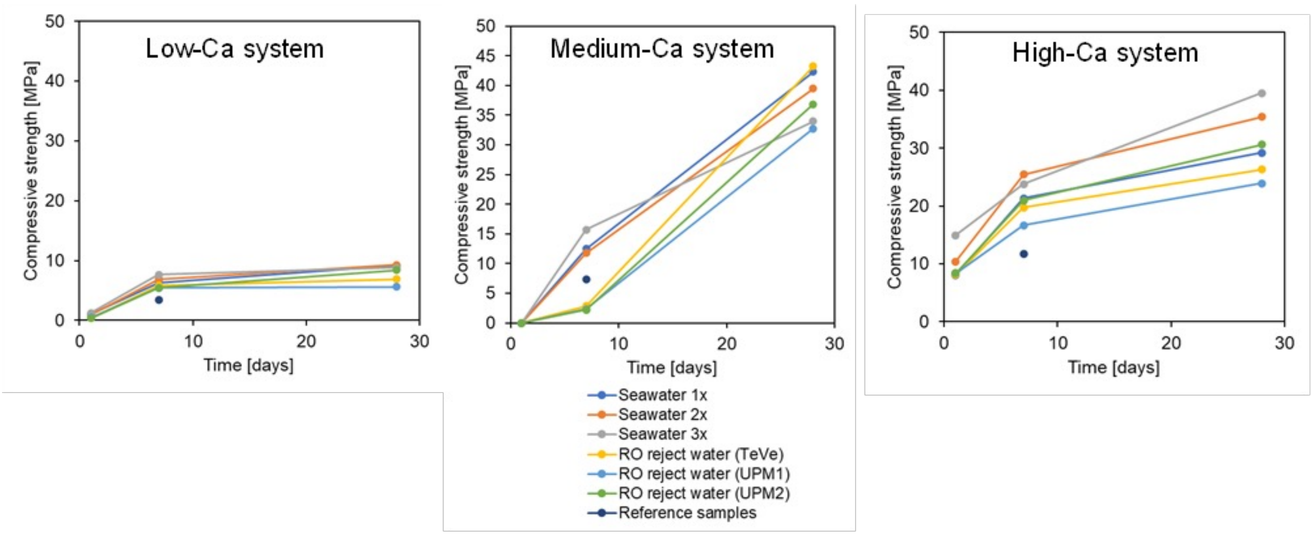

Figure 13: Compressive strength of binders prepared with different high salinity waters using metakaolin (low-Ca system), mixture of metakaolin and blast furnace slag (medium-Ca system), and blast furnace slag (high-Ca system). Seawater 1x, 2x, and 3x refer synthetic seawater with 1x, 2x, or 3x salt content.

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Development of membrane technology

Description

Membrane filtration is an attractive alternative to recirculate process waters e.g. in the P & P industry. It offers a possibility to tailor the purified water quality and even replace the fresh water with recirculated water in the mills. Most of the membranes are used today in desalination processes. It is predicted that the annual number of discarded EoL (mostly RO) modules from desalination processes will exceed 2 million by the year 2025. These modules, which are mainly disposed of in landfills today, could be reused after proper treatment [1–3].

Herein, to fully implement the European Directive 2008/98/EC guideline on sustainable waste management [4], the main effort has been put in the development of a reusing method for EoL membranes as UF/NF membranes for treatment of P&P effluents. The proposed method includes prior cleaning procedures followed by controlled chemical oxidation either as direct reuse as UF membrane or after conversion to NF membranes through layer-by-layer (LBL) polyelectrolyte deposition technique.

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Results

The first stage in the recirculating of EoL membranes was their cleaning. The Ultrasil 110 cleaning agent was found to be the most promising cleaning agent for the removal of fouling in the precleaning step. Moreover, the same cleaning agent (0.2 w-%) was sufficient for flux recovery after filtration of waters from P & P industry without compromising the MgSO4 rejection (>90%) in most cases. LBL-coated membrane (Figure 14 C) demonstrated higher stability against NaOCl exposure compared to the commercial NF270 membrane. This could open possibility to use oxidative agent for cleaning of LBL-coated membranes.

It is possible to produce membranes possessing various cut-off (Figure 14 D), salt rejection, and pure water flux through direct controlled chemical oxidation of polyamide layer of EoL membranes using NaOCl at different exposure times. By altering the oxidation time, membranes with 12, 21, 45, and 175 pure water permeability (LMHb) were obtained (permeability of EoL membrane was 4–5 LMHb). The inherent trade-off between permselectivity and permeability led to the decrease of MgSO4 salt retention from ~90–93% to ~0–3% (Figure 14 A). It was also observed that the higher oxidation level of EOL membrane and further LBL polyelectrolyte deposition led to higher rejection of neutral PEG and higher pure water permeability compared to milder oxidation without LBL modification (Figure 14 B).

The oxidised membranes up to the permeability of 45 LMHb, and LBL-modified ones (EOL-45-5 Bilayers (45 LMHb) & LBL-175-5 Bilayers (175 LMBb)) demonstrated the potential to remove the colour of alkali filtrate feed completely where commercial UH004 P (4 kDa cut-off) was not able to completely remove the colour.
Another important finding of this study is that the higher oxidation of EOL membranes with further LBL coating and/or controlled mild oxidation can lead to membranes possessing better performance in terms of permeability, cut-off value (rejection of neutral PEG) and total dissolved carbon (TDC) and chemical oxygen demand (COD) removal compared to the commercial UF (4 kDa) membrane during the filtration of alkaline filtrate (Figure 15). The nessesity of LBL-coating technique for tuning the structure of oxidised membrane is of particular importance for achieving the industrial requirements of TOC and COD removal in P & P mills' effluents. The results showed that EoL membrane can be converted to useable membranes for the purification of P & P industry waters.

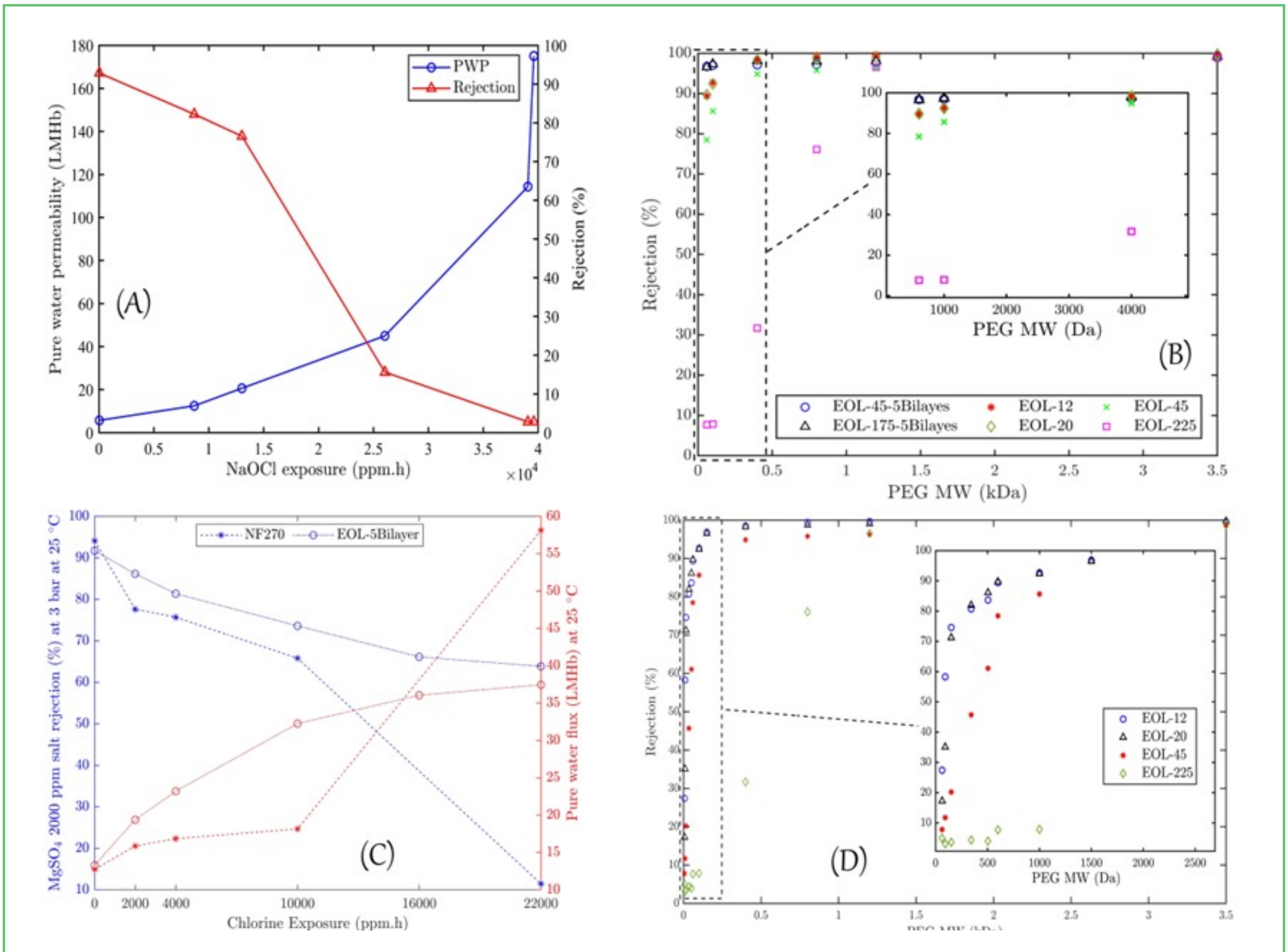

Figure 14: The effect of NaOCl exposure on: PWP and salt rejection (A); Retention of PEGs and PWPs of oxidised and LBL-coated membranes (B&D); Stability of 5 bilayer coated and commercial membrane NF270. (The Numbers denoted to the name of EOL membranes are the permeability of membranes).

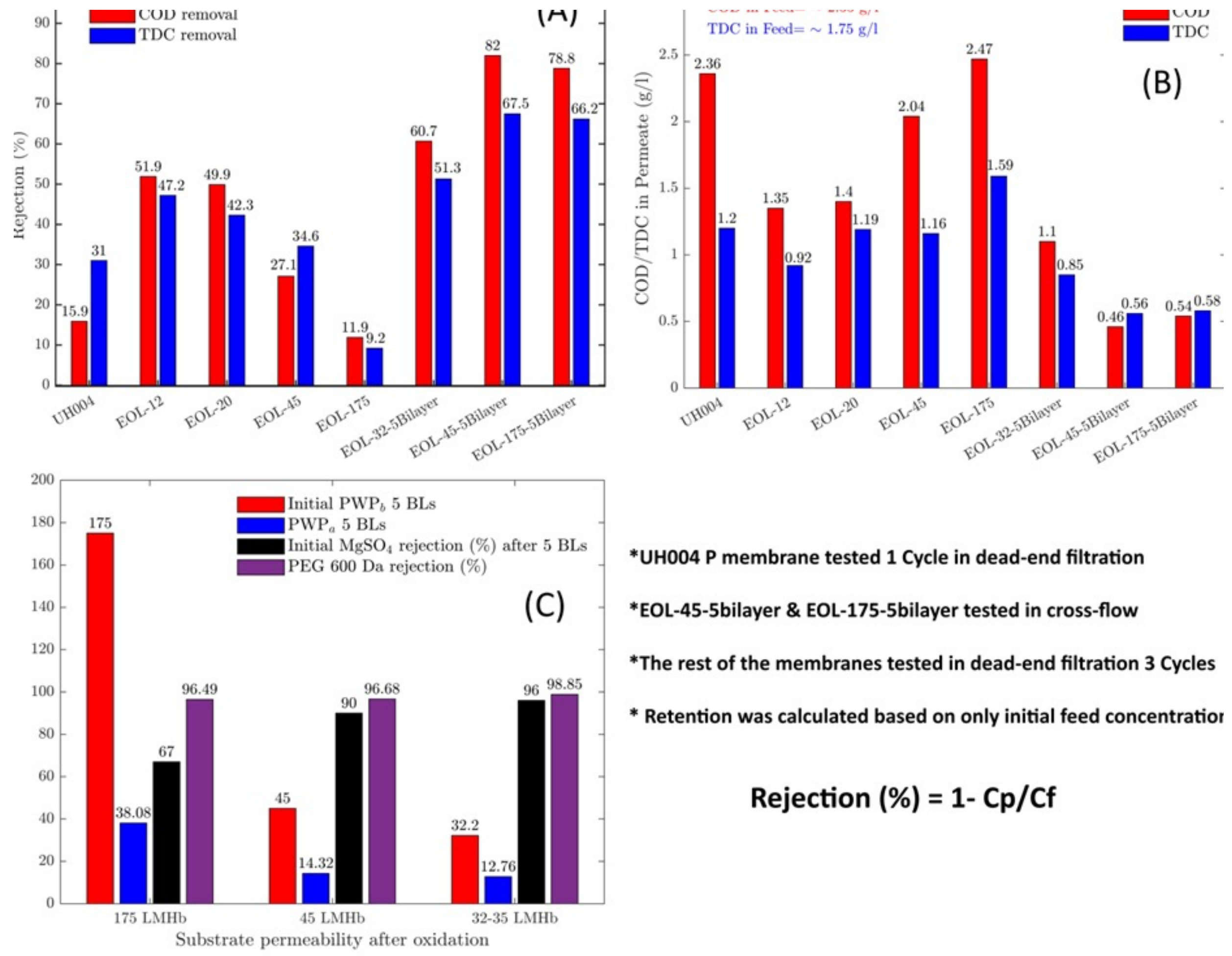

Figure 15: The performance of the commercial UH004 p membrane, oxidised membranes at different oxidation level (i.e., different permeability), and LBL-coated membranes in terms of: (A) TDC and COD removal; (B) Quality of permeate in terms of COD and TDS (g/l); (C) the effect of initial substrate possessing different permeability on the performance subsequent 5 bilayers polyelectrolyte coating.

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Micro- and nanoplastics in industrial waters

Summary

Micro- and nanoplastics (MNP) are an emerging environmental concern in all ecosystems. Microplastics, often defined as plastic particles with size between 1 µm and 5 mm, and nanoplastics (particles sized between 1 nm and 1 µm) are insoluble to water and they degrade chemically very slowly in ambient conditions. Hence microplastics are widespread and persistent pollutants, regardless of their origin (intentionally manufactured, i.e. primary microplastics, or fragmented from larger plastics, i.e. secondary microplastics).

The abundance of MNP in industrial discharge waters and matrices (e.g. sludges) has already been widely reported. However, there is practically no information of microplastic abundance in industrial process waters. To ensure clean enough water for recirculation in industry, the accumulation of contaminants, such as microplastics, in process waters should be studied and prevented. In addition, water purification and subsequent sludge treatment processes should be developed, as the industrial discharge presents potential sources for micro- and nanoplastics to end up in the environment.

Hence, there is a need to characterise microplastics from industrial sample matrices (e.g. process water, wastewater and sludge). To fulfil the need, development of reproducible methods for microplastic separation and identification is required considering the high organic content of these matrices. Furthermore, instead of laborious analytical processes in the laboratory, there is a need for novel methods for in situ measurements being able to monitor microplastic abundance and the effects of processes.

Microplastics are not currently regulated, because there are no standardised methods available for characterisation of MNP from industrial water and sludge. Here, the methods for sampling, separation and measurement of MNP were developed. In the industrial piloting set-ups, the effects of selected processes for wastewater and sludge treatment on MNP abundance were determined for the first time. Also, a prototype for in situ monitoring was introduced and tested in an industrial pilot. Through these efforts, we enable the industry to be prepared for potential future legislation (as studied in WP1 of this project).

In this work package, efforts were focused on four tasks (see Figure 16). Namely, in Task 4.1 the aim was to develop reproducible and optimised methods for pretreatment and measurement of microplastics from industrial samples. Task 4.2 aimed to test filtration methods and membranes to concentrate and remove microplastics from industrial waters. In Task 4.3, we aimed to develop a prototype for in situ optical measurement of microplastics directly in water. Finally, in Task 4.4. the methods developed in other tasks were utilised for measuring microplastics from industrial water and sludge streams provided by the company participants

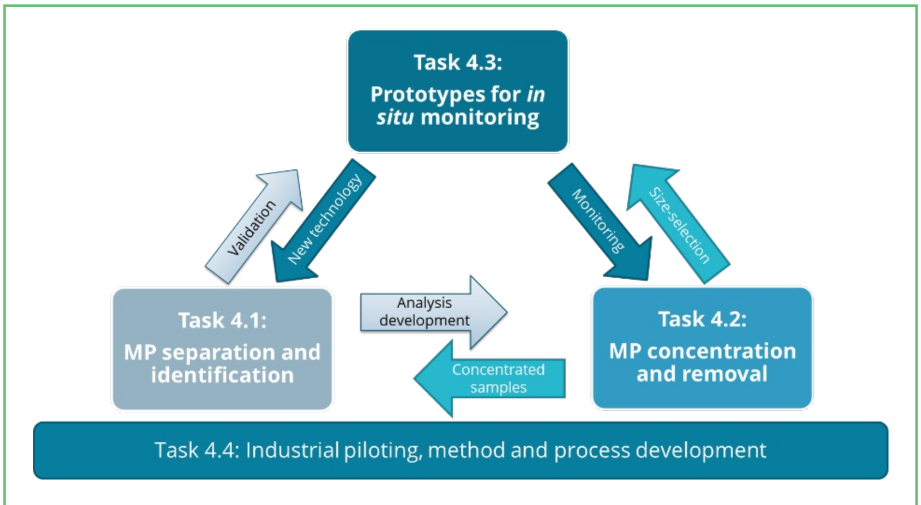

Figure 16: Interlink between tasks in work package 4.

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Microplastic separation and identification

Description

This task covers the development of sample preparation and validation of measurement methods for detection and quantitation of microplastics (MPs) [1] from industrial wastewater and sludge samples. The aim of sample preparation is to separate MPs from other solid materials. Efficient sample pre-treatment is essential, because MPs must be isolated to be measured accurately. Current sample preparation methods are insufficient for industrial samples, which are complex and diverse, containing many different types of solid materials.
Considering possible future regulations for monitoring MP abundance in industrial wastewaters and sludges, more efficient sample preparation methods enabling reproducible MP analysis needs to be developed. Current measurement methods also need to be tested and validated to measure their accuracy and uncertainties.

The aims of this task were to develop enzymatic-chemical digestion protocols for industrial wastewater and sludge samples, and validate spectroscopic measurement methods for MPs. Sample preparation methods were validated by confirming that enzymes and other reagents do not degrade MPs. Measurement methods were validated by measuring samples containing known amounts of intentionally added MPs. Moreover, inter-laboratory comparisons of sample preparation and measurement methods were done between the universities participating in this task.

Results

Enzymatic digestion protocol published by Löder et. al. [2] was used as a basis for developing sample preparation methods for the industrial samples obtained from the company partners. The enzymatic treatment protocol contains multiple steps, which can be selected according to the sample composition. Usually, all samples are treated with hydrogen peroxide. Typically, this does not remove all non-plastic materials, and enzymes such as cellulase, protease or lipase are used to target the materials which remain in the samples. If samples contain inorganic materials, they need to be removed by density separation. In density separation, a sample is mixed with e.g. liquid with high density (about 1.8 g/cm^3) resulting in plastics floating on the surface and inorganic particles sinking to the bottom. The effect of each enzyme on MPs was observed to ensure that MPs were not degraded by the treatments. The process was optimised for the studied sample types and a general protocol applicable to majority of the samples was developed.

Protease was shown to increase the number of detected MPs significantly in all cases. This may be due to protease dissolving a protein film that could have formed on the MP surface and caused errors in detection. Cellulase and amylase did not cause any similar phenomenon, but they caused other kinds of challenges for MP analysis, such as solid formations in many different process parameters, which make it impossible to analyse some samples. This means working with those enzymes reserved for specific cases and specific parameters. Optimal results were observed by first treating the samples with hydrogen peroxide (H_2O_2) for 24/48 h (depending on the sample composition) at 50 °C with 100 rpm stirring. Subsequently, the samples were filtered and submerged in phosphate buffer, adjusted to pH 9 and protease was added to digest for 2 days at 50°C. Density separation was done afterwards if needed. In the case of amylase, optimal digestion results were observed at pH 4–4,5 and digestion for 3 days at 37°C. Similarly, cellulase worked best at pH 4.5–5 and 4 days digestion at 37°C. Though tested temperatures and pH values ranged from 37° to 50°C and 4 to 8, respectively. Digestion times were tested between 1 days and 6 days for each enzyme. If all enzymes in the Löder's protocol were used, the digestion process of a sample took about 12 days, but the optimised process took about 4–5 days instead.

In the case of sample preparation of sludges originating from a biogas process, the starting point was the protocol optimised and reported earlier [3]. This 5-day sample preparation protocol relied solely on a chemical digestion at 35 °C which combined the use of a surfactant, sodium dodecyl sulphate (SDS), and H_2O_2. However, the protocol was further streamlined in this task by omitting the prefiltration (a possible MP contamination source) by halving the sample size and increasing the filtering area of the vacuum filtration. Density separation at 1.75 g/cm^3 was added to the end of the protocol, extending the duration of the sample preparation to one week.

The development of sample preparation of sludges originating from pulp & paper industry was challenging due to the high cellulose fibre content. The sample preparation protocol was optimised by monitoring the reduction in total solids and organic content of the samples. As the chemical digestion alone was not efficient enough, the protocol was enhanced using cellulase enzyme. Finally, the most efficient digestion protocol for both sample types turned out to be as follows: 1 days SDS, 3 days H_2O_2, 4 days cellulase enzyme and 3 days H_2O_2 (10 days in total). The temperature was increased to 45 °C to boost the cellulase enzyme activity and to enhance peroxide digestion. A density separation step was needed in the case of a sludge having many heavy non-plastic particles, extending the sample preparation time to two weeks for this type of sludge.

For method validation purposes, synthetic MPs were prepared via cryogenic milling, using commercially available plastic beads. A grinding protocol was optimised for each plastic type, as the grinding parameters depend heavily on the properties of used polymers. These micrometer-scale particles (i.e. synthetic MPs) were then sieved to different-size fractions and used for method validation purposes across the entire work package. Return rate tests from the enzymatic digestion protocol were conducted and the same samples were analysed with imaging FTIR and Raman spectrometers to confirm return-rate results and compare the methods. The particles were also observed under Scanning Electron Microscopy to study the morphology, shapes and sizes of the manufactured synthetic MPs.

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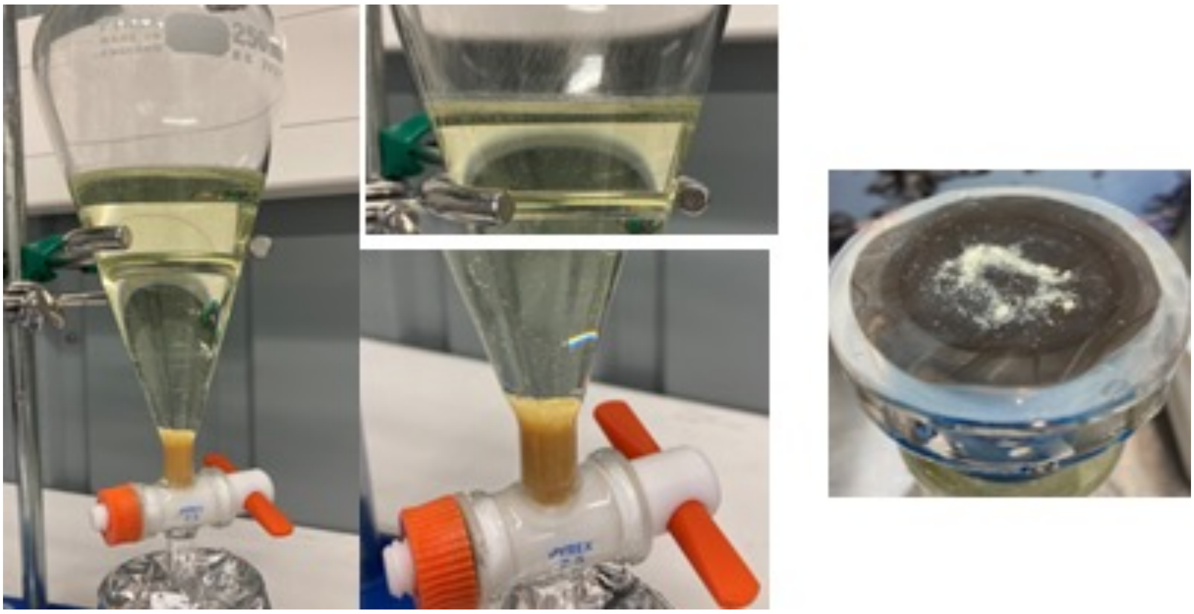

Figure 17: MP separation process optimisation of the fibrous sludge. Despite the successful density separation step, the process still required optimization of the chemical-enzymatic phase to reduce the amount of remaining solids to be analysed with spectroscopy.

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BENEFITS FOR PARTICIPATING COMPANIES

Gasum

Circular economy of water related to biogas production

Gasum is Nordic leader in biogas production, having 17 biogas plants in Finland and Sweden. In Finland, Gasum is treating a significant part of sewage sludge, formed in Finnish wastewater treatment plants.

Gasum joined CEIWA public research for two principal reasons: 1. to increase understanding of microplastics, present especially in sewage sludge coming to biogas plants, and 2. to study potential new industrial wastewater streams as feeds to biogas production. In addition, the regulative aspects were an important CEIWA work package for Gasum.

The CEIWA project was able to increase expertise in microplastic analytics and somewhat of their presence in different streams – although the project also showed that it is a very complex topic. Furthermere, research done in CEIWA provided important new knowledge on biogas production from industrial wastewater and widened the understanding of the regulative landscape internationally.

Gasum
Viljami Kinnunen,
Senior process engineer
CEIWA Steering Committee member

CEIWA

Microplastic concentration and purification

Description

This task covers the testing and development of concentrating and purifying industrial process waters to allow reliable microplastic analysis from a larger volume of a wastewater sample. Overall, the aim of this task was to develop a novel concept for collection and concentration of micro- and nanoplastics from different water streams. After the selection of various sludge samples by other collaborators in WP 4 (Tasks 4.1 and 4.4), this task was focused on the effluent from pulp and paper (P&P) industry.

The expected deliverables were a protocol to collect and concentrate nano- and microplastics as well as methods to purify concentrated nano- and microplastic samples on the membrane surfaces. In addition, a report on the usability of different membranes to recover nano- and microplastics was expected.

Results

In the beginning, over hundred litres of P&P effluent was concentrated with an ultrafiltration membrane with a volume reduction factor (VRF) of 63. The subsamples of concentrated effluent were treated thrice with hydrogen peroxide (H2O2, 25%, 2–3 d at RT) and concentrated with two types of membranes (RC10, 10 kDa; MFP2, 0.2 µm). As a result, only 200-ml subsamples of the original effluent were able to be analysed with Raman imaging microscope (>100 µm) at LUT University or FPA-FTIR (>20 µm) at UEF. According to these results, it was clear that the tested membranes were efficient to concentrate solids, including microplastics. On the other hand, the collection of fractions of all sizes above the porosity of the membranes (starting from 0.1 µm) made the analysis of microplastics from a reasonable sample volume impossible with the currently available spectroscopic methods. As far as the results are aimed to be reported as number of particles per volume or weight, the inclusion of fractions of all sizes in one sample would not be possible. For that kind of samples, thermoanalytical techniques, such as gas chromatography with mass spectrometer (GC/MS) or thermogravimetric analyses (TGA), could be tested to provide mass concentrations of possible microplastics concentrated in the sample. However, during the implementation of WP4, the analytical methods were limited to spectroscopic measurements.

Thus, the original plan of concentrating samples with membranes was shifted to the idea of concentrating larger liquid samples (1 m^3) with a metal sieve with a mesh size of 20 µm. In that way, the volume of the analysed subsample could be increased from hundreds of millilitres to dozens of litres – depending on the effectivity of the purification. As a disadvantage, the smallest microplastics and nanoplastics would also be excluded from the analysis. The reliability of their quantification would nevertheless have been low with the available instruments in this WP. The purification of the sample was also further improved by testing different methods to degrade non-plastic materials remaining in the P&P effluent. These methods included various combinations of oxidation with H_2O_2, enzymatic degradation with cellulase [1], treatment with sodium hydroxide (NaOH) and urea [2], as well as with N-methylmorpholine N-oxide (NMMO) [3]. Out of the tested purification methods, NaOH-urea treatment along with oxidation with H_2O_2 was the most effective to remove non-plastic materials from the P&P effluent (Figure 18). Later, the most promising concentration and purification method was further optimised and validated with the various artificial MPs created in Task 4.1. This work was not finished by the time of writing this report.

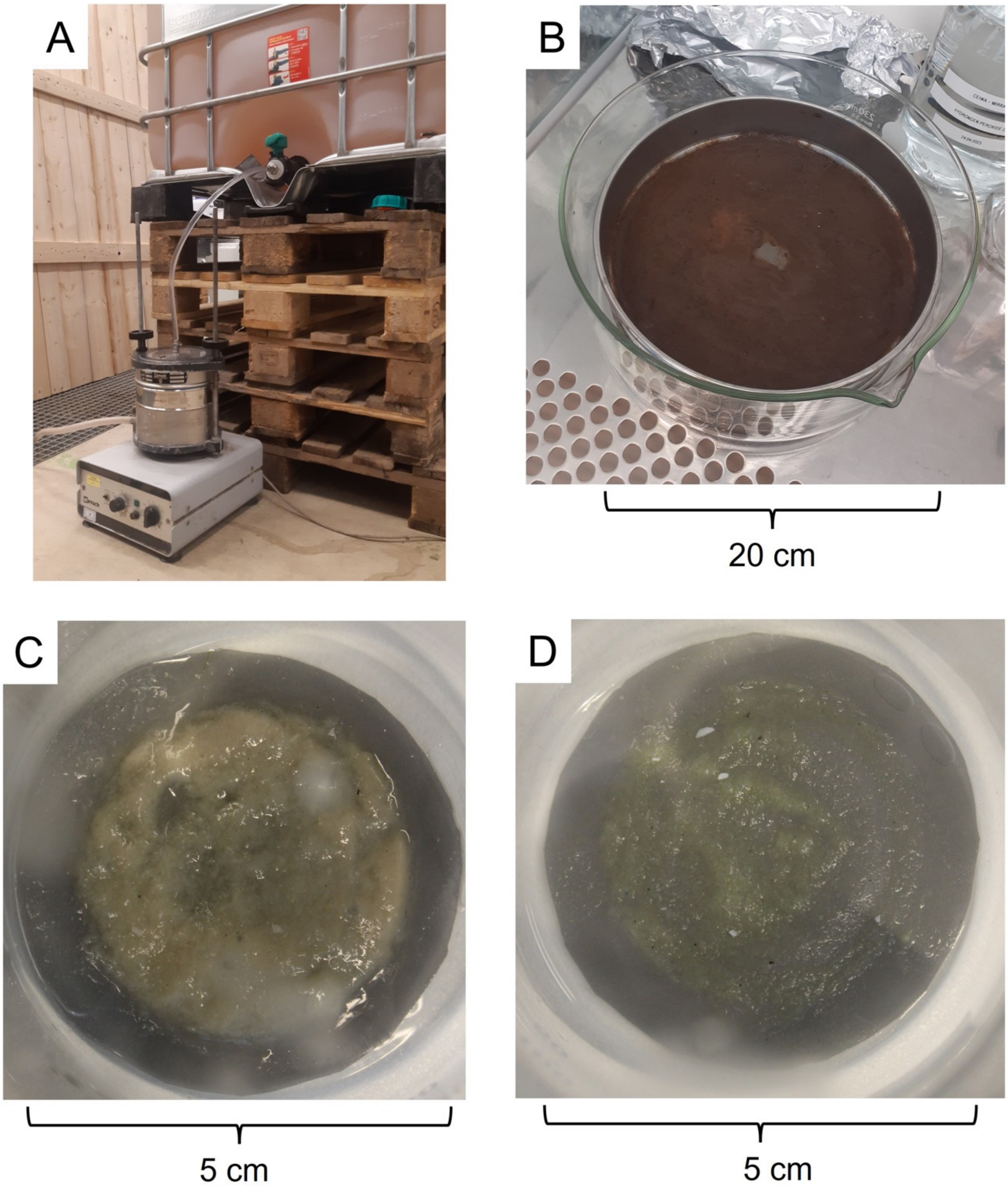

Figure 18: A) Filtration of 1 m3 of P&P effluent, B) the untreated sample representing solids (>20 µm) from 1 m3 of P&P effluent, C) the solids (>20 µm) from 250 L of P&P effluent after one H2O2 treatment, and D) the solids (>20 µm) from 250 L of P&P effluent after two rounds of NaOH-Urea treatment in combination with H2O2 treatment.

CEIWA

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BENEFITS FOR PARTICIPATING COMPANIES

UPM

Population growth, urbanisation and rising living standards, particularly in emerging markets, create new consumer demand. In the meantime, natural resources are dwindling. Mitigating climate change and tackling other environmental challenges require sustainable choices. At UPM, we respond to the growth in consumer demand with recyclable products that are made of responsibly sourced, renewable raw materials and offer alternatives to fossil materials. The circular economy and resource efficiency offer solutions to climate change and the scarcity of natural resources, such as virgin raw materials and water. Water fuels most life and ecosystems on our planet. It also flows through every part of our business. Therefore, we seek to make the most of it, and apply our circular thinking to water, just as we do with any other natural resource – as per UPM's Biofore strategy. Responsibility and innovations to replace fossil materials with bio-based alternatives are focus areas of our business strategy – beyond fossils.

"We decided to join and support CEIWA project as it offers us the right platform to look beyond business as usual, testing and developing new tools to monitor and remove detrimental substances from our processes, ensuring the sustainability value proposals of our products and operation and staying abreast of future changes in regulation. In practice, CEIWA consortia has supported the UPM target by improving our ability to foresee the effects of tightening water-related regulation, developing new measurement methods for microplastic, and modelling biological treatment for process optimisation."

UPM
Corinne Le Ny Heinonen
Environmental Manager
CEIWA Steering Committee member

Prototypes development for in situ monitoring

Description

The objectives of this task are three-fold: 1) Determining what is the best solution based on photonics methods [1] to detect and eventually identify microplastics in water, 2) Designing and realising a prototype based on those methods in view of testing in an industrial environment, and 3) realising the test in-situ.

Several challenges had to be tackled prior the construction of the prototype, namely, the means of detection and the optical process or method to be used for the detection of MP. During the prototype development, we kept in mind the fact that the plastic samples are in water, since the detection is supposed to be done in the line of treatment of wastewaters. Moreover, water is in this case a complex environment with possible particle pollution or colouring effect (typically yellow coming from the presence of lignin).

Results

We started the project with the hope of using a combination of direct imaging and speckle contrast monitoring. Based on previous research [2–5] this was an obvious initial choice. However, we realised that it would not give us a complete understanding of the particle being analysed. We therefore opted for the development of an integrated spectrometer. Considering the limited time, the number of challenges to be faced beside optical tools development, and the fact that measurements are made through water, we decided to design the spectrometer for operation in the visible range of light, where water does not present strong absorption peaks. This means a longer detection cell. No specific absorption bands for plastics are present in this wavelength range but it allows for the determination of transmission variation (from one medium to another) and a simplified alignment and optimisation of the device. We chose to set up the spectrometer as a nephelometer (tilted orientation of the grating) because of the additional potential of measuring turbidity in the sample volume. Figure 1 shows the device as constructed so far (June 2023). It is LabVIEW controlled and pipes can be plugged on in order to bring water into the measuring zones. It is using two monochrome cameras (one for imaging, one for spectrometry) and a white light LED illumination. The overall cost of such a prototype is about €4,000 per unit. Two steps are currently ongoing. The adaptation to short wavelength infrared range to match the specific absorption peaks of several plastics and a test is planned in a papermill for on-site testing. In this view, an adaptation of the device to the industrial pipe is to be done.

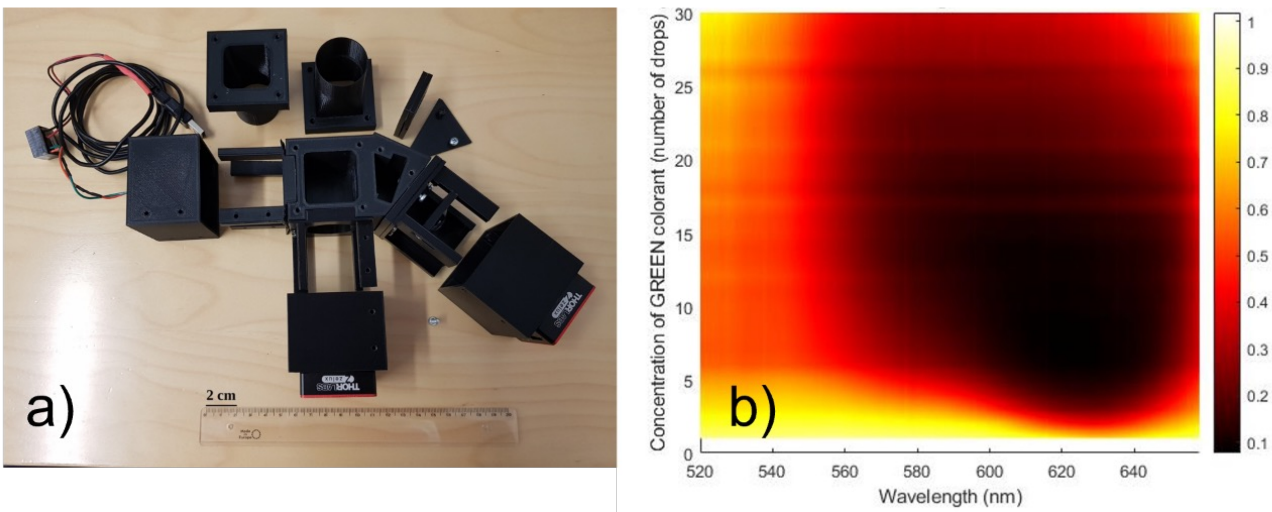

Figure 19: a) Unassembled prototype including all the parts for imaging and spectroscopic measurements. b) example of results, i.e., a map showing the spectra as a function of red-dye concentration in water.

In parallel to this development, we performed additional investigation to determine better solutions, We first tested Valmet FS5 commercial device with artificial microplastics (performed by Blaž Hrovat, SIBlab). High-resolution imaging entails extremely good results both on direct identification of the MP and MP type allowing a fast sorting of MPs [Pub1, see Figure 2] and on the motion of plastics and 3D representation of them [Pub3]. We conducted theoretical work and initiated experiments on aggregates of nanoplastics leading to a third type of MPs [Pub2]. For this we used measurements of the Hamaker's constant to predict the aggregation. Finally, we investigated the potential of hyperspectral imaging for direct measurement of MPs in water. We obtained very good results, and the publication is in preparation [Pub4]. This work led to a PREIN-funded project (Flagship PREIN, Academy of Finland) run jointly with UEF, Aalto University, Tampere University, and VTT on the detection of black microplastics. It led also to an EU HORIZON-RIA project IBAIA involving 20 partners for the monitoring of water pollution, and UEF/Photonics is part of a consortium for the preparation of an EU-HORIZON-RIA project for the study of sediment in Danube water.

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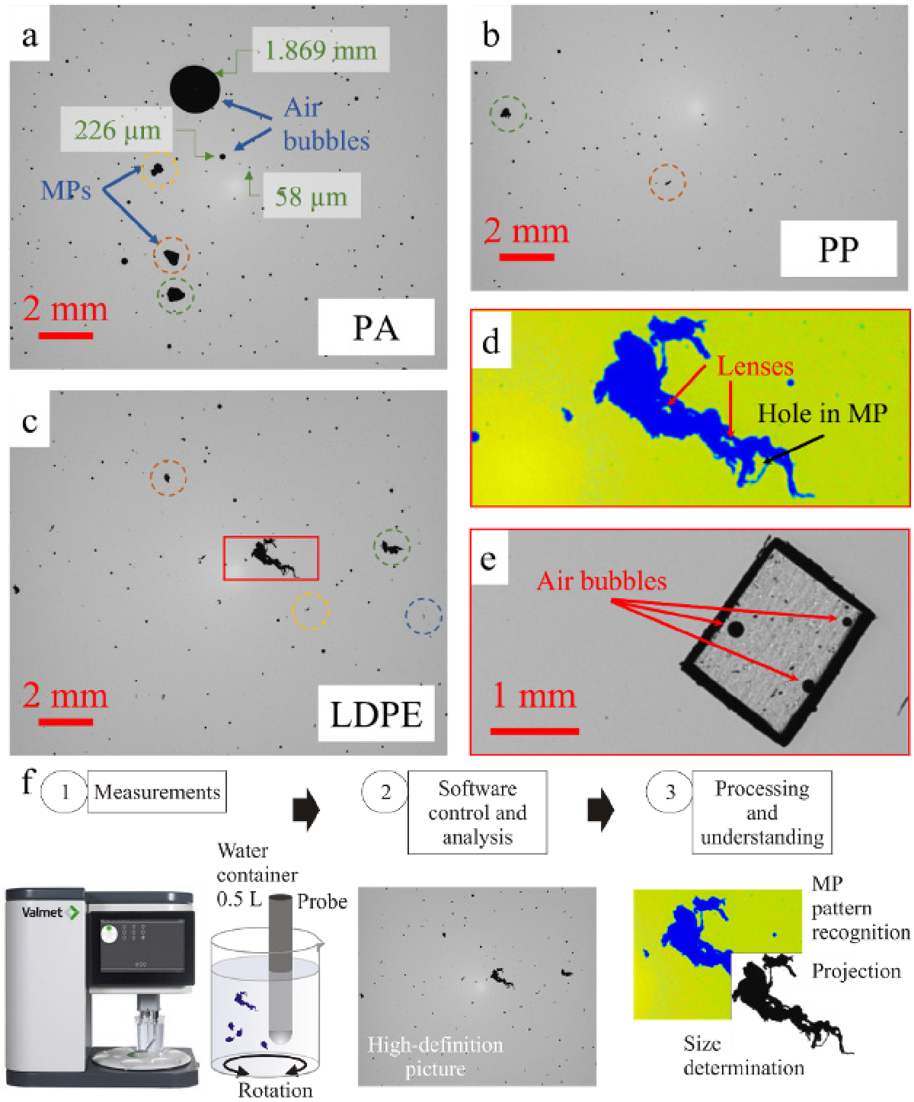

Figure 20: Images acquired with the Valmet FS5 UHD device for different samples in water including a) PA particles, b) PP particles, and c) LDPE particles. d) zoomed-in and enhanced image of a microplastic particle from c) (red contour). Red arrows in d) highlight bright "lensing" areas in the microplastic particle. Black arrows in d) highlights a hole in the MP. e) air bubbles on a PET MP. f) Procedure to image and recognise MPs in a water sample [Pub1].

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Publications

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Industrial piloting

Description

This task combined the application of technologies developed in tasks 4.1 and 4.2, providing information on the effects of industrial processes and wastewater treatment technologies on MPs in process waters, wastewaters and sludges. The produced information included the number, size and polymer content of MPs detected in selected industrial water and sludge streams. As MPs form an emerging type of contaminants, this data could serve many useful purposes for the companies. For example, this type of data can be used to 1) evaluate the utilisation potential of the studied streams, 2) evaluate the efficacy of the applied process/waste water treatment technologies and 3) identify possible internal or external sources of MPs.

Results

When planning for MP characterisation, the sampling plays a crucial role as defects in sampling can create a huge error source for the results. Thus, sampling protocols should be clear and concise. For example, in this project there were concerns that certain industrial samples were contaminated with fibres. Sampling time also plays a crucial role. For example, when analysing sludge samples in this study, the sampling time had a considerable effect on the number and type of MPs identified, and the deviation in the results was large between the different sampling times. Another issue to consider is the sampling volume vs. representativeness of the sample when considering large volumes of wastewaters and sludges. For example, with sludge samples, only 0.5 g of TS has been utilised for the MP characterisation in this study.

When optimising the separation of MPs from wastewater and sludge matrixes, the removal of organic matter has to be done without degrading or harming the MPs. Thus, for example, temperature plays a crucial role and, in this study, for sludge samples, it was not increased above 50°C. As the current MP separation methods last for days, the optimisation of the separation step should consider the length of the separation and try to minimise the duration of the procedure. The same applies for characterisation of MPs that is also time-consuming.

Various issues need to be considered upon MP characterisation. The size limit for detection of MPs in this study was ca. 20 µm. For example, there is a potential to misidentify MPs by the methods used. This was demonstrated with return rate tests using synthetic MPs. Certain types of plastics (PET, PVC) were often misidentified as something else and detection parameters needed to be adjusted, while others (PP, PE) would be recovered perfectly. Furthermore, fibres and other shapes have been identified, but human correction is still necessary to determine whether agglomerated particles are detected as one particle or as fibre loops to prevent being misidentified as another shape. In Raman spectroscopy, identification of MPs can also be complicated by the shape of the MPs and the pigments used in plastics. Furthermore, as the size of the MPs decreases, the identification becomes more difficult.

When characterising industrial wastewaters, in all but one case the most prevalent MPs were spherical/rectangular particles that were mostly made of polypropylene (PP), polyethylene (PE) and low amounts of polyethylene terephthalate (PET). In one case, there were mostly fibres present. It is not known whether this was due to contamination during the sampling. The most common polymer type in all cases was still PP.

When characterising industrial sludge samples related to anaerobic digestion of sewage sludge, MPs identified included PET, PE, PP, polyamide (PA) and polystyrene (PS). A large fraction of the MPs ended up in the solid fraction of the digestate (the effluent of the anaerobic digestion), while in the liquid fraction of the digestate the amounts of MPs were much smaller and the polymers were mostly composed of light plastics, i.e., PE fragments and PP fibres.

Various separation and characterisation methods for MPs exist and have also been developed and utilised in this project (see Tasks 4.1 and 4.2). However, it must be acknowledged that samples from different plants, processes, etc. can have very different composition of organics, inorganics and MPs and thus, methods must be optimised for every sample type. No universal method exists for industrial wastewaters and sludges.

Using the results of this analysis, industrial partners received information on the amount and characteristics of MPs in their wastewater and sludge samples as well as on the efficacy of their wastewater treatment plants or other purification processes to assess whether additional MP removal steps are necessary to satisfy future law regulations.

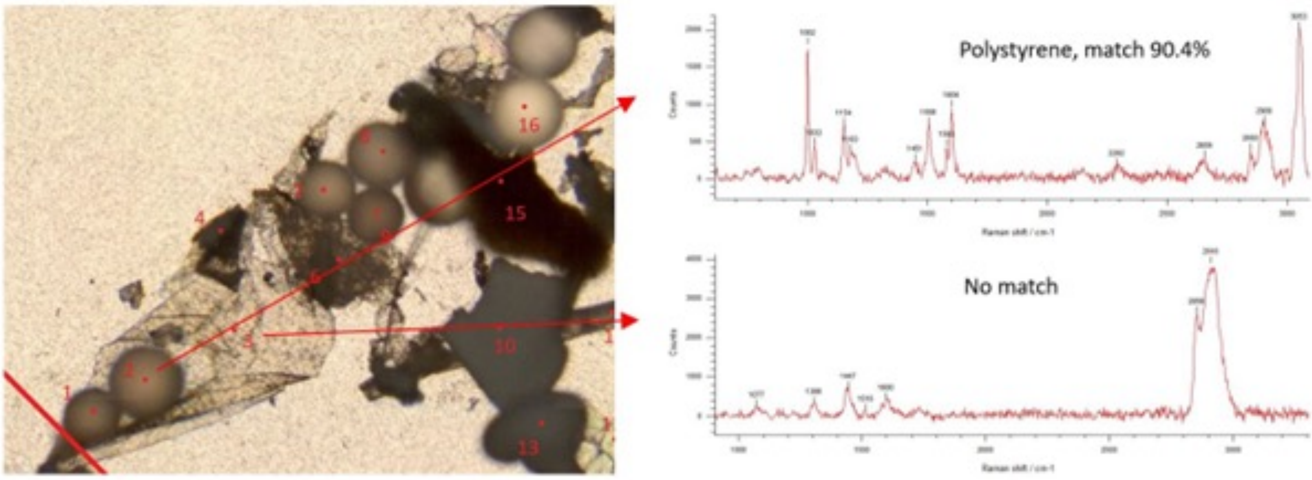

Figure 21: Left: Particles extracted from sewage sludge for Raman analysis on a filter. Right: Examples of Raman spectra of the analysed particles.

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