ULTIMATE

WATER SMART INDUSTRIAL SYMBIOSIS

Deliverable D1.5

New approaches and best practices for closing the material cycles within symbiosis cluster

Author(s): M. Sgroi, J. González Camejo, F. Fatone

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Technical References

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Executive Summary

Summary of Deliverable

The EU Horizon 2020 ULTIMATE promoted circular economy concepts within the framework of water smart industrial symbioses. It focused on industrial wastewater streams as resource for water, energy and material recovery. ULTIMATE developed and demonstrated 24 circular economy related technologies. In six out of nine case studies (i.e.; N. Prinsenland, Rosignano, Nafplio, Karmiel, Tain and Kalundborg), symbiosis network in regional area were demonstrated towards the implementation of different material recovery routes, which included recovery of nutrients from industrial wastewaters, use of by-products of local industries for wastewater treatment, recovery of high-value products (e.g.; antioxidant, polyphenols, sulphurs, metals). In addition, in this document are also reported results related to the use of innovative fluorescence sensors to monitor the removal of organic micropollutants during quaternary treatments of wastewater to comply with recent EU regulations on urban wastewater treatment and reuse.

Recovery of nutrients from industrial wastewater

Solutions for nutrients recovery were investigated in the ULTIMATE case studies in the Netherlands (Nieuw Prinsenland), Lleida (Spain), Tain (Scotland).

Case study 2 - Netherland

The Dutch case study (N. Prinsenland) analysed the feasibility to use Electrodialysis (ED) technologies to recover nutrients from greenhouse wastewater by avoiding accumulation of salts in the recirculated water. For this scope, monovalent selective membranes were modified and tested in reducing concentration of detrimental ions (Na+ and Cl-) and improving nutrient reuse potential in greenhouse cultivation. It was estimated that the ULTIMATE solution can achieve up to NO^{3-} (30%), K^+ (33%), Ca^{2+} (70%), Mg^{2+} (76%), SO_4^{2-} (84%), PO_4^{3-} (93%) nutrient recovery by treatment of greenhouse wastewater. However, still enhancements are needed in the development of high selective monovalent membranes to improve the treatment process. To scale up and replicate on a large scale this material recovery technology, it should be considered that high concentration of nutrients in the feed water is beneficial to improve the recovery rate of the ED technology. On the other side, tests are needed to evaluate the uptake by plants of recovered nutrients. In addition, inputs for further development of this technology may derive by new regulatory indications on the management of this type of wastewater.

Case study 5 - Spain

At CS#5 in Lleida (Spain) a concept study has been conducted to recover struvite by Aquavite® process from supernatant of sludge dewatering and nutrients from hydrochar obtained by hydrothermal carbonization of the brewer’s spent grain and of the municipal sludge from Lleida WWTP. Outputs of the study are that struvite recovery is not economical in the investigated scenario, and it is limited to applications with streams with high P loads. On the other side, a detailed chemical/physical characterization of hydrochar are necessary to evaluate the feasibility of fertilizers recovery, which remains only theoretically possible at concept study level.

Case study 7 - Scotland

At CS#7 in Tain (Scotland), the wastewater of a distillery for whisky production, which is treated by an AnMBR reactor, is still rich of phosphorus and ammonia. The ULTIMATE project tested a precipitation system for the formation of struvite from the AnMBR effluent, and a following ammonia stripping unit, where nitrogen can be recovered in the form of ammonium sulphate solution. The trials carried out with this two-stage treatment process led to a total nitrogen removal and recovery of 80%, while 80% recovery of phosphorus was achieved only by the struvite precipitation unit. To scale up and replicate on a large scale this material recovery technology, it is suggested the application of the technology to a high strength water in terms of either phosphorus or ammonia content. In addition, a membrane filtration unit is beneficial to avoid any impact of solids during the nutrient recovery process. Furthermore, the use of waste heat or heat production from biogas onsite is beneficial to control the temperature in the stripping process and improve performance. Finally, a pH control of the feed to the nutrients recovery systems may be required to avoid uncontrolled precipitation leading to clogging problems

Recovery of industrial by-products and test of innovative fluorescence sensors

Investigations about the possibility to use industrial by-products for wastewater treatment were accomplished in the Italian case study of Rosignano.

Case study 3 - Italy

The Italian case study (CS#3) analysed the possibility to use by-products from the industrial area of Rosignano (Livorno, Italy) as alternative material to produce treated wastewater of suitable quality for industrial reuse and agriculture reuse. Tested industrial by-products included bentonite, partially cooked limestone, soda out of specification, hydrochar from sewage sludge, aluminium sludge, H_2O_2 from Solvay plant. Successful pilot test showed the possibility to use out of specification soda Solvay as alternative coagulant in the clariflocculation process with the advantage of a concurrent removal of COD and hardness. Requirements for the use of out of specification soda for coagulation process are continuous pH control and dosage in powdered form.

In this case study, fluorescence probes were successfully tested as innovative real-time sensors to monitor the removal organic micropollutants from wastewater during GAC adsorption processes and AOP (UV/H_2O_2) treatments. It was observed that application of fluorescence sensors for micropollutants monitoring during quaternary treatments (i.e.; AOP, GAC filtration) requires regular cleaning as well as installation

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in place protected by the sunlight to avoid interferences. In the case of monitoring of adsorption processes, unchanged physical characteristics of the absorption system (i.e., carbon type, bed high) are required.

Recovery of added values compounds from industrial wastewater

Technological solutions for the recovery of high-value compounds from wastewater were investigated in the cases study in Greece, Israel and France.

Case study 4 - Greece

In the frame of Ultimate, Greener than Green (GtG) Technologies developed VesperX, a mobile unit that treats and recycles water and nutrients present in aqueous industrial by-products. Particularly, in a fruit processing wastewater, value added compounds were selectively adsorbed on a solid phase material that exhibits high affinity towards phenolic compounds relative to other chemical species. Application of the technology in the GreeK CS#4 showed the possibility of 90% recovery of water (compared to the water present in industrial by-product) and 75% recovery of total phenolic content (as of total phenolics present in industrial by-product). To scale up and replicate on a large scale this material recovery technology, it is strategical to reduce the treatment costs by developing new and low-costs adsorption media as well as convenient extraction methods. Phenols extraction was tested by three different methods, including conventional extraction, Subcritical Water Extraction and Supercritical CO_2 extraction with the last two methods resulting very promising to significantly improve the process's overall effectiveness.

Case study 6 - Israel

The case study 6 (Karmiel) tested also the innovative VesperX adsorption/extraction system developed by Greener than Green Technologies (GtG) to remove and recover polyphenols from olive mill wastewater (OMW) and to serve as pre-treatment for the following anaerobic biologic treatment process. The polyphenols adsorption on the resin was followed by extraction of high value-added compounds as a crude extract. An average reduction of 38% of the polyphenols content in wastewater was observed during the pilot tests. Even in this case, crucial factor for technology implementation and its optimal performance and replicability on large scale is the optimization of capital expenditure (CapEx), which needs research and investments on cost-effective adsorption materials and advanced extraction methods.

Case study 8 - France

At case study 8 (Chemical Platform Roussillon), to reduce the pollutant load in water from flue gas cleaning, the recovery of sulphur from flue gas of the incineration facility was tested at pilot demonstration under real conditions with different process steps involving condensation, dust cleaning and scrubbing. The objective of the process was to produce sodium bisulfite (NaHSO3) solution from SO_2 contained in flue gas of the

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hazardous incineration plant. The treatment system, which still has room for improvement, was able to obtain a recovery of 80% of organic sulfur waste. Particularly, improvements can be obtained by treating the flue gas upstream the sulphur recovery unit ensuring an effective cleaning of dust and salts and preserving the sulphur dioxide concentration. Then, crucial factors to scale-up the system and replicate it on large scale include: i) contractualization for the management of the upstream organic sulphur waste and of the downstream sodium hydrogen sulphite; ii) regulations and research grant to further promote the development of the recovery treatment system

In this case study, it was also conducted a feasibility study for molybdenum recovery from flue gas washing waters. The study was based on laboratory tests where different ion exchange resins were investigated for molybdenum adsorption capacity as well as for their capacity to restore it during the elution stage. Results showed the possibility to obtain >99% adsorption yield and under optimal condition elution yield in the range 66 – 87%. To scale up the treatment process the recommendations are related to: i) the identification of the most suitable and economic resin for the metal to be recovered, allowing both effective adsorption from the aqueous effluent and effective elution to produce a recoverable solution.

Case study 9 - Denmark

At case study 9 (Kalundborg), a concept study was conducted about the recovery of valuable compounds from the industrial wastewater, which results from enzyme, insulin and pharmaceutical protein production processes. It was concluded that reduction of the overall water consumption via hybrid-membrane schemes in the industrial production lines generate water for reuse within industry. Thereby this scheme also results in concentrates with high nutrient, ion and protein content, which serve as ideal streams for material recovery. Overall, a high recovery potential for phosphate and sulphate was simulated as apatite, gypsum or syngenite. On the contrary, inconvenient seems to be the recovery of proteins. To scale up the system, laboratory tests and pilot tests are advised to confirm the expected recovery opportunities.

EU-added value of the deliverable

Material-recovery technologies were studied in six different European countries and Israel, and the concepts and results were discussed in workshops (Kleyböcker et al. 2024a, D1.10) and allowed the project partners, together with the partners of their sister projects, to learn from each other and to identify the need for common policy recommendations. Particularly, ULTIMATE promoted, established and extended water smart industrial symbioses (WSIS) between the industrial sector and service providers of the water sector. WSIS are the foundation for a successful implementation of circular economy technologies, because one partner produces a resource or product, and the other partner has the demand for it. Table provides an overview about the obtained results during ULTIMATE project, which are related to material recovery and reuse in typical water and industrial symbiosis systems. Below, are briefly highlighted the innovative aspects of proposed ULTIMATE technologies operated at pilot scale.

Monovalent selective membranes were modified and tested to reduce the concentration of detrimental ions (Na+ and Cl-) in greenhouse wastewater. In this way, it becomes possible to recover water rich in nutrients for fertigation. However, to scale-up and replicate the technology on a large scale, still research is needed in the development of low-cost and high selective monovalent membranes.

A treatments train that includes precipitation for struvite formation and a following ammonia stripping unit was tested successfully for the recovery of nutrients from wastewater of a distillery for whisky production. Applications of this process are suggested in streams with high load of nutrients. The same conclusion is reported in other concept studies dealing with struvite precipitation described in this report.

The possibility to remove and recover polyphenols from olive mill wastewater (OMW) and from a fruit processing wastewater was successfully demonstrated by testing the innovative VesperX adsorption/extraction system developed by Greener than Green Technologies (GtG). However, research and optimization of the process are needed to reduce capital and operational costs and to boost a large-scale application of this technology.

Recovery of sodium bisulphite was successfully demonstrated by applying condensation, dust cleaning and scrubbing processes in the flue gas cleaning at a plant for the incineration of industrial liquid hazardous wastes. Economical interests and funding for recovery products and management of wastes are crucial factors to scala-up this system.

The use of out of specification soda as alternative coagulant in the clariflocculation process for treating wastewater was successfully demonstrated at pilot scale with the advantage of a concurrent removal of organic material and hardness. Use of industrial-products within a public-private partnerships/symbiosis can be used to foster circular economy and reduce costs for industrial water reuse.

Finally, ULTIMATE project tested successfully the application at pilot scale of fluorescence sensors for monitoring in real-time organic micropollutants during quaternary treatments (e.g., adsorption ad AOP) of municipal wastewater. This important result can support water utilities/managers to satisfy requirements from recent EU legislations, such as the EU regulation 741/2020 for wastewater reuse in agriculture and the new proposal of directive concerning urban wastewater treatment.

Reassuming, ULTIMATE project demonstrated and tested technologies that are in line with the ambitions of the European Green Deal its Action Plan for Circular Economy to reduce waste production and costs for their treatment and management. Particularly, different pilot plants implementing innovative technologies were tested for recovery of different materials, including fertilizers, high value compounds (i.e.; antioxidants, polyphenols, sodium bisulphite), coagulants for wastewater treatment. Creation of public-private symbiosis networks are strategical requisites for the full implementation of circularly economy routes, since they may facilitate the economical convenience to fulfil the end of waste criteria for products recovery from wastes. However, still fundings are needed to make some of the studied technologies ready for the market and to promote the creation of private-public industrial symbiosis networks.

Within ULTIMATE project, to boost the promotion and replication of the ULTIMATE technologies in Europe and worldwide, the technologies have been presented in the

Technology Evidence Base of the Water Europe Marketplace. The Water Europe Marketplace is a flexible platform for finding and sharing information about innovative economy solutions and systems in the domains Water, Energy and Materials. It is also a place to get in contact with other stakeholders in the Circular Economy, share ideas, arrange meetings and join forces. Through the scientific assessment of the technologies, as presented in this deliverable, problem owners can have access to an honest and neutral assessment of the technology performance, which may increase their confidence in the technologies and hence, their willingness to invest in them.

Table 0 Summary of material recovery technologies with TRL increase in ULTIMATE, symbiosis application, KPIs and their feasibility

CS	**ULTIMATE Technology**	**TRL**	**Material(s) recovered**	**Symbiosis application**	**Performance (KPIs)**	**Feasibility and/or successful operation**
2	Monovalent selective electrodialysis	4→6	Nutrients	Recovery of nutrients from greenhouse wastewater	Nutrient recovery up to 30% (NO_3^-), 33% (K^+), 70% (Ca^{2+}), 76% (Mg^{2+}), 84% (SO_4^{2-}), 93% (PO_4^{3-})	Successful system operation
3	Clariflocculation	5→7	Soda out of specification (industrial by-product)	Use of industrial by-products for wastewater treatment	100% replacement of commercial coagulant	Successful pilot operation
3	Adsorption	4→6	Hydrochar from sewage sludge	Use of industrial by-products for wastewater treatment	The material activated at lab scale has very good adsorption capacity	Hydrochar activation procedures are not available for pilot scale application
3	Fluorescence sensors to monitor Adsorption and AOP (UV/H_2O_2) quaternary treatments	4→7	Treated wastewater, H_2O_2 from Solvay plant	Water quality monitoring to assure compliance with EU regulation for reuse	Observed correlations with six organic micropollutants Promising performance in water quality monitoring	Successful pilot operation
4	Hybrid adsorption/subcritical water extraction (VesperX)	5→7	Value added Compounds (i.e., antioxidants)	Recovery of high-value products from industrial wastewater	75% recovery of total phenolic content in the food industry wastewater	Successful pilot operation
5	Aquavite(R).	-	Struvite	Recovery of fertilizers from industrial wastewater	-	Concept study
5	Hydrothermal carbonization (HTC)	-	Hydrochar from brewer's spent grain and sewage sludge	Recovery of fertilizers from industrial wastewater	-	Concept study

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6	Adsorption on resins and extraction	4→6	Value added Compounds (i.e., polyphenols)	Recovery of high-value products from industrial wastewater	Reduction of 38% of the polyphenols content in wastewater	Successful pilot operation Resin extraction operated in the lab
7	Struvite precipitation and ammonia strippring	5→7	Fertilizers	Recovery of fertilizers from industrial wastewater	80% nitrogen recovery 80% phosphorus recovery	Successful pilot operation
8	Condensation, dust cleaning and scrubbing	4→6	Sodium bisulfite ($NaHSO_3$)	Recovery of sodium bisulfite and reduction of pollutants load in water from flue gas cleaning in industry	80% organic sulfur waste recovery	Successful pilot operation
8	Ion exchange resins	-	Molybdenum	Metals recovery from flue gas washing waters in industry	-	Concept study
9	Concentration by hybrid-membrane schemes and precipitation	-	Value added Compounds (i.e., phosphate and sulphate)	Recovery of high-value products from industrial wastewater	-	Concept study

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Abbreviations

AAT	Advanced anaerobic treatment: high-rate immobilised anaerobic reactor
AC	Activated carbon
AD	Anaerobic digestion
AD	Anaerobic Digestion
AGb	AGROBICS LTD
AnMBR	Anaerobic membrane bioreactor
AnMBR	Anaerobic membrane bioreactor
AOPs	Advanced oxidation processes
ASM	Activated sludge model
ATEX	Atmospheres explosibles
BSGs	Brewer's spent grain
CAPEX	Capital expenditure
CE	Circular Economy
CECs	Contaminants of emerging concern
COD	Chemical Oxygen Demand
CS	Case Study
DA	Poly-dopamine
DAF	Dissolved air flotation
EBCT	Empty bed contact time
EC	Electrical Conductivity
ED	Electrodialysis
ED	Electrodialysis
EGSB	Expanded granular sludge bed reactor
EIC	Extracted Ion Chromatogram
ERS	Electrode rinse solution
ERS	Electrode rinse solution
GAC	Granular activated carbon
GSR	Galilee Society Institute of Applied Research
GtG	Greener Than Green Technologies AE
HTC	Hydrothermal carbonization
IC	Internal circulation
IEMs	Ion-exchange membranes
IS	Industrial symbiosis
KPI	Key Performance Indicator
LOD	Limit of detection
MBR	Membrane Bio-Reactor
MEK	Mekorot company
MLD	Minimal liquid discharge
MSED	Mono selective electrodialysis

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MSED	Monovalent selective electrodialysis
NF	Nanofiltration
OLR	Organic Loading Rate
OMW	Olive mill wastewater
P&ID	Piping and instrumentation diagram
PAC	poly aluminium chloride
PHAs	Polyhydroxyalkanoates
PLC	Programmable logic controller
PPP	Public-private partnership
RF	Response factor
RO	Reverse osmosis
SCADA	Supervisory Control and Data Acquisition
SFE	Subcritical Fluid Extraction (SFE)
SOP	Standard Operating Procedure
SubW	SWE with 100% water
SWE	Subcritical Water Extraction
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TRL	Technology Readiness Level
TS	Total Solid
TSS	Total Suspended Solids
UASB	Up-flow anaerobic sludge blanket
UF	Ultrafiltration
UV	Ultraviolet
UV_{254}	UV absorbance at 254 nm
VACs	Value Added Compounds
WRF	Water Reclamation Facility
WSIS	Water-smart industrial symbiosis
WW	Wastewater
WWTP	Wastewater Treatment Plant
XRD	X-ray diffraction

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1. Introduction

Water scarcity is a worldwide concern affecting both domestic and industrial users that can potentially “compete” for the consumption of water, thus delaying the continuous development of society (Thomé et al., 2019). It is thus necessary to transform the water sector to a model based on Circular Economy (CE) and water-smart principles (WE, 2022). CE applied to water is based on improving resource efficiency by reusing treated wastewater, taking advantage not only of the reclaimed water, but also of the valuable compounds contained in it, also minimising waste production, reducing (and recovering) energy, and decreasing environmental impacts of current economic activities (Nika et al., 2020).

Industrial symbiosis (IS), and more specifically, water-smart industrial symbiosis (WSIS) is a particular form of Circular Economy applicable to industrial contexts where wastewater plays a key role as reusable and exchangeable resource. With the creation of closed cycle links, industrial symbiosis seeks to design an industrial system characterised by functional interdependence relationships in which the waste products of a process become a valuable input to the production lines of other companies to create important advantages for the business system and the community, both in economic and environmental terms. For instance, industries can be strongly favoured by reusing urban wastewater for specific process operations (such as air cooling, cooling of metallurgical workpieces, various washing operations in the textile industry etc.) and urban WWTP can provide quite stable source of water unlike natural sources, especially in water-scarcity regions. Apart from this, wastewater contains some materials (nutrients, cellulose, organic matter, etc.) that can be recovered, reused or transformed in energy or bio-products (Figure 1):

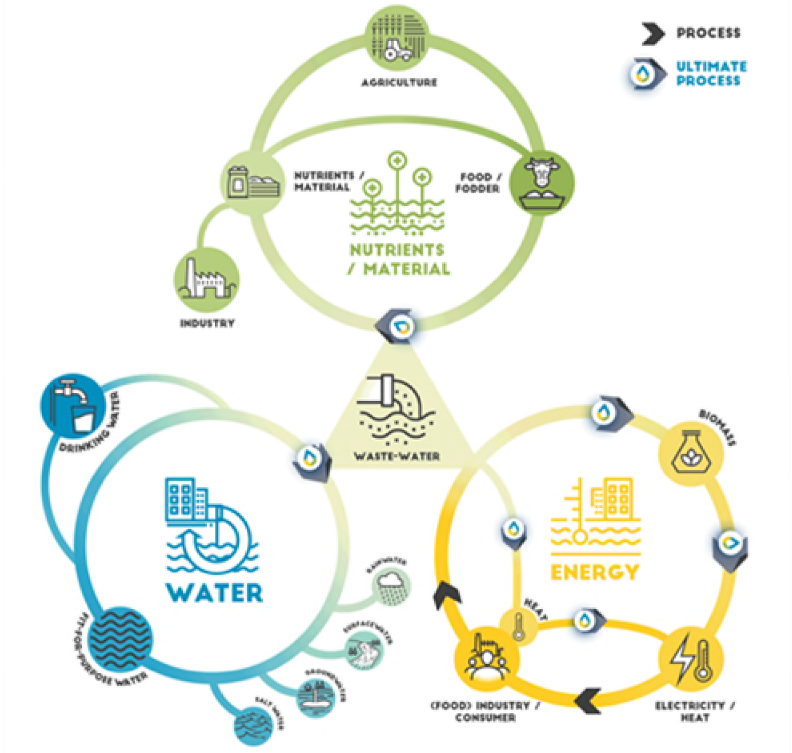

Figure 1. Water, material and energy recovery from wastewaters: ULTIMATE icon indicates, where the ULTIMATE technologies contribute to recover the corresponding products.

In ULTIMATE project, 24 circular technologies were developed, investigated, optimized and demonstrated in 9 different case studies across Europe and Israel (Figure 2). These technologies aim to recover water, energy, and/or materials from wastewater sources (industrial and/or urban), following WSIS approach.

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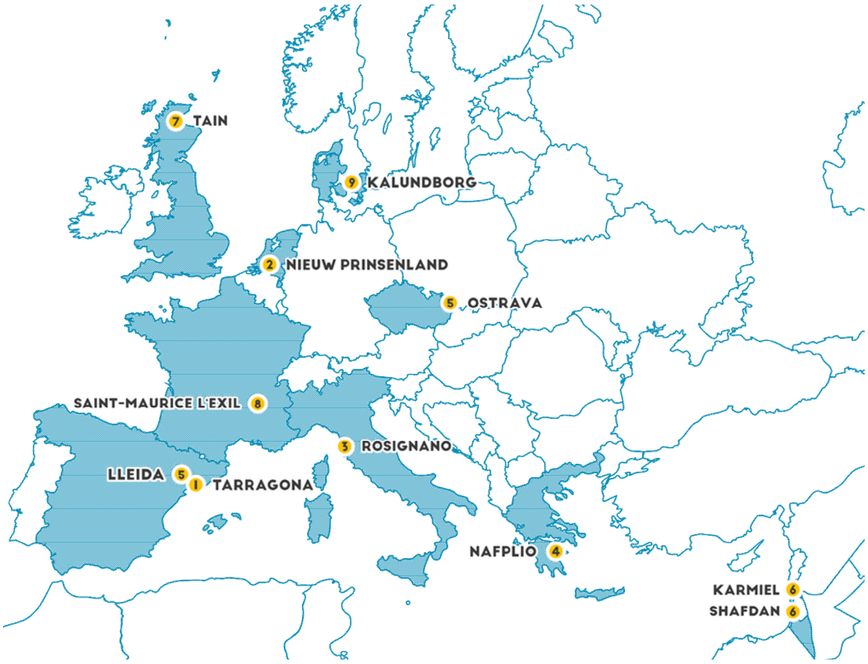

Figure 2. Left: Water Smart Industrial Symbioses (WSIS) between the industrial and water sector; right: location of ULTIMATE case studies

This deliverable is one of three deliverables presenting the results of the ULTIMATE technologies and focuses on material recovery. D1.3 (Naves Arnaldos et al. 2024) and D1.4 (Kleybocker et al. 2024) deal with water recovery and reuse and energy recovery, respectively.

Table 1 provides an overview about the case studies and material recovery technologies, which were conceptualized, developed, optimized and demonstrated in ULTIMATE.

Table 1 Overview about the material recovery related case studies in ULTIMATE showing the resource for material recovery, the used technology and the end product. Concept studies are indicated in grey.

Case study	Resource	Technology	Recovered materials
CS2 Nieuw Prinsenland	Greenhouse wastewater	Monovalent selective electrodialysis	Nutrients in wastewater with tolerable salinity
CS3 Rosignano	Industrial by products, Municipal wastewater	Clariflocculation, Adsorption, Advanced Oxidation Pocesses, Fluorescence sensors to monitor micropollutants	Reagents and material for water treatment, treated wastewater
CS4 Nafplio	Fruit & Vegetable processing wastewater	hybrid adsorption/subcritical water extraction	high-value products, e.g. antioxidants
CS5 Lleida	Brewery wastewater	Aquavite® for struvite recovery, Hydrothermal Carbonization	Fertilizers
CS6 Karmiel	Olive mill wastewater	Adsorption on resins	high-value products, e.g. polyphenols
CS7 Tain	Distillery Wastewater	Struvite precipitation, ammonia stripping	Fertilizers
CS8 Saint Maurice	Industrial liquid waste	Condensation, dust cleaning and scrubbing	Sulphur products
CS8 Saint Maurice (conceptual study)	Industrial liquid waste	Ion exchange resins	Heavy metal (i.e., Molibdeno)
CS9 Kalundborg (conceptual study)	Industrial wastewater	Concentration by hybrid-membrane schemes and following precipitation	high-value products, e.g. phosphate and sulphate

The objective of this deliverable is to explain the innovative ULTIMATE material recovery solutions, to present their performance to demonstrate their feasibility and to provide recommendations for best practice implementation and application of the technologies under different process conditions.

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2. ULTIMATE technologies and new approaches for material recovery

The next paragraphs present the concepts and outcomes of the case studies related to material recovery.

2.1. Recovery of nutrients from greenhouse wastewater in Nieuw Prinsenland (NL)

2.1.1. Case study and ULTIMATE concept

Coöperatieve Tuinbouw Water Zuivering de Vlot is a wastewater treatment facility located at ‘s-Gravenzande treating wastewater (40-60 m^3/h) from 160 hectares (60 companies) of greenhouses mainly growing ornamental and vegetable crops. In the coming years, this sector is faced with water availability (need for alternative high-quality irrigation water) and discharge regulation challenges (removal of plant protection products by 2021 followed by limitations in nutrient discharge by 2027). Thus, De Vlot (Figure 3) aims to explore water and nutrient reuse opportunities from their wastewater (approx. 10% of the total water input) by optimizing their system for internal symbiosis within their own facility and external symbiosis with neighboring greenhouses and industries (supported by extensive survey conducted in 2021), to reach (nearly) zero liquid discharge.

Figure 3. Greenhouse Horticulture in the Netherlands (left) and Wastewater Treatment Plant at De Vlot (right).

In ULTIMATE, nutrient recovery from De Vlot will be demonstrated as follows: The wastewater stream from the greenhouses, which contains valuable nutrients including Ca2+, Mg2+, K+, SO42-, NO3-, and PO43- that can be retained/recovered, is currently discharged to the sewer. Reclamation of the (water and) nutrients is hampered by the risk of accumulating salinity (specifically Na+<0.1 mmol/l) and the additional requirement to selectively separate, concentrate and recover valuable nutrients from the undesired ones. In ULTIMATE, advanced electro-chemical membrane wastewater treatment technologies are investigated for retention/recovery to achieve maximum nutrient recovery and reach (near) zero liquid discharge (Figure 4). Here,

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electrodialysis (ED) utilizing state-of-the-art commercial monovalent selective membranes, as well as a one-step separation process (by employing modified novel Na+/K+ selective membranes) are investigated.

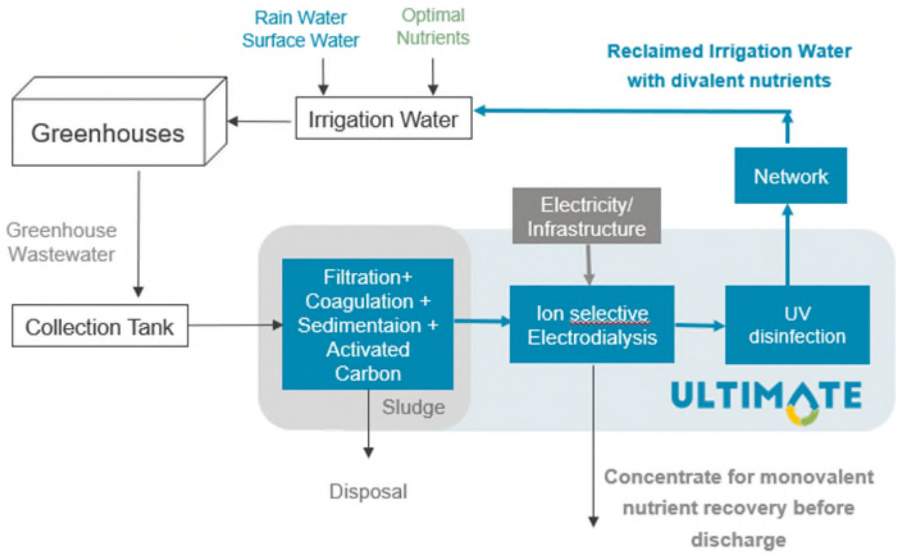

Figure 4. Treatment scheme and proposed ULTIMATE technology solution for the wastewater treatment plant at De Vlot.

Electrodialysis is an electrochemical separation process that can (selectively) transport ions through electrostatically charged ion-exchange membranes (IEMs), driven by an electrical potential difference (applied electric field). In contrast to other separation technologies that separate large water volumes from solutes, electricity-driven processes remove ions, enhancing ion-selective recovery (Tarpeh and Chen, 2021). ED is a well-established technology with applications in treating brackish water, industrial wastewater, municipal wastewater, table salt production, heavy metals removal, and acid and bases production (Strathmann, 2010). The increase in popularity and application of ED has been accelerated by its selective ion separation potential for high product (e.g. nutrient) recovery, compatibility with renewable energy, low fouling potential, improved process control and development of novel IEMs with improved target ion selectivity. ED is a promising technology for the application of treating and potentially reusing nutrients from greenhouse wastewater, as it can selectively remove ions such as sodium (which is harmful for crop growth) and retain/separate nutrients (which can be used as fertilizers).

For optimizing nutrient recovery, the (selective) membrane plays an important role. Most ED applications employ ion-exchange membranes (IEMs) (Guleria et al., 2024). However, conventional IEMs are limited in ion selectivity; thus, important plant nutrients, including potassium (K+), calcium (Ca2+), magnesium (Mg2+), nitrate (NO3-), sulphate (SO42-), phosphate (PO43-) are transported along with the unwanted Na+ ions in the concentrate. Monovalent selective electrodialysis (MSED) utilizing monovalent selective membranes to separate divalent and monovalent ions is a promising alternative to selectively retain divalent nutrients in reclaimed water, thus facilitating reuse of these nutrients. Studies with MSED at lab scale have demonstrated

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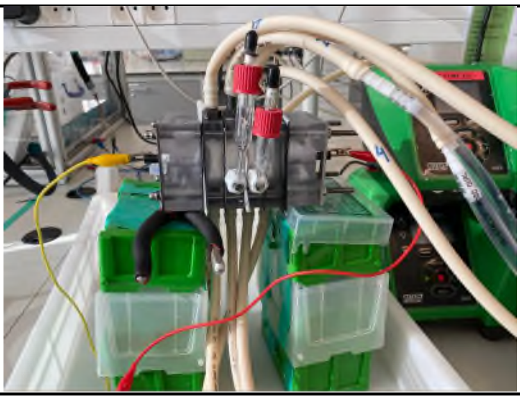
the separation of monovalent including Na+ and K+, and retention of divalent Ca2+ and Mg2+ ions for reuse as irrigation water from wastewaters such as greenhouse wastewater (Andab et al., 2021). In this case study, the application of MSED to the effluent of the wastewater treatment at De Vlot was investigated. This technology had a starting TRL of 4. Additionally, to further optimize resource recovery and move toward minimal liquid discharge (MLD) in the greenhouse horticulture sector, selectively differentiating between Na+ and K+ ions is required. However, the effectiveness of currently available conventional and selective commercial ion-exchange membranes is limited by their physical and chemical properties. Development of such membranes by modification or synthesis is being researched, and in this case study, Na+/K+ selective membranes were fabricated using a promising methodology from extensive literature research. Thus, in ULTIMATE, the efficacy of electrodialysis with monovalent selective commercial membranes and modified Na+/K+ selective membranes were investigated and demonstrated, for nutrient recovery from greenhouse wastewater.

Electrodialysis (ED) set-ups for nutrient recovery from commercial and developed Na^+/K^+ selective membranes

Mono-Selective Commercial Membranes (MSED)	**Na^+/K^+ selective membranes**
PC Cell ED stack	6-compartment ED cell
Neosepta membranes (10 – 20 cell pairs (scalable))	Modified Fujifilm Type 2 membranes with crown ethers (15-crown-5 and 18-crown-6)
Batch mode (active membrane area 64 cm^2)	Batch mode (active membrane area 16 cm^2)
Flow rate 1-2 cm/s	Flow rate 1-2 cm/s
50% water recovery	50% water recovery
	

For ED and processes founded on ED, the treatment potential can range from below 100 m3/d to 20,000 m3/d (Strathmann, 2010). The two main ED geometric patterns

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include sheet flow and the tortuous path, and it can operate in batch or continuous mode (Gurreri et al., 2020). Table 2 provides the range of typical operating parameters.

Table 2 Typical range for ED operating parameters.

Parameter	Units	Range	Reference
Cell pairs	no.	<10 (bench) – 100s (pilot/full)	**(Gurreri L, 2020)**
Active area per membrane	m^2	0.01 – 0.06 (upto 1)	**(Gurreri L, 2020) , (M. Demircioglu, 2003)**
Spacer thickness	mm	0.3 - 2	**(Campione, et al., 2018), (M. Demircioglu, 2003)**
Fluid velocity	cm/s	1-10 (upto 50)	**(Campione, et al., 2018)**
Applied voltage	V	7-30 (lab scale)	**(Sajjad Al-Amshawee, 2020)**
Current density	mA/cm^2	5 - 60	**(Rubaba Mohammadi, 2021)**
Running time	h	24, 30, 55, 72	**(Sajjad Al-Amshawee, 2020)**

2.1.2. Results of new approaches

ED set-up with monovalent selective membranes (MSED)

The performance of ED in nutrient retention for reuse was assessed with the MSED set-up with various water qualities representative of greenhouse wastewater.

Figure 5 illustrates the concentrations of various ions (Na+, K+, Ca2+, Mg2+, Cl-, NO_3-, $SO_4$2-, $PO_4$3-) in the recovered water stream (the diluate from the membrane process).

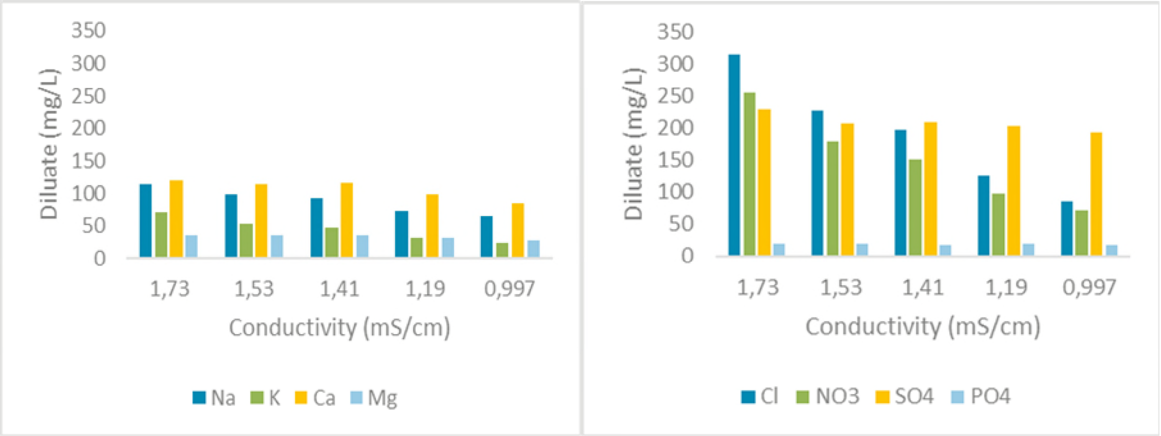

Figure 5. Reduction in concentration of ions as conductivity decreases during treatment of greenhouse wastewater with MSED: a) cations; b) anions.

As conductivity decreases from 1.73 to 0.98 mS/cm, the concentration of the cations - Na+, K+, Ca2+, Mg2+ also decreases, indicating effective ion removal. The removal rates recorded were 44%, 67%, 29% and 23%, respectively for Na+, K+, Ca2+, Mg2+, showing higher retention of divalent ions in the diluate for reuse. Among the

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monovalent ions, it is interesting to note that removal of Na+ is lower than K+, possibly due to the higher initial concentration of Na+ (114 mg/l) over K+ (71 mg/l) or possibly some Na+ leakage from the electrode rinse solution (ERS) with Na2SO4 when very low concentrations of diluate are reached. However, it can be expected that this effect is minimized when the membrane set-up is upscaled, resulting in higher Na+ removal. Overall, for cations, the Neosepta mono-selective membranes demonstrated 70-75% retention of divalent nutrients (Ca2+, Mg2+) for reuse, for the current operating conditions. And, in the concentrate, 45-70% of the monovalent ion are transported. For the anions, removal rates were 73%, 72%, 15% and 6% for Cl-, NO_3-, $SO_4$2-, $PO_4$3- respectively. This again shows higher retention of divalent ions in the diluate for reuse. Among the monovalent ions, both Cl- and NO_3- show almost identical removal percentages. Thus, for the anions, the Neosepta mono-selective membranes demonstrated 85-95% retention of divalent nutrients ($SO_4$2-, $PO_4$3-) for reuse, for the current operating conditions. And, in the concentrate, 70% of the monovalent ions are transported. These results underscore the effectiveness of MSED in reducing ion concentrations and improving nutrient reuse potential, with monovalent ions detrimental to plant growth such as Na+ and Cl- being removed more efficiently than divalent and trivalent ions, that can be recirculated and reuse as nutrients in the diluate.

Furthermore, the ionic transport was assessed based on normalized concentrations to understand their removal behaviour (Figure 6). Na+ dropped significantly to 0.56 by the 105th minute, and K+ levels even more steeply to 0.34, demonstrating the membranes' higher removal for these monovalent ions. In contrast, divalent ions such as Ca2+ and Mg2+ showed lower transport, up to 0.71 and 0.76 respectively, indicating a preference for monovalent ions over divalent ions. Similarly for anions, Cl- and NO3- also exhibited low values of 0.27 and 0.28, highlighting the membranes' effectiveness in removing monovalent anions. However, SO42- and phosphate PO43- displayed moderate to minimal removal efficiencies, with retained levels of 0.85 and 0.94 respectively being observed, consistent with the membranes' lower affinity for divalent anions. These trends corroborate the results observed in the ionic removal percentage for MSED.

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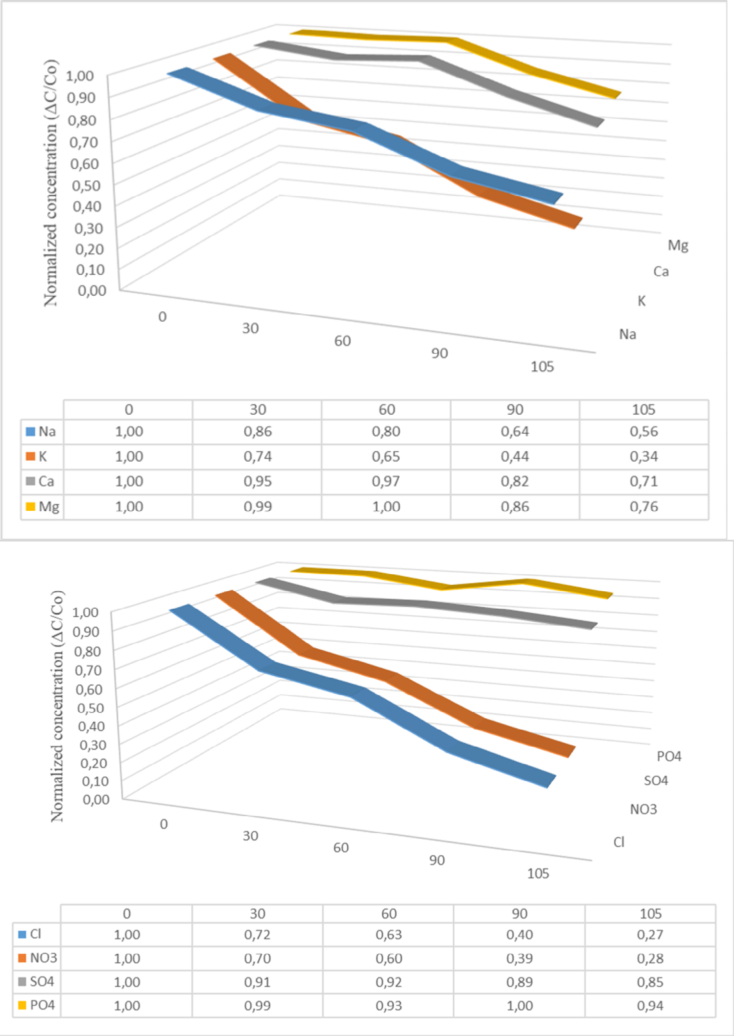


	0	30	60	90	105
■ Na	1,00	0,86	0,80	0,64	0,56
■ K	1,00	0,74	0,65	0,44	0,34
■ Ca	1,00	0,95	0,97	0,82	0,71
■ Mg	1,00	0,99	1,00	0,86	0,76

	0	30	60	90	105
■ Cl	1,00	0,72	0,63	0,40	0,27
■ NO3	1,00	0,70	0,60	0,39	0,28
■ SO4	1,00	0,91	0,92	0,89	0,85
■ PO4	1,00	0,99	0,93	1,00	0,94

Figure 6. Normalized transport of cations (above) and anions (below) over time in the MSED set-up.

The potential amount of nutrients that can be reclaimed is estimated based on the performance of the MSED and results from deliverable D1.3 (for ED with conventional IEMs). Table 3 gives an overview of the amount of nutrients in t/y and g/m3 that can be reused. The Fujifilm Type 10 conventional membrane shows nutrient reclamation capacities for various ions, including potassium (3 t/y or 21.6 g/m^3), calcium (4.47 t/y or 35.2 g/m^3), magnesium (1.7 t/y or 13.44 g/m^3), nitrate (11 t/y or 92.82 g/m^3), sulphate (9.6 t/y or 75.5 g/m^3), and phosphate (1 t/y or 8 g/m^3). In comparison, the Neosepta Mono-selective membrane demonstrates slightly higher values for potassium (3.07 t/y or 24.14 g/m^3) and significantly higher values for calcium (19.58 t/y or 154 g/m^3), magnesium (3.43 t/y or 27 g/m^3), sulphate (24.64 t/y or 194 g/m^3), and phosphate (2.39 t/y or 18.8 g/m^3). The Neosepta membrane does show slightly lower nitrate recovery (9.76 t/y or 80 g/m^3), however, this can be attributed to the lower initial concentration of nitrate in the Neosepta membrane runs, suggesting the importance of feed concentration on recovery potential of the nutrients. These estimations highlight the Neosepta membrane's higher potential in reclaiming nutrients (specifically divalent ions) compared to conventional membranes. It should be noted that the operation of the ED and MSED set-up (for the data used to estimated nutrient reclamation potential in Table 3), were based on water recoveries of 50%. With higher water recoveries (up to 80%), higher nutrient concentrations can be obtained. Moreover, this study also provides an overview of the concentrate composition from the set-ups used. This aids in assisting the selection of additional recovery technologies for further nutrient valorisation.

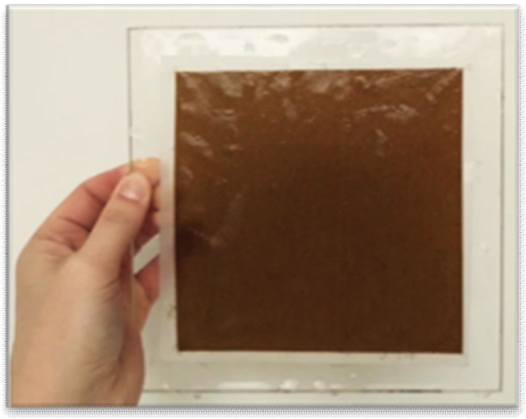
Table 3 Estimated nutrient recovery potential with conventional and mono-selective ion-exchange ED membranes.

Membrane	**Unit**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**NO_3^-**	**SO_4^{2-}**	**PO_4^{3-}**
Fujifilm Type 10 IEM	ton/y	3	4.47	1.7	11	9.6	1
	g/m^3	21.6	35.2	13.44	92.82	75.5	8
Neosepta MSED IEM	ton/y	3.07	19.58	3.43	9.76	24.64	2.39
	g/m^3	24.14	154	27	80	194	18.8

ED with modified Na^+/K^+ selective membranes

In order to achieve better separation performance, in ULTIMATE the development of Na^+/K^+ selective membranes was investigated. The development potentially offers a significant advancement in electrodialysis technology for (near) complete nutrient valorisation from greenhouse wastewater. On the basis of a review of the state-of-the-art, surface modification with crown ethers was identified as the most promising development approach for Na+/K+ separation membranes with potential for application at a relevant scale under process conditions. This was concluded on the basis of a selectivity-resistance-scalability assessment of the available development methods for selective membranes.

Following the selected surface modification approach, two commercial membranes were successfully modified via co-deposition with crown ethers 4′ -aminobenzo-15-crown-5 (15C5) and 4′ -aminobenzo-18-crown-6 (18C6) and poly-dopamine (DA) (



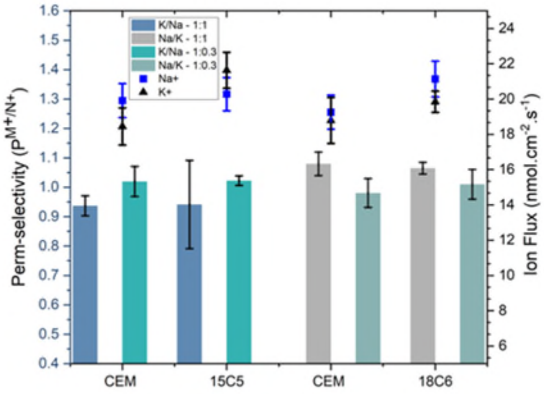
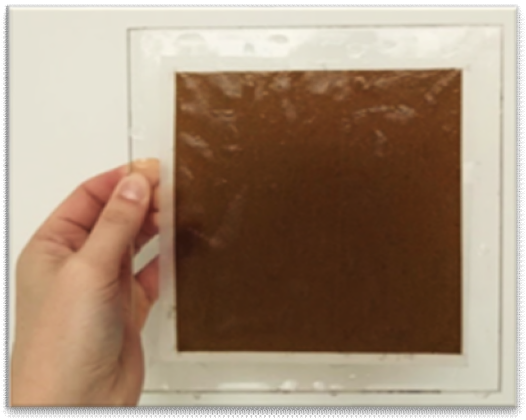


Figure 7). The modified membranes were characterized, and their separation performance was evaluated under real greenhouse operating conditions. The separation performance results revealed low Na⁺/K⁺ selectivity (



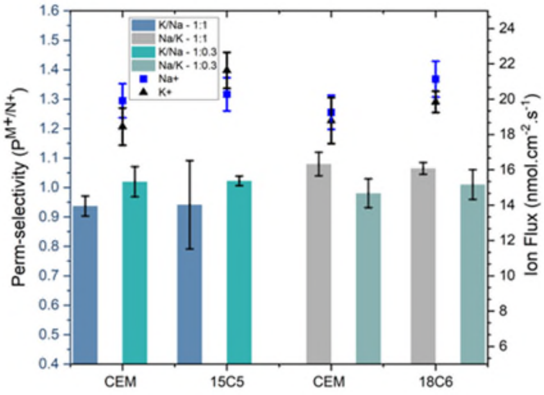


Figure 7). Marginally enhanced selectivity for K+ was observed with the 15C5 modified membrane. This enhanced selectivity can potentially be attributed to partially dehydrated ion size exclusion or mobility retardation due to stable complexation with the target ion. The exact mechanisms behind the selectivity were not further investigated, as the selectivity achieved is insufficient to meet the requirements of the greenhouse application.

It was concluded that while the modification approach has potential, it does not yet achieve the desired differentiation between Na+ and K+ ions. Additionally, the challenge of scaling up this technology for practical applications remains a significant hurdle. To better understand the potential of crown ether-functionalized membranes for selective Na+/K+ separation, further research should focus on the incorporation of crown ether ligands into the polymer network. Optimized copolymerization, involving the controlled integration of various functional groups within the membrane, could. Furthermore, the development process can significantly benefit from machine learning (ML)-assisted membrane design, specifically in combination with computational methods and data augmentation techniques. Finally, process technologies such as Donnan Dialysis and ion-exchange could be explored for efficient Na+/K+ separation for practical application from greenhouse wastewater.

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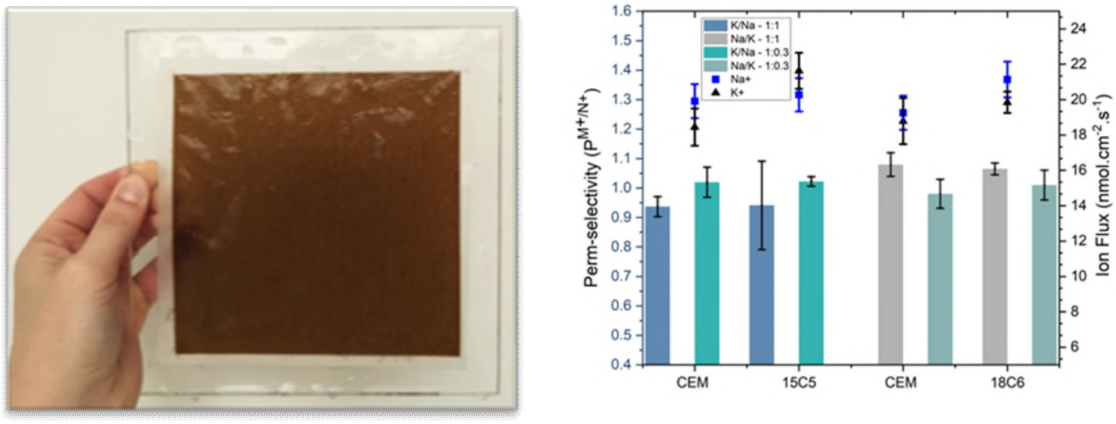

Figure 7. Image of the crown ether- modified membrane developed (left) and Perm-selectivity and ion flux of the non-modified and modified membrane (15C5 and 18C6) conducted with an equimolar NaCl and KCl solution (Na:K; 1:1) and a greenhouse wastewater solution (Na:K; 1:0.3) (right).

The demonstration and results show that there is potential in ED as a solution for nutrient reclamation from greenhouse wastewater. The results of this case study are summarised using the ULTIMATE KPI's in *Table 4*.

Table 4 Overview of the ULTIMATE KPI's for nutrient recovery for case study 2.

KPIs specified in GA	**Achievable targets - Full scale**
Material recovery (30%)	NO_3^-(30%), K^+(33%), Ca^{2+} (70%), Mg^{2+} (76%), SO_4^{2-} (84%), PO_4^{3-}(93%) (with MSED, when compared to nutrients contained in wastewater)

In comparison to the baseline situation with no nutrient recovery (Figure 2), the ultimate solution can achieve up to NO3-(30%), K+(33%), Ca2+ (70%), Mg2+ (76%), SO42-(84%), PO43-(93%) nutrient reuse (reuse percentages calculated in relation to the total mass of nutrients contained in the effluent of the De Vlot greenhouse wastewater treatment plant). These figures indicate that while the ED process could allow for recovery of a substantial portion of these essential nutrients in a reused water stream, there is still significant room for improvement to maximize recovery efficiency. Enhanced techniques and further optimization/additional recovery step are necessary to increase the recovery rates and fully capitalize on the nutrient content in greenhouse wastewater

2.1.3. Conclusion

The case study investigated the potential of electrodialysis utilizing commercial state-of-the-art mono-selective (MSED) and modified commercial membranes, to reclaim nutrients from greenhouse wastewater. Site experiments with MSED showed nutrient retention for reuse up to NO3-(30%), K+(33%), Ca2+ (70%), Mg2+ (76%), SO42- (84%), PO43-(93%), compared to nutrients contained in the wastewater treatment plant effluent. Furthermore, the potential of separating Na+/K+ using electrodialysis for circular greenhouse wastewater reuse was explored, focusing on developing Na+/K+ selective membranes for this application. Surface modification with crown ethers (15-crown-5 and 18-crown-6) was identified as the most promising approach based on a literature scan. Commercial membranes were successfully modified and characterized. However, the modified membranes showed low selectivity, with only marginally enhanced K+ selectivity observed with the 15-crown-5 modified membrane over the non-modified membrane. The selectivity achieved is currently insufficient for the greenhouse application. Future research could focus on enhancing membrane selectivity by incorporating crown ether ligands into the polymer network and optimizing copolymerization with various functional groups to enhance ion separation efficiency by selectively binding Na+ and K+ ions. Additional recommended technologies include target specific ion-exchange and Donnan Dialysis to achieve further ion selective recovery. Operational challenges included careful membrane maintenance and conditioning before application. The potential for reuse of the nutrients investigated at De Vlot were estimated as follows: potassium (3.07 t/y or 24.14 g/m^3), calcium (19.58 t/y or 154 g/m^3), magnesium (3.43 t/y or 27 g/m^3), sulphate (24.64 t/y or 194 g/m^3), phosphate (2.39 t/y or 18.8 g/m^3), and nitrate (9.76 t/y or 80 g/m^3). This highlighted the potential of MSED in retaining divalent nutrients for reuse in the recovered water stream compared to conventual IEMs. This promotes circularity and symbiosis between in the greenhouse horticulture sector to reclaim nutrients and reduce the total discharge from greenhouse wastewater. Further optimization of the processes and exploration of concentration, along with assessment of potential revenue (D1.2) from the nutrients recovered from the wastewater can help realize maximum benefits.

Crucial factors for the recovery of nutrients from greenhouse wastewater

- Selective electrochemical membrane processes such as MSED have the potential recover nutrients ions from greenhouse wastewater. Discharge management (technical & regulatory) such as for monovalent ion recovery/treatment before discharge needs more investigation.
- Concentration of the feed water impacts the concentration of nutrient recovery. Higher concentration for recovery is economically beneficial.

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- For complete nutrient recovery robust and proactively monovalent-monovalent ion selective membranes are promising, however, their selectivity and feasibility is still a challenge. Furthermore, the cost of selective ion-exchange membranes and energy required can be bottleneck for economic feasibility.
- Criteria for reuse directive/selling permits should be more pro-recovery and needs more clarity.
- The final uptake of the reclaimed nutrients would need testing, incentive and trust building to overcome the risk-averse nature of farmers/end-users in this sector.

2.2. Use of by-products of local industries for wastewater treatment in Rosignano (IT)

2.2.1. Case study and ULTIMATE concept

One practical example of WSIS is the ARETUSA public-private partnership (PPP) that was established in 2001 in the region of Tuscany, Italy. It is formed by a water utility (ASA Livorno), a technology provider (Termomeccanica Ecologia), and a chemical industry (Solvay Chimica Italia). The main objective of the Consortium's agreement is to increase the amount of reused wastewater coming from two municipal wastewater treatment plants (WWTPs) nearby, i.e. Cecina and Rosignano WWTPs. In this respect, the reclamation plant of Aretusa produces 3,8 Mm^3/y of reclaimed water to be reused for the industry, mainly for the cooling towers, but also for agricultural irrigation.

To do so, it is necessary to reach the quality standards required by both the company and the legislation. In this respect, incoming update of the wastewater treatment directive foresees to increase the demands for the removal of contaminants of emerging concern (CECs) such as pharmaceuticals, personal care products and many others, which are common in the effluents of municipal WWTPs and can hinder the safe use of reclaimed water (Sgroi et al., 2018; Radini et al., 2023; Tran et al., 2018). (Lenka et al., 2021; Wu et al., 2022). In general, there is no single technology to fully allow the reuse of urban wastewater, but it takes place by combining different processes or technologies to reach the appropriate water quality, such as biological or physic-chemical treatment, clarification, filtration, disinfection and/or advanced oxidation processes (AOP).

CS3 of ULTIMATE focuses not only on maximizing the amount of reclaimed water recovered for industrial reuse (which is explained in detail in D1.3, i.e., Naves et al., 2024), but also on recovering by-products from Solvay chemical industry to be used for advanced wastewater treatment. In this respect, the technologies tested, and materials recovered in this case study are:

- Clariflocculation: using "Soda Solvay light", which is out of specification for Solvay; granulated limestone rocks ("precotto"), which are only partially calcinated and slacked, or their mixture.

- Advanced oxidation process (AOP): Solvay produces H2O2, which is a promoter of OH radicals when coupled with UV radiation. This H2O2/UV technology has been tested as improved advanced oxidation process (AOP).

- Adsorption: Activated hydrochar from hydrothermal carbonization (HTC) of sewage sludge was used as adsorbent in GAC process. In addition, coupled to this process, UV absorbance at 254 nm and fluorescence sensors were tested as surrogate parameters to monitor the performance of the tested quaternary treatment and to monitor the quality of the effluent water.

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In Figure 8 is reported the schematic of Aretusa Water Reclamation Facility (WRF) with indication of the technologies where industrial by products (i.e.; Solvay by-products, alternative adsorbent material, H2O2) have been tested for wastewater treatment. In Figure 8 is also indicated the monitoring point of water quality by the innovative spectroscopic sensors.

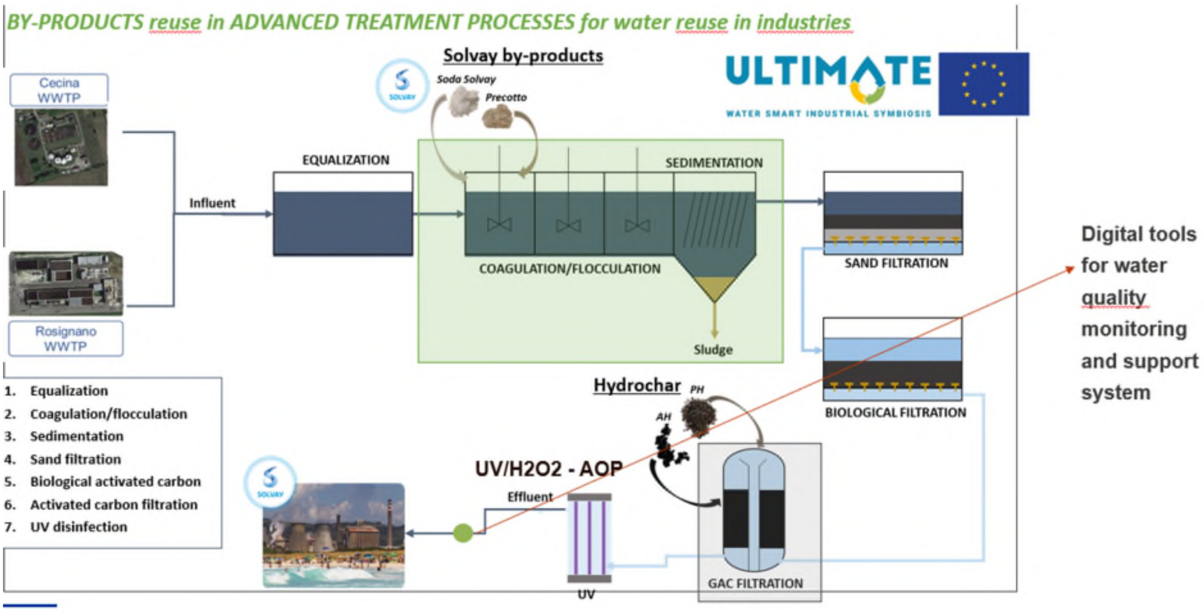

Figure 8: Schematic of ARETUSA WRF with indication of tested industrial by-products for wastewater treatment

Due to technical issues, some of the full-scale technologies for wastewater treatment are out of service at Aretusa WRP. In this study, available industrial by-products and alternative material for water treatment were tested at pilot-scale.

Clariflocculation Pilot Plant

The clariflocculation unit at ARETUSA WRF has the scope to reduce the hardness of water and the content of COD to allow reuse of treated wastewater for cooling the evaporation tower of the Solvay plant. Poly Aluminum Chloride is used as coagulant in the process. Objective of this research was to test Solvay by products (i.e., Soda Solvay light, which is out of specification for Solvay and granulated limestone rocks “precotto”), as alternative coagulants for the clariflocculation process. The use of soda and lime as coagulants provides the advantage to remove organic material and hardness during the same treatment process.

Chemical precipitation is one of the more common methods used to soften water. The most common chemicals used are lime (calcium hydroxide, $Ca(OH)_2$) and soda ash (sodium carbonate, Na_2CO_3). Lime is used to remove chemicals that cause carbonate hardness (temporary hardness). Soda ash is used to remove chemicals that cause non-carbonate hardness (permanent hardness).

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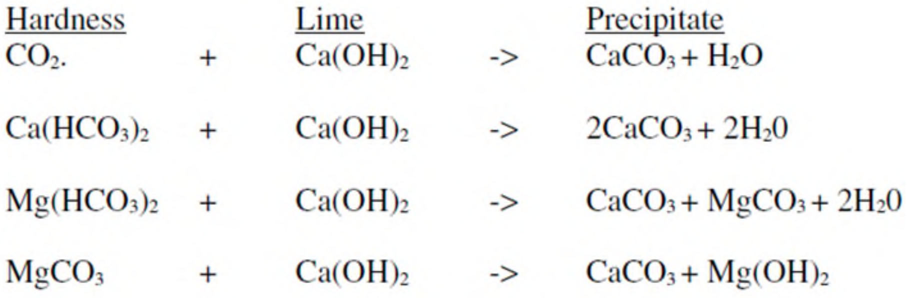
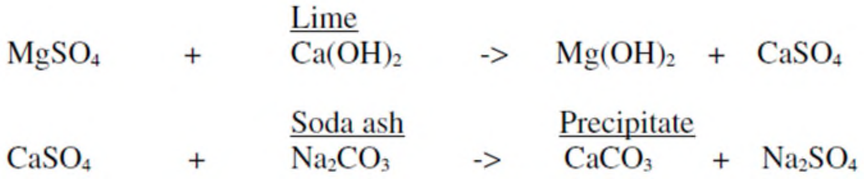
When lime and soda ash are added, hardness-causing minerals form nearly insoluble precipitates. Calcium hardness is precipitated as calcium carbonate ($CaCO_3$), whereas magnesium hardness is precipitated as magnesium hydroxide ($Mg(OH)_2$). These precipitates are then removed by conventional processes of coagulation/flocculation, sedimentation, and/or filtration. As precipitates are very slightly soluble, some hardness remains in the water-usually about 50 to 85 mg/L (as $CaCO_3$). This hardness level is desirable to prevent corrosion problems associated with water being too soft and having little or no hardness.

Lime addition



Hardness		Lime		Precipitate
CO_2.	+	$Ca(OH)_2$	->	$CaCO_3 + H_2O$
$Ca(HCO_3)_2$	+	$Ca(OH)_2$	->	$2CaCO_3 + 2H_20$
$Mg(HCO_3)_2$	+	$Ca(OH)_2$	->	$CaCO_3 + MgCO_3 + 2H_20$
$MgCO_3$	+	$Ca(OH)_2$	->	$CaCO_3 + Mg(OH)_2$

Lime and soda addition



		Lime				
$MgSO_4$	+	$Ca(OH)_2$	->	$Mg(OH)_2$	+	$CaSO_4$
		Soda ash		Precipitate		
$CaSO_4$	+	Na_2CO_3	->	$CaCO_3$	+	Na_2SO_4

As previously discussed, in the framework of ULTIMATE project, two materials from the Solvay Chimica Italia Spa plant were tested as alternative chemicals to remove hardness.

The clariflocculation pilot plant (specifically built for the ULTIMATE project, Figure 9) consists of two sections: the first is positioned on a skid where are located the two agitated tanks T01 and T02, the power panel, the inverter panel, the granular solid substance dosing unit, and the liquid substance dosing pump. The second section consists of a truncated cone settler. A flow meter is installed on the inlet pipe. The characteristics of the system are as follows:

Maximum flow rate: 240 L/h.

T01: 50 L square tank with truncated cone bottom

T02: 200 L cylindrical tank

DG01: gravimetric dosing unit for granular solids

PD01: dosing pump

T03: settling tank with truncated cone bottom

Operational parameters and characteristic of the clariflocculation plant include:

Influent water: wastewater coming from the equalization tank fed by the wastewater treatment plants of Cecina and Rosignano, which corresponds to the influent water to Aretusa reclamation plant (as explained in D1.3, Naves et al., 2024).

Influent flow: 240 L/h. Preliminary tests were done in this pilot plant, showing that this flow was enough to achieve conditions close to steady state for the three reactors in reasonable time of 4 hours.

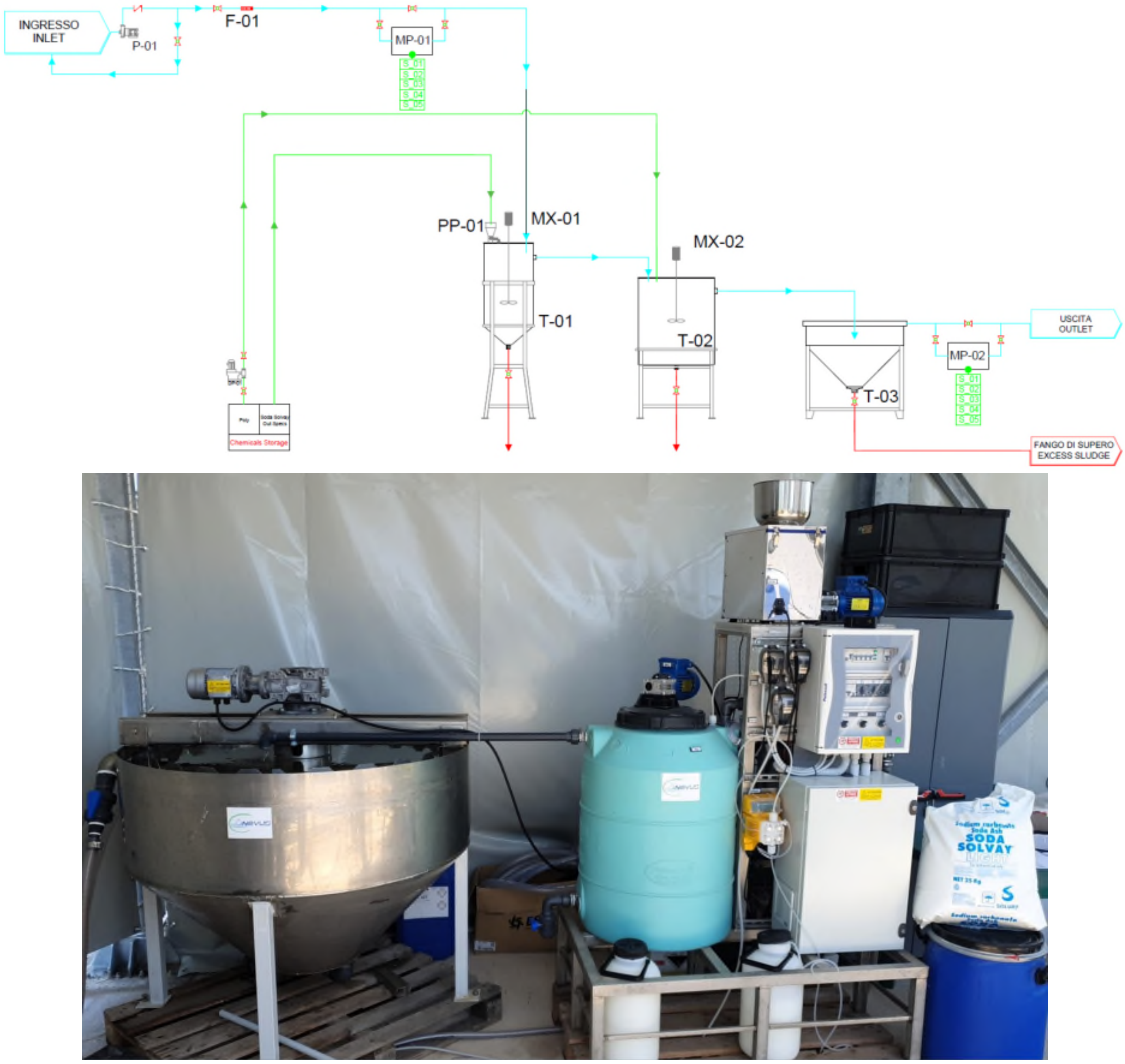


Figure 9 Clariflocculation pilot plant: a) flow diagram; b) picture of the plant.

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The selected alternative reagents were tested in three different pilot tests:

i) Test with “Precotto” P2000: It must be noted that for the pilot conditions, the material has to be screened and only the fraction < 2.9 mm was used. This problem should not be encountered in the eventual industrial-scale plant.

The amount of lime present in the *precotto* is variable but was estimated to be around 10±2% by weight. With a fed water flow rate of 240 L/hr, 8 g/min of precotto was dosed, which corresponds to a concentration of 200 mg/L. The test lasted a total of 4 hours.

ii) Test with Soda light-SL 600: it was possible to use this by-product as it was. With a fed water flow rate of 240 L/hr, 2.4 g/min of soda ash was dosed, which corresponds to a concentration of 600 mg/L. The test lasted a total of 4 hours.

iii) Test using a mix of “Precotto” P2000 and Soda light-SL 600: With a fed water flow rate of 240 L/h, 8 g/min of lime and 2.4 g/min of soda was dosed, corresponding to concentrations of 2000 mg/L and 600 mg/L respectively. During this test, it was not possible to use the DG01 gravimetric dosing unit to feed both chemicals because, as soon as they come into contact, an exothermic reaction occurs that leads to the consumption of the lime and sodium carbonate: the soda ash was therefore fed manually in this test, which lasted a total of 4 hours.

Adsorption Pilot Plant

The adsorption pilot-system has been realized with the scope to test alternative adsorbent materials to replace GAC during wastewater treatment, and to investigate the use of innovative sensors based on fluorescence and UV absorbance spectroscopy for process control and monitoring. Particularly, UV absorbance at 254 nm (UV_{254}) and fluorescence signals, which are surrogate parameters to evaluate organic matter content in wastewater, have been tested to monitor the breakthrough curve of organic material (in terms of dissolved organic carbon), but also the adsorption process of organic micropollutants (e.g., pharmaceuticals and personal care products).

The adsorption pilot system has been equipped with different on-line sensors for real-time measurements, which included an electromagnetic flow meter (SIEMENS - SITRAN FM MAG 5100W), pressure transmitters (SIEMENS – SITRANS P200), a pH probe (Hach Lange 1200-S sc); a conductivity probe (Hach Lange 3798-S sc), an UV absorbance sensor reading at 254 nm (Hach Lange UVAS sc), and a fluorescence sensor (Cyclops-7F Submersible Fluorometer). All sensors are connected by a control unit (Hach Lange - ICS-1000).

The pilot system has four adsorption columns hydraulically connected to be operated in series or in parallel. Considering a design empty bed contact time (EBCT) of 10 min, the big columns can be operated with a flow rate of around 3.5 m^3/h, whereas the small columns can treat around 0.5 m^3/h of wastewater. The design parameters of the adsorption columns are reported in Table 5.

Pressure transmitters are installed in line to control the pressure within each column, whereas all the other sensors are placed in a monitoring tank. The P&ID of the adsorption pilot system is reported in Figure 10, whereas a picture showing all the components of the adsorption pilot plant is shown in Figure 11.

Table 5. Design parameters of the adsorption columns.

Big Columns			Small Columns		
EBCT	10	min	EBCT	10	Min
Flow rate per each column	3.6	m^3/h	Flow rate per each column	0.5	m^3/h
Area	0.5	m^2	Area	0.07	m^2
Radius	0.40	m	Radius	0.15	m
Bed height	1.65	m	Bed height	1.30	m
Surface Load	7.2	m/h	Surface load	7.5	m/h

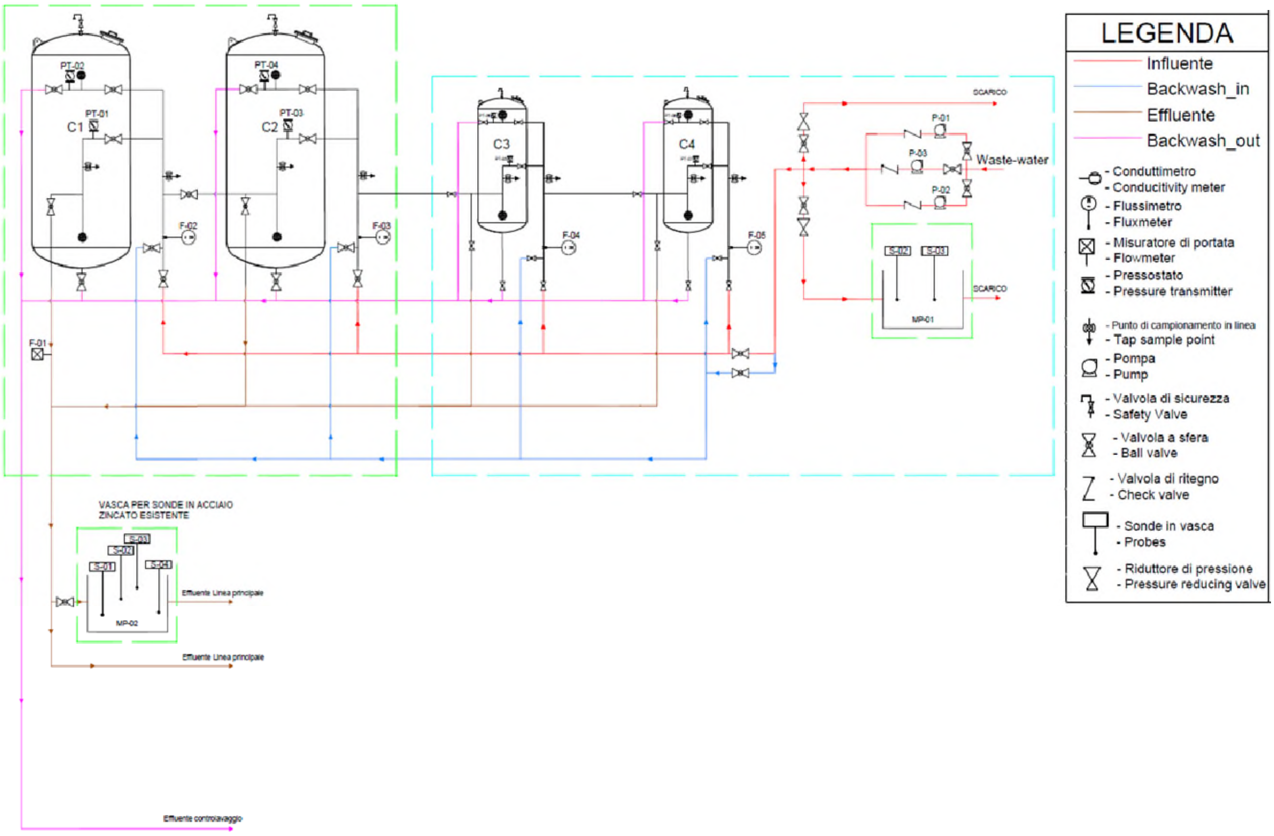

Figure 10. P&ID of the adsorption pilot plant

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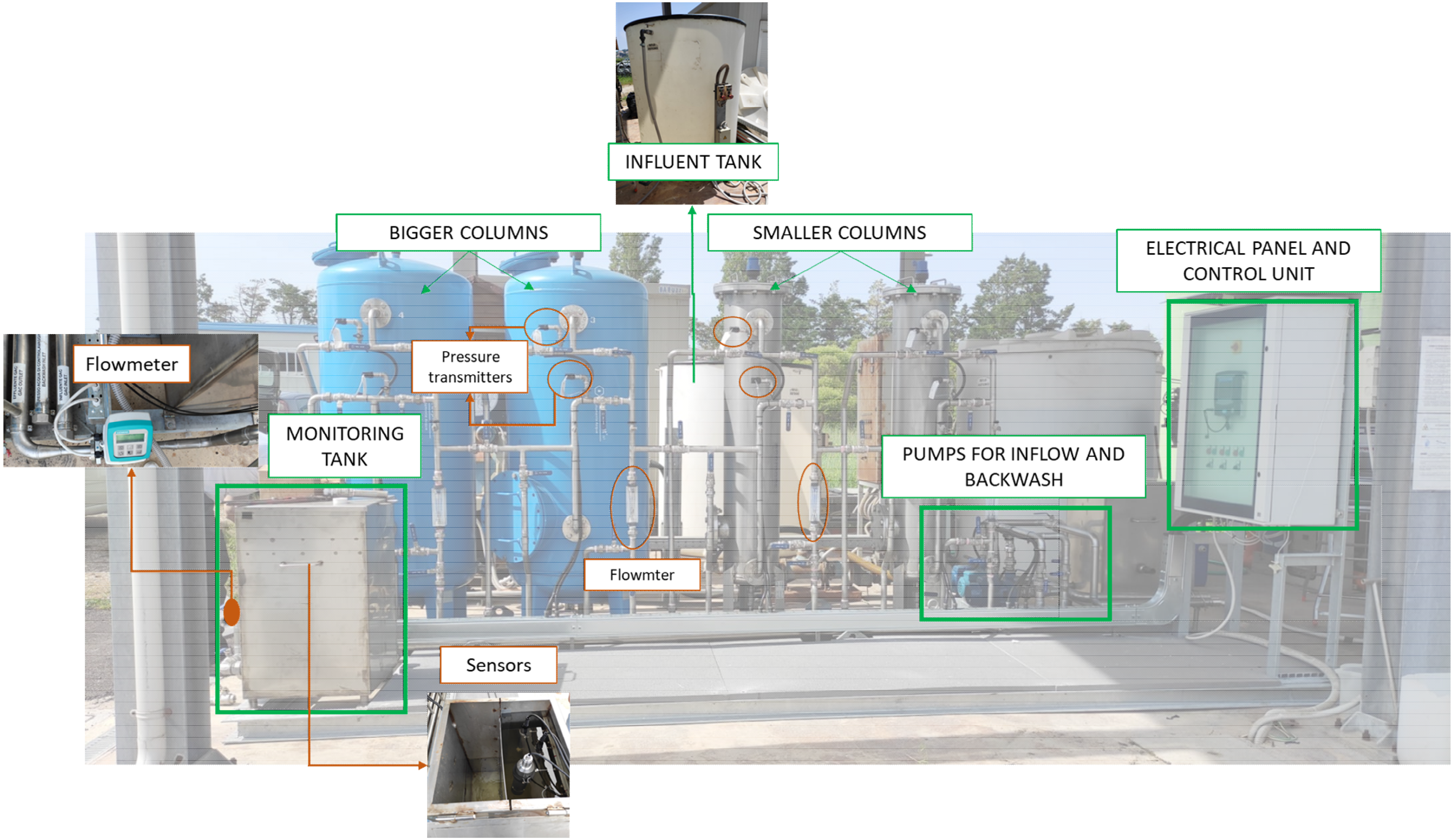

Figure 11. Adsorption pilot plant

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Preparation of test with alternative adsorbent material (hydrochar)

Hydrothermal carbonization (HTC) is a non-oxidative thermochemical process able to convert biomass (e.g., sewage sludge) into value-added products, including a carbon rich solid (i.e., hydrochar), a liquid (i.e., process water rich of nutrients) and gases (primarily CO_2) *[9]*. The hydrochar investigated in this study was produced by HTC of sewage sludge. Particularly, a pilot-scale HTC system for sewage sludge treatment was operated in Tuscany (Italy), during a previous research project, with the aim to gather knowledge and design parameters for a full-scale installation. Hence, it was possible to obtain around 100 kg of hydrochar produced from sewage sludge to be tested during ULTIMATE research activities.

The solid hydrochar has been proposed in literature as an alternative adsorbent material for wastewater treatment (Gao et al., 2020). However, a preliminary activation procedure is needed before using hydrochar as an adsorbent. Typical chemical or physical activation procedures reported in literature studies have always been accomplished at laboratory scale (Gao et al., 2020; Kazak and Tor, 2020), and it was not possible to find facilities able to activate large amount of hydrochar that can be utilized for a pilot-scale test.

As previously discussed in Deliverable D1.9, non-activated hydrochar cannot be utilized for water treatment process, since it releases high amount of organic material in water, and it has not adsorption properties. Hence, it was decided to treat hydrochar by a slow pyrolysis process to remove the leaching organic material.

The slow pyrolysis of hydrochar was committed to the company RE-CORD (https://www.re-cord.org/), which has a registered office in Viale Kennedy, 182, Scarperia e San Piero (FI), Italy. RE-CORD performed the slow pyrolysis of around 100 kg of hydrochar using a pilot plant (Figure 12) able to treat 100 kg/h of biomass.

Figure 12. Rotary kiln for slow pyrolysis (PYROCK).

The plant operated at a process temperature of around 450°C (maintained inside the rotating drum) for a residence time of the material not exceeding 2 hours. For safety reasons, the char leaving the plant was wetted with water using nebulizers, allowing to

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limit the production of dust. In Table 6 are summarized the operative conditions maintained during the test.

Table 6. Operative conditions of slow pyrolysis performed at pilot scale.

Temperature (°C)	450
Flowrate of hydrochar (kg/h)	40
Residence time (min)	90

After the slow pyrolysis process around 30 kg of pyrolyzed hydrochar have been obtained (Figure 13) from an initial amount of 100 kg of raw hydrochar.

Figure 13. Pyrolyzed Hydrochar.

As discussed in Deliverable D1.9, the pyrolyzed hydrochar coming from sewadge sludge has not adsorption properties, and it cannot be utilized as alternative material for GAC. Several tests were performed with pyrolyzed hydrochar obtained from sewage sludge that confirmed the absence of adsorption properties of the material. Because of that, further efforts in the research work were addressed to test the suitability of spectroscopic on-line sensors (UV absorbance at 254 nm and fluorescence) to monitor adsorption processes in wastewater operated at pilot scale using commercial GAC.

AOP Pilot Plant

The Advanced Oxidation Process (AOP) pilot plant was realized to test possible upgrade of the disinfection unit at ARETUDSA WRF. Indeed, by increasing the UV fluence of the system and by injecting H_2O_2 it possible to implement an AOP process, which is one of the suggested technologies for the removal of emerging contaminants in wastewater. Particularly, the new Proposal for a Directive concerning urban wastewater treatment introduces new criteria to control micropollutants. For example, quaternary treatments are required for the reduction of micropollutants in urban wastewater discharges. To verify the compliance of the quaternary treatment, it is

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sufficient to monitor the removal efficiency of a limited set of representative micropollutants listed in the proposal of directive.

H_2O_2 is one of the chemicals produced at the Solvay industrial plant of Rosignano (Italy). Hence, within the WSIS envisioned in ULTIMATE, H_2O_2 (30% concentration of H_2O_2 in water) produced by Solvay was used to perform AOP treatment monitored by innovative spectroscopic sensors.

A picture of the realized AOP pilot plant is reported in Figure 14.

Figure 14. AOP Pilot Plant

The schematic of the AOP pilot plant includes a sand filter to remove solids avoiding lamp fouling and an (optional) filter cartridge for further protection. A peristaltic pump is present to inject H_2O_2 by using a static mixer. Two UV lamps PRO24-186 VIAQUA provide UV irradiation. The obtained UV fluence is a function of the UV transmittance of the tested water and of the applied flowrate (Figure 15). The UV transmittance of the tested water was around 75%, whereas the pilot plant can be operated with a flowrate ranging from 0.5 to 3.0 m^3/h.

The AOP pilot plant was equipped with the same on-line spectroscopic sensors used to monitor adsorption processes, which included an electromagnetic flow meter

(SIEMENS - SITRAN FM MAG 5100W), a pH probe (Hach Lange 1200-S sc); a conductivity probe (Hach Lange 3798-S sc), an UV absorbance sensor reading at 254 nm (Hach Lange UVAS sc), and a fluorescence sensor (Cyclops-7F Submersible Fluorometer). All sensors were connected by a control unit (Hach Lange - ICS-1000).

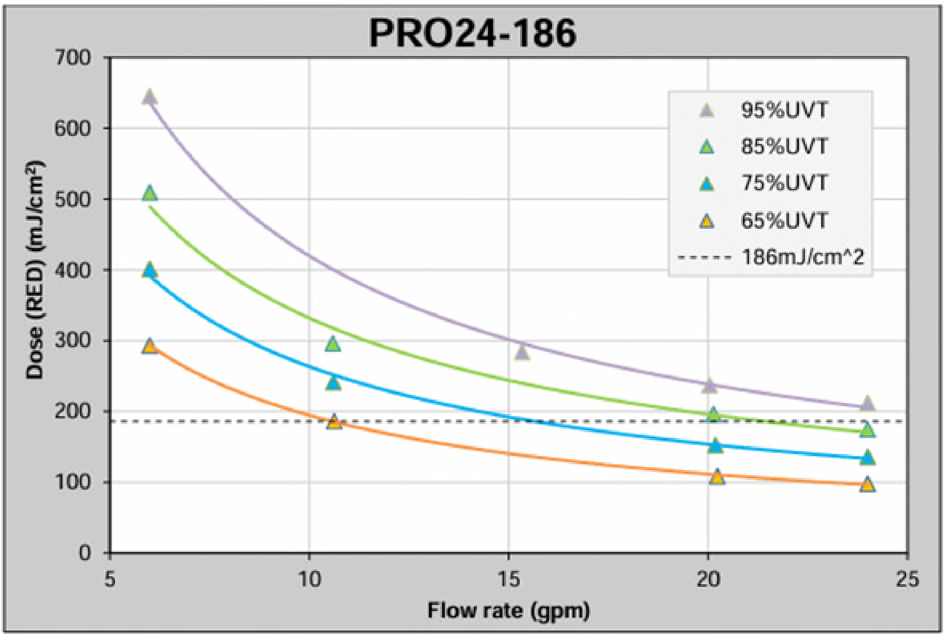

Figure 15. Dose curve of the AOP Pilot Plant

During the experimental test with the AOP pilot plant, spectroscopic sensors were tested to monitor the removal of organic micropollutants as required by the new proposal of directive concerning urban wastewater.

2.2.2. Results of new approaches

Clariflocculation Pilot Plant

The soda and Precotto concentrations tested in the Clariflocculation Pilot Plant are those resulting from previous laboratory-scale experiments, the results of which have already been shown in previous deliverables (D1.9) and reported in Table 8. The effectiveness of calcium or manganese removal was dependent on the reached pH during the test. The target pH influenced the amount of Solvay by-product to dose. The best results during operation at laboratory scale were obtained when dosing soda light Solvay (dosage of 0.3 – 0.5 g/L). During the flocculation test, 1 mL of flocculant CATFLOC SD 7085 was dosed.

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Table 7. Hardness and COD removal during laboratory tests.

Softening agent	**Final pH**	**Conductivity**	**TSS**	**COD**	**Mg**	**Ca**	**COD Removal**	**Mg Removal**	**Ca Removal**
-	**-**	**µS/cm**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**%**	**%**	**%**
INFLUENT WW - ARETUSA WWTP	**8.0**	**2130**	**50**	**23.9**	**46.1**	**164**	**-**	**-**	**-**
Precotto	8.7	1920	30	13	42.4	152	45.45	8.13	6.8
Precotto	9.1	1964	30	8.7	42.1	162	63.64	8.64	1.0
Soda light Solvay	9.0	2180	20	-	48.5	157	na	-5.26	4.3
Soda light Solvay	9.2	2310	10	6.52	52.3	89.7	**72.73**	-13.44	**45.2**
Mix	8.9	2180	10	8.26	46.6	154	65.45	-1.13	6.0
Mix	9.3	2270	0	10.9	49.6	130	54.55	-7.49	20.3

**na = non-available*

Water quality of influent to ARETUSA changes over time. During pilot-tests, the inlet COD was found to be always less than 15 mgO_2/L, and consequently, also non-measurable values were detected on the outlet from tank T02 (Figure 9).

The inlet TSS are quite variable but have rather low values. At the outlet, samples were under the limit of detection (LOD).

It was therefore decided not to proceed with the flocculant dosing tests, which would not lead to analytically determinable results for TSS and COD.

The following graphs show the inlet-to-outlet variations in pH and conductivity that occurred as a result of the various dosing of Solvay by-products. As can be seen in Figure 16, the precotto P-2000 was the only flocculant capable of reducing the total conductivity of the wastewater. However, this product increased pH values significantly, reaching up to 10.5. Similar pH was obtained by the mixed flocculant. On the other hand, the Soda Light SL 600 maintained the pH under the maximum limit for water reuse, i.e., < 9.5. Hence, this material would be the only one capable of producing reclaimed water under appropriate pH conditions without further post-treatment such as dilution. Hence, pilot tests confirmed results obtained at laboratory scale.

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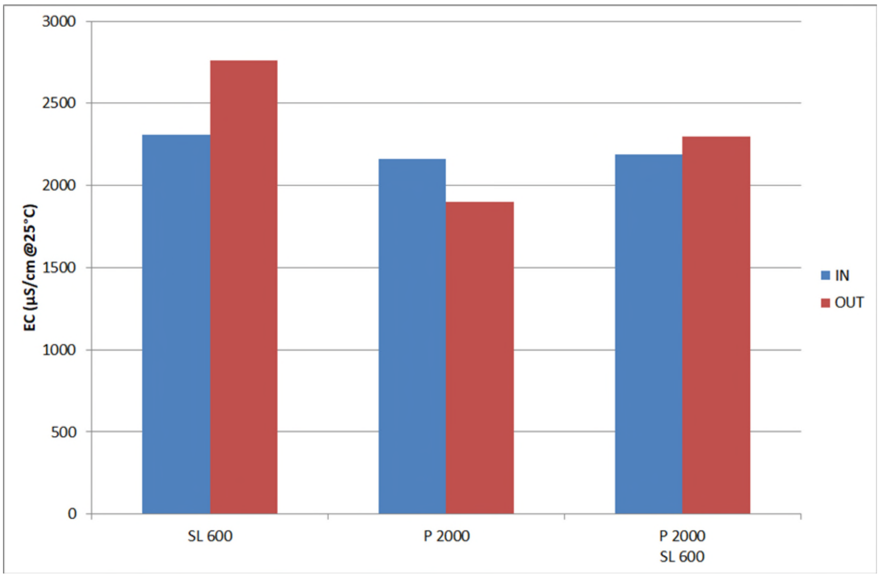

Figure 16 Conductivity values in the inlet and outlet streams

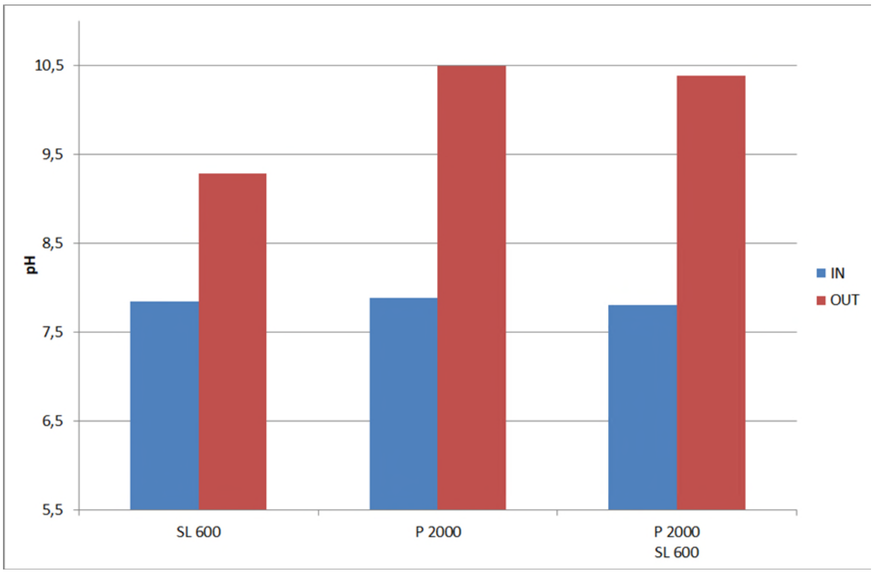

Figure 17 pH values in the inlet and outlet streams.

Regarding inorganic carbon species, total alkalinity, which is the sum of bicarbonate, carbonate, and hydroxide alkalinity is shown in Figure 18. Carbonates, bicarbonates and hydroxide concentrations are displayed Figure 19, Figure 20 and Figure 21.

In the incoming stream (influent), the pH is less than 8.3 so that there are no carbonates but only bicarbonates. After dosing soda (SL-600), pH increases, alkalinity almost doubles, and obviously carbonates are present together with bicarbonates (Figure 17).

By dosing lime (P2000), pH increases further, alkalinity is greatly reduced and bicarbonates disappear as the chemical equilibrium moves to hydroxides. With soda and lime, pH is high, alkalinity remains the same and carbonates and hydroxides appear.

Summarizing, when pH is less than 8.3, all alkalinity is in the bicarbonate form and is commonly referred to as natural alkalinity. When pH is above 8.3, alkalinity may consist of bicarbonate, carbonate, and hydroxide. As pH increases the alkalinity progressively shifts to carbonate and hydroxide forms.

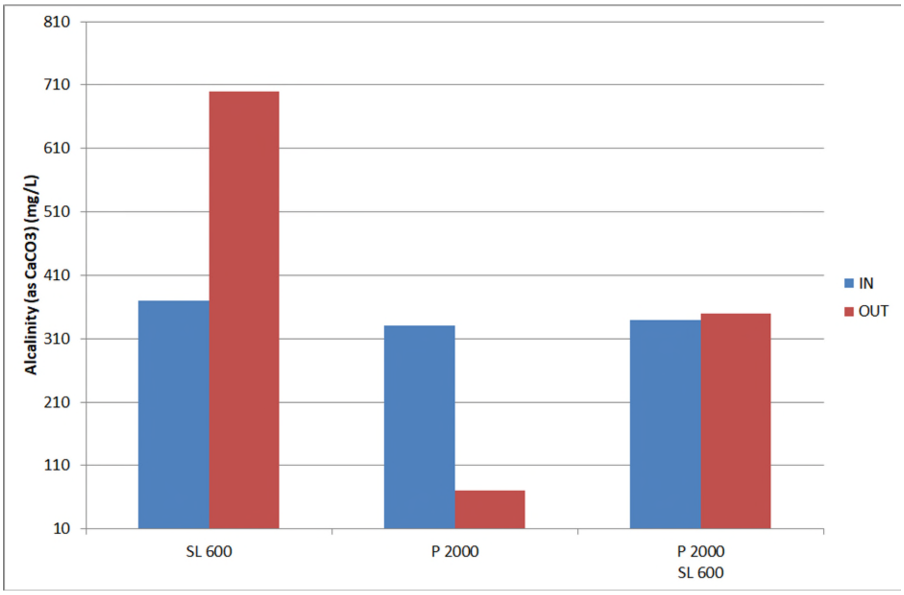

Figure 18 Alkalinity values in the inlet and outlet streams.

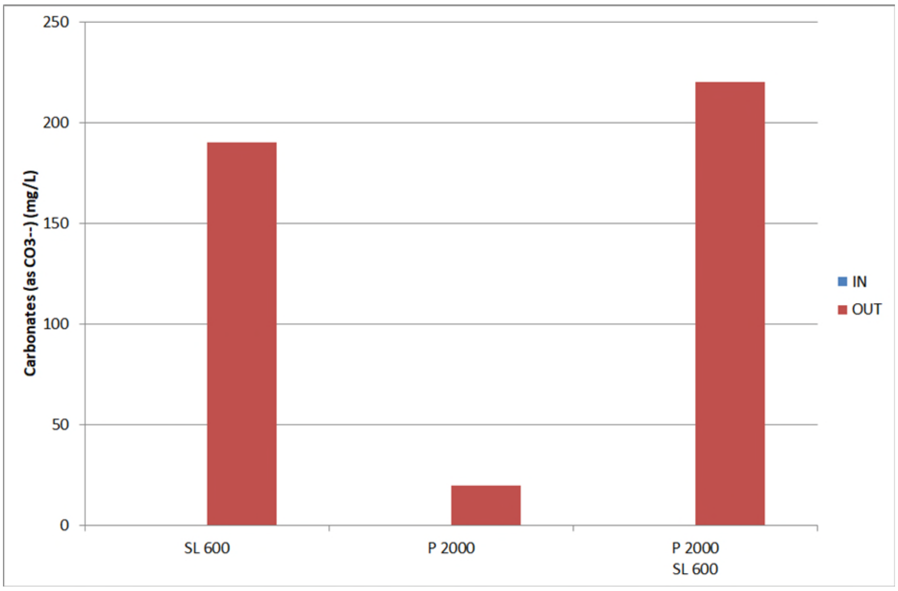

Figure 19 $CO3^{-}$ concentration values in the inlet and outlet streams.

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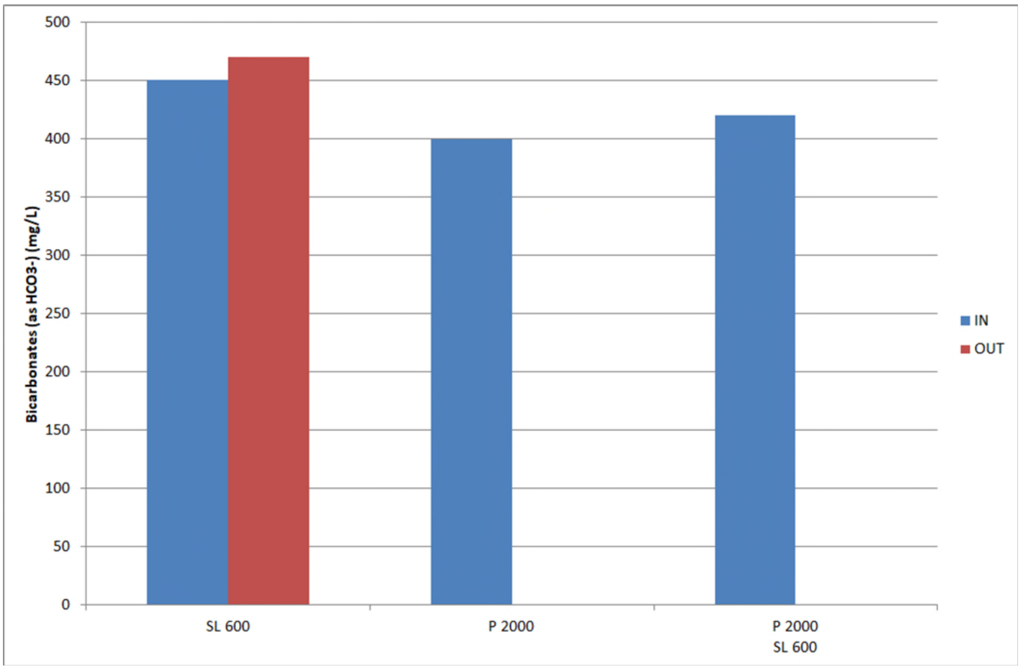

Figure 20 HCO_3^- concentration values in the inlet and outlet streams.

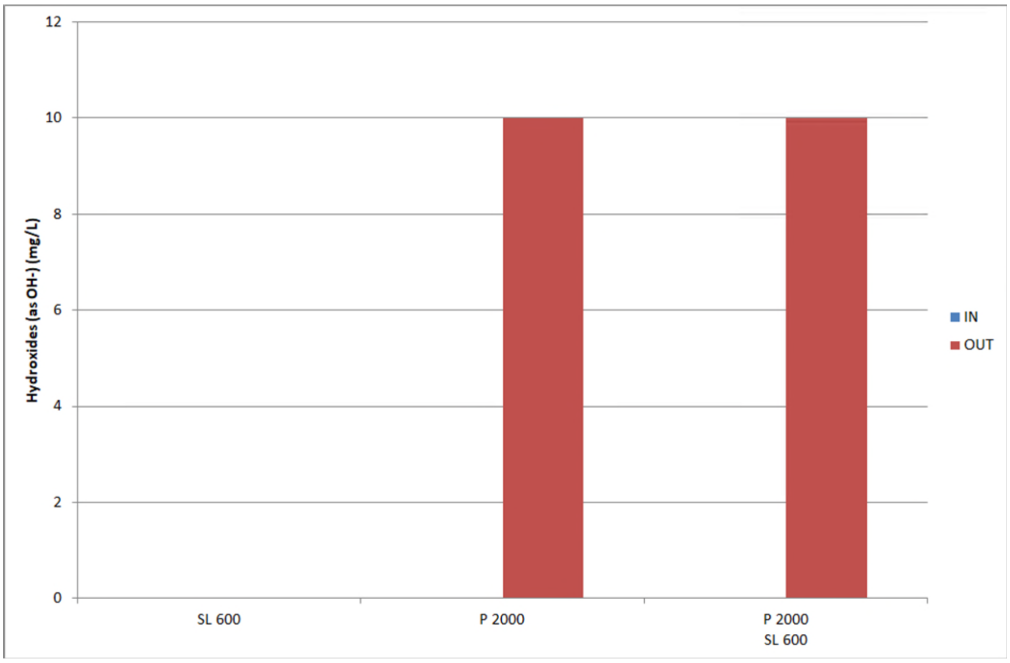

Figure 21 OH^- concentration values in the inlet and outlet streams.

The most significant parameter for the process is hardness. The following graphs (Figure 22, Figure 23) show the variations in hardness and their relative abatement.

It can be seen that the abatements of total hardness when soda ash or Precotto was dosed were similar but in the case of SL 600, permanent hardness was abated more significantly than in P2000, which removed more temporary hardness. In the test where the reagents were dosed together, there were significant abatements of both temporary and permanent hardness, resulting in a greater abatement of total hardness than in the previous cases.

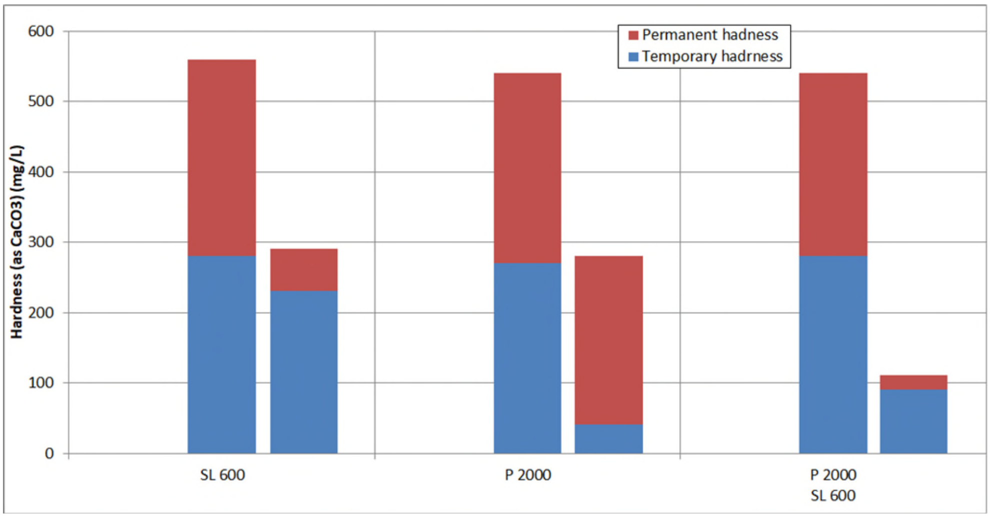

Figure 22 Temporary and permanent hardness removal.

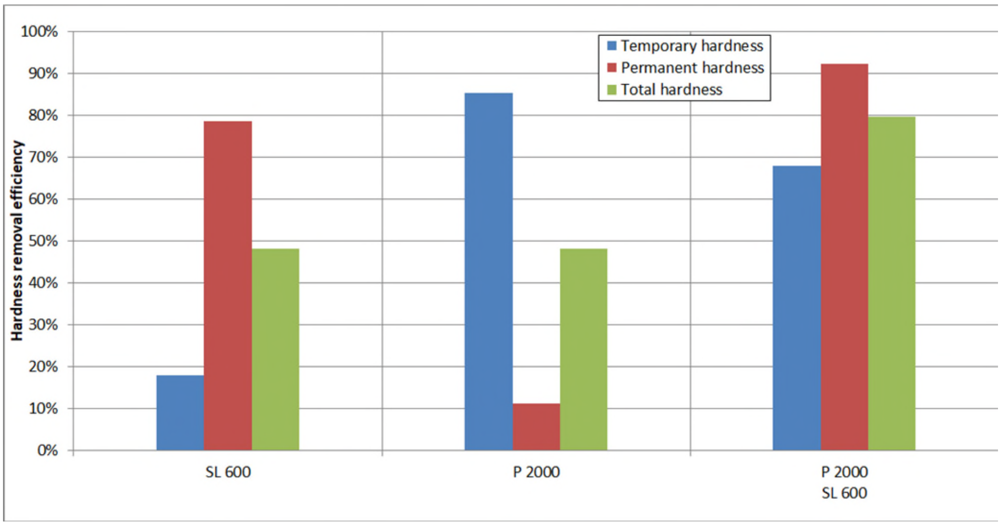

Figure 23 Hardness removal efficiency.

In this study was also tested the possibility to re-use the chemical (alum/ferric) sludge produced as a waste in drinking water treatment plants of the area to be reused during coagulation/flocculation processes according to the Alu Circles initiative. However, the use of aluminum sludge is not suitable for the treatment of tertiary wastewater effluent, but it can have application to improve the sedimentation process in primary clarifier treating raw wastewater.

Aluminum sludge from the drinking water treatment plant of Castriccioni (Marche Region) was acidified (Figure 24) using sulfuric acid to recover the coagulants. Particularly, 6 g of sludge were added in 300 mL volume of distilled water, where it was dosed sulfuric acid 3N at different amount (20, 30, 40, 50 mL/L,). Each sludge samples was mixed with the respective acid amounts using a jar test at 150 rpm for 60 min and then allowed to settle for a further 60 min to separate the supernatant. The collected supernatant was dosed to wastewater samples using a jar test to simulate the coagulation and flocculation stage (Mora-León A.G et al., 2022).

Figure 24 Aluminium Sludge acidification process

Coagulation and flocculation tests accomplished using a typical wastewater effluent produced an increase of COD in the water matrix at the end of the test. This fact confirms that the recovered coagulant from aluminium sludge cannot be used to treat the tertiary wastewater effluent at ARETUSA WRP. Hence, aluminum sludge was not used during tests with the Clariflocculation pilot plant.

Laboratory tests were also accomplished by simulating by Jar Test a coagulation/flocculation and sedimentation process for the primary effluent of Falconara WWTP. The best performance obtained in COD removal was obtained when using extracted coagulant from aluminium sludge using 30 mL/L of sulphuric acid 3 N. In this condition, the observed COD removal was significant at low dosage of the recovered coagulant (Table 8)

Table 8. Results of Jar Test experiments using coagulant solution recovered from aluminium sludge

N. Test	Wastewater Volume	Coagulant dosage	TSS	pH	Temp	COD	COD removal
	L	**mL**	**mg/L**	**-**	**°C**	**ppm**	**%**
Raw wastewater	0.5	-	29	8.2	17.9	69.75	
0	0.5	0	31	8.14	18.1	43.24	38
1	0.5	5.0	8	8.0	17.6	4.32	90.0
2	0.5	7.5	12	7.8	17.5	25.95	40.0
3	0.5	10.0	16	7.8	17.6	8.65	80.0
4	0.5	12.5	9	7.7	17.7	4.32	90.0
5	0.5	15.0	12	7.6	17.9	12.97	70.0
6	0.5	20.0	13	7.6	18.0	25.95	40.0

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Adsorption Pilot Plant

Two commercial GAC were used during the pilot experiments. General characteristics of the used carbon are reported in Table 9. The pilot system was continuously fed with the wastewater effluent of the Falconara Marittima wastewater treatment plant (WWTP).

Table 9. General characteristics of the activated carbon used

Parameter	Filtercarb CSC5 (Test 1)	Filtercarb GBC 8x30 (Test 2)
Iodine number	-	950 ± 50
Surface area - BET (m^2/g)	500 ± 50	1000 ± 50
Bulk density (g/cm3)	0.50-0.55	0.50 ± 0.05
Material	Mineral coal	Bituminous coal
Ash content (%)	<10	12 ± 2
Grain size (mm)	> 5 (0.5%) < 2 (1.5%)	> 2.4 (<0.5%) < 0.6 (<0.5%)

The list of monitored micropollutants is reported in Table 10, which were analysed by LC-MS/MS following the UNI EN ISO 21676 method.

Table 10. List of monitored micropollutants

Compound	**Use**	**MW (g/mol)**
Atenolol	Beta blocker	266.34
Azithromycin	Antibiotic	785.02
Carbamazepine	Antiepileptic	236.27
Clarithromycin	Antibiotic	748.00
Sulfamethoxazole	Antibiotic	253.28
Primidone	Anticonvulsant	218.25
Trimethoprim	Antibiotic	290.32

The first experimental test was accomplished using the carbon Filtercarb CSC5, whereas during the second experimental test it was used the carbon Filtercarb GBC 8x30. In Figure 25 is shown the breakthrough curve of UV_{254} and fluorescence signal from real-time sensors during adsorption Test 1, whereas in Figure 26 are reported the breakthrough curve of UV_{254} and fluorescence signals during adsorption Test 2.

In both the figures it is possible to observe that fluorescence signal was much more sensitive to track variation of organic carbon content. In addition, the fluorescence breakthrough was much slower than UV_{254} breakthrough.

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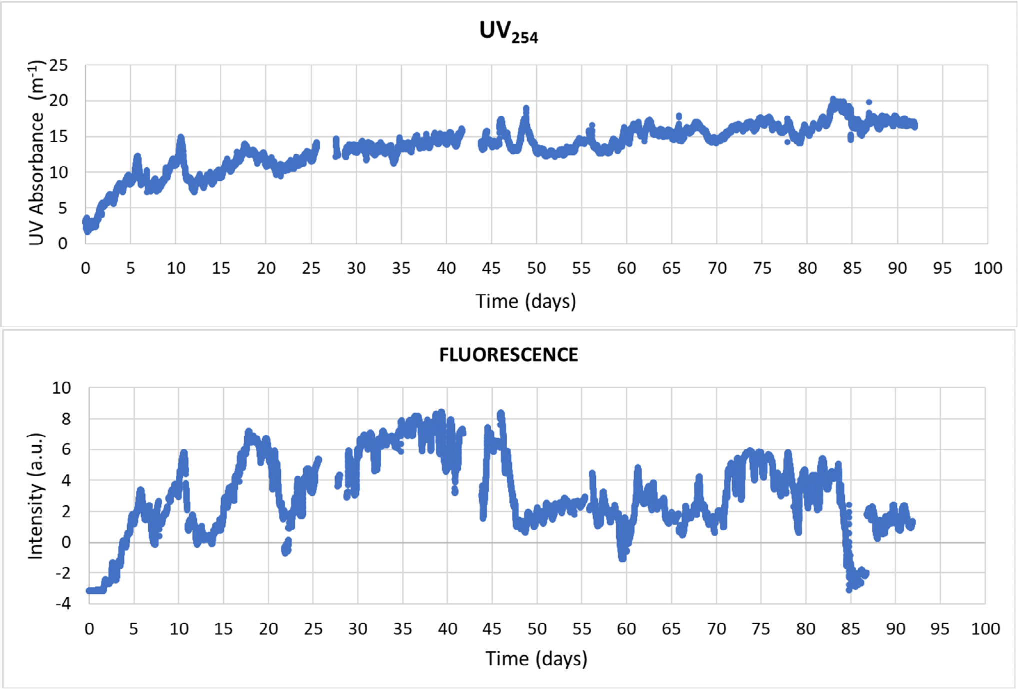

Figure 25 Breakthrough curve of UV$_{254}$ and fluorescence signal from real-time sensors during adsorption Test 1.

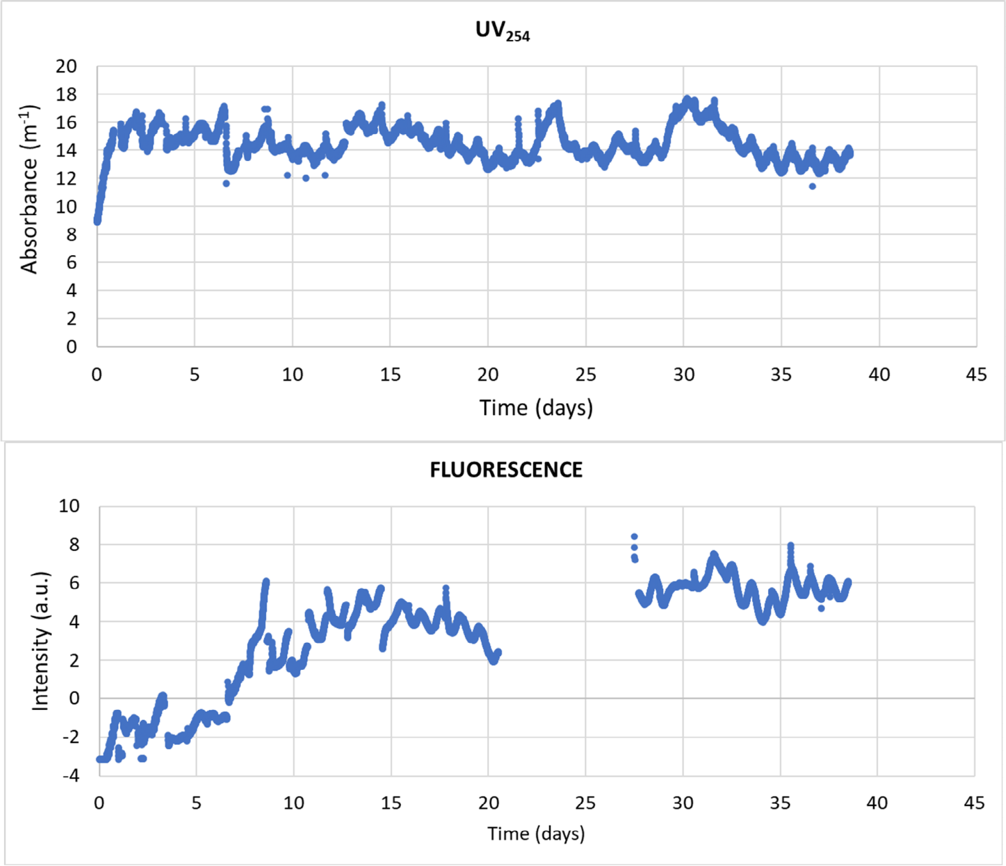

Figure 26 Breakthrough curve of UV$_{254}$ and fluorescence signal from real-time sensors during adsorption Test 2.

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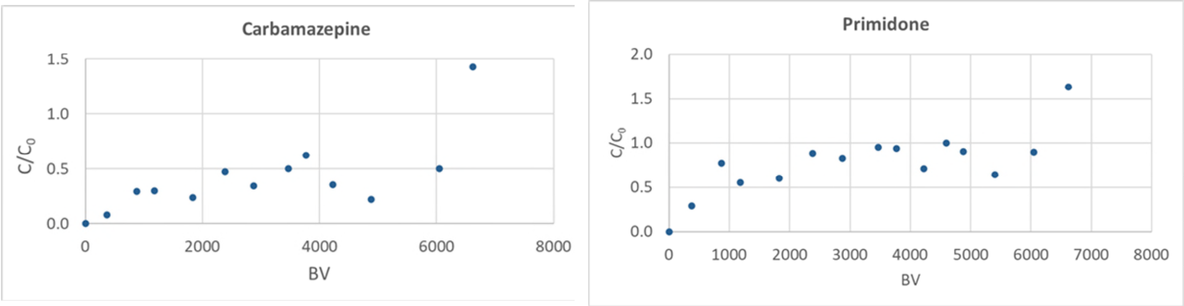
As an example, in Figure 27 are reported the breakthrough curves observed for the micropollutant primidone and carbamazepine during the two experimental adsorption tests.

Adsorption Test 1



Adsorption Test 2

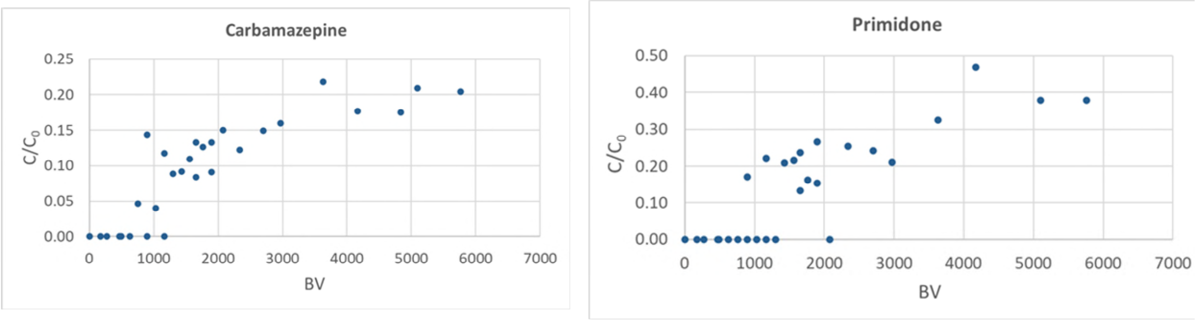


Figure 27 Breakthrough curve of carbamazepine and primidone during the two adsorption experimental tests

Results of the correlation analysis (Table 11 and Figure 28) showed a very good correlation between micropollutants breakthrough and fluorescence breakthrough, whereas UV254 was not correlated with any monitored compound.

Table 11. Observed correlation between spectroscopic sensors' signals and monitored emerging contaminants

Adsorption test	**Correlation coefficient r**			
	Test 1		**Test 2**	
Compound/signal	**UV_{254} probe**	**Fluorescence probe**	**UV_{254} probe**	**Fluorescence probe**
Atenolol	-0,17	0,89	-0,70	0,91
Azithromycin	0,36	0,88	0,14	0,59
Carbamazepine	0,04	0,71	0,30	0,69
Clarithromycin	0,12	0,50	0,29	0,77
Sulfamethoxazole	-0,62	0,59	0,47	0,82
Primidone	-0,39	0,72	0,34	0,75

As an example, in Figure 28 are reported graphical representation of observed correlation between the micropollutant sulfamethoxazole and fluorescence probe signal during adsorption Test 2.

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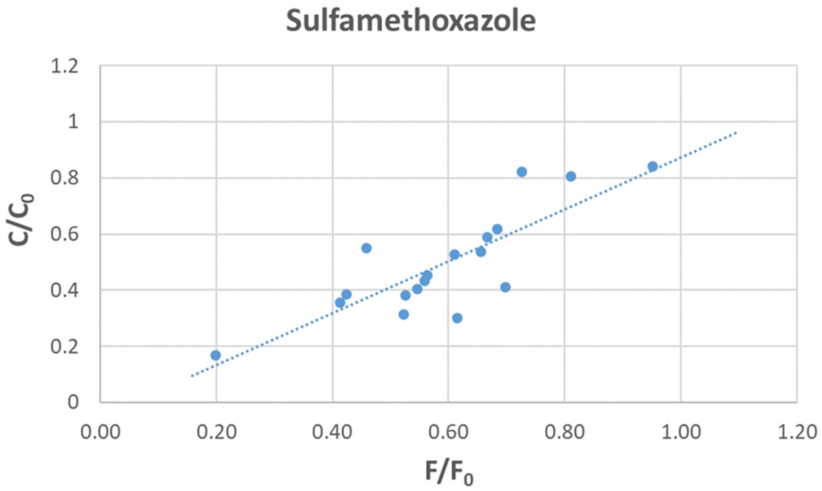

Figure 28 Observed correlation between sulfamethoxazole and fluorescence during adsorption Test 2. C_0 and F_0 are observed concentration of the contaminant and fluorescence signal in the influent, respectively

These observed results suggest the possibility to use real-time sensors to monitor micropollutants removal during GAC filtration as required by the proposal of new directive concerning urban wastewater treatment.

Observed correlations were independent of water quality, but were different when using carbon with different adsorption capacity.

AOP Pilot Plant

The AOP pilot plant was also equipped with the spectroscopic sensors for the measurements of the UV absorbance at 254 nm and fluorescence. The pilot plant was operated by dosing around 20 mg/L of H_2O_2 and with an influent flowrate ranging between 1.2 and 1.8 m^3/h. The observed water quality was variable over time as can be observed by analysing fluorescence spectra of samples collected in different days and measured at the laboratory (Figure 29).

Real-time signals were recorded for both fluorescence and UV_{254} sensors (Figure 30), and it is possible to observe that fluorescence was able to discriminate degradation of organic matter in wastewater during AOP process. On the contrary, signals of UV_{254} probe before and after treatment were very similar.

The micropollutants listed in Table 10 were also monitored during the AOP tests.

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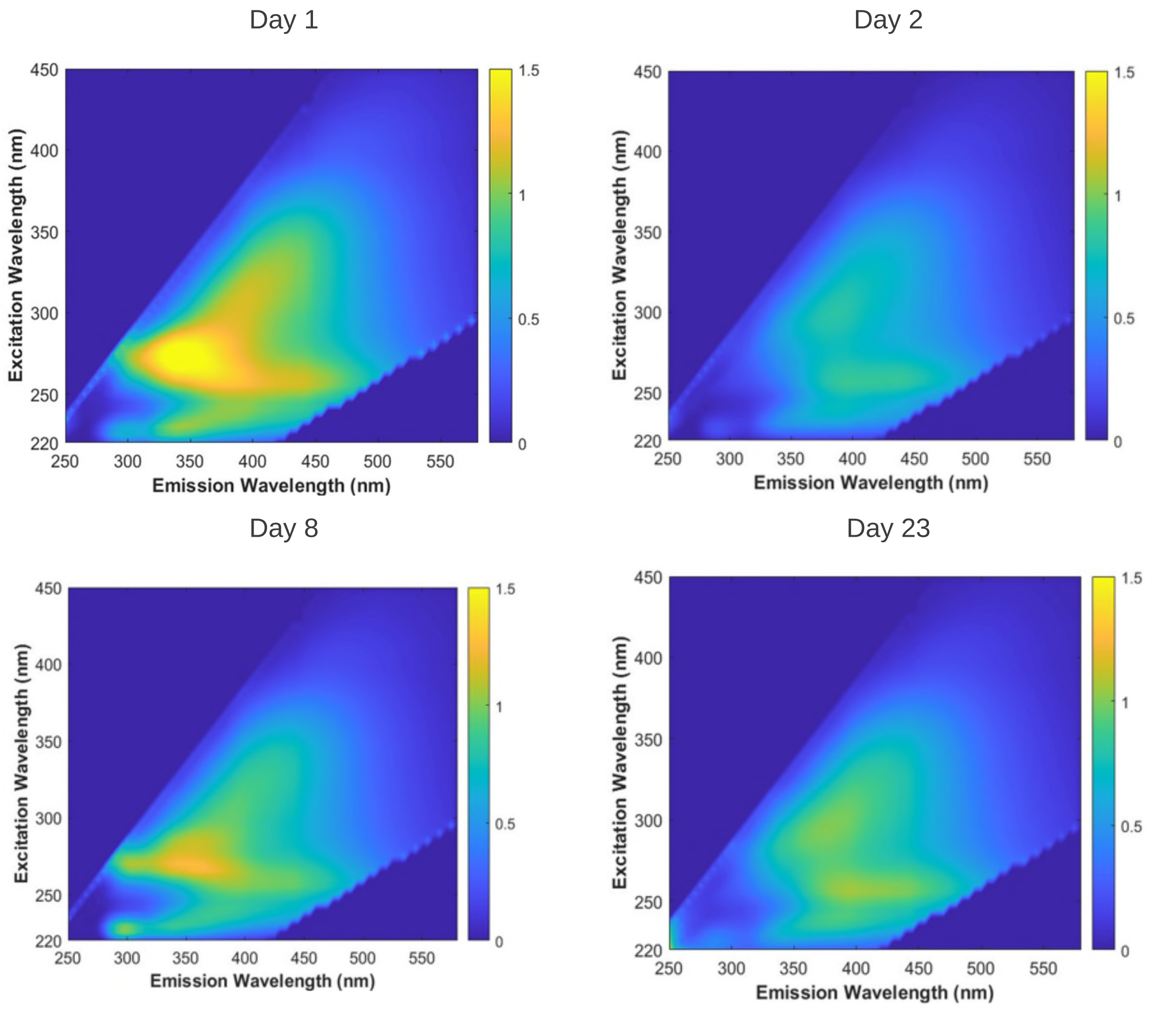

Day 1

Day 2

Day 8

Day 23

Figure 29 Fluorescence spectra of the wastewater influent to the AOP pilot plant collected at different days

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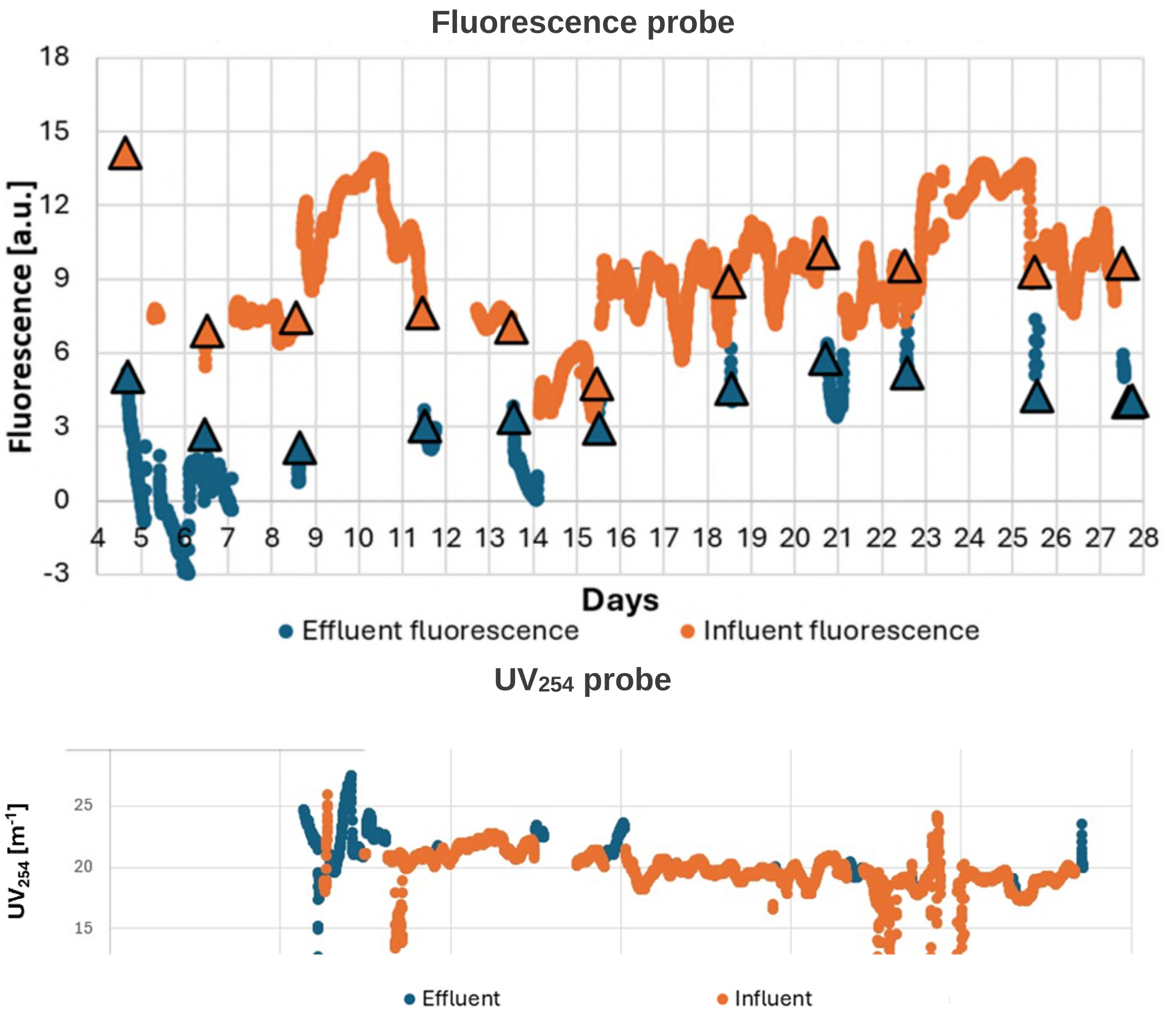

Figure 30 Fluorescence signal of the influent and effluent of the AOP pilot plant recorded in real-time

In Figure 31 are reported, as an example, observed concentration of primidone and clarithromycin in the influent and effluent of the AOP pilot plant, where it possible to observe changes of concentration and removal of contaminants during the treatment process.

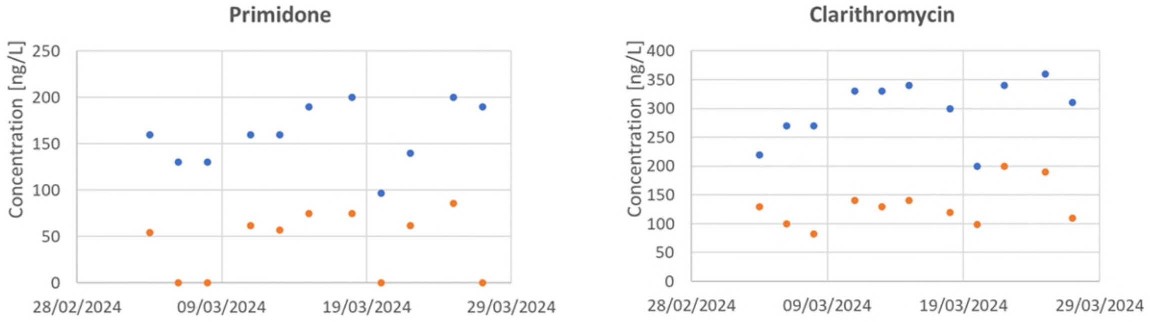

Figure 31 Observed concentrations of primidone and clarithromycin in the influent (blu indicator) and effluent (orange indicator) of the AOP pilot plant

A correlation analysis was accomplished between removal of fluorescence signals and removals of emerging contaminants observed during the AOP process. Results of the analysis are reported in Table 12 for all the contaminants and Figure 32 for the compound Azithromycin and Carbamazepine. On the contrary, no correlations were found between UV_{254} removal and emerging contaminants removal.

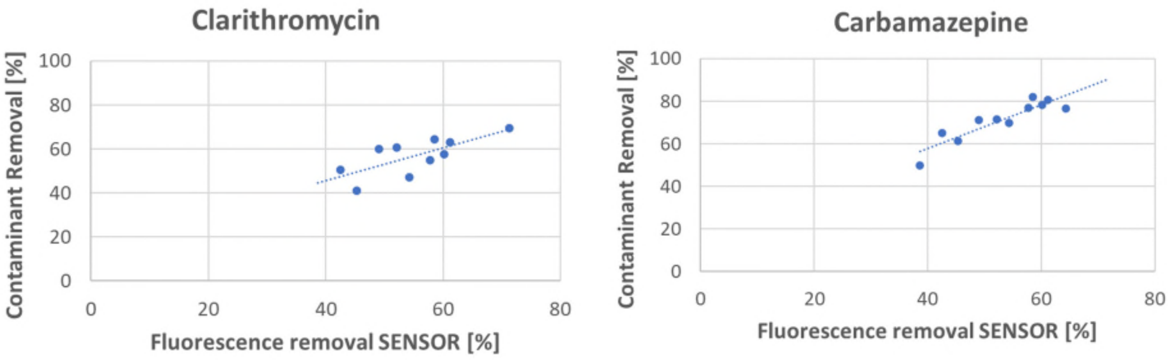

Figure 32 Correlation analysis between fluorescence removal and emerging contaminants removal during AOP process

Table 12. Observed correlations between removal of fluorescence signal and organic micropollutants during AOP process

Compound	**Probe Fluorescence**	
	R	n
Azithromycin	0.15	10
Carbamazepine	0.90	12
Clarithromycin	0.73	10
Atenolol	Non detected	
Primidone	0.50	11
Sulfamethoxazole	0.90	5

Data in Table 12 and Figure 32 support the possibility to use fluorescence sensors to monitor the removal of emerging contaminants during quaternary treatment processes as required by the new proposal of EU directive concerning urban wastewater treatment.

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2.2.3. Conclusion and recommendation

Key performance indicators and comparison with baseline situation

A comparison to the baseline situation, which highlight the benefits that can be obtained by implementing ULTIMATE solutions, is reported in Table 13.

Table 13 Potential benefits obtained by the implementation of ULTIMATE solutions

Implemented solution	Obtained results	Benefits for WSIS	observation
Use of the by-product Soda light Solvay	Concurrent removal of hardness and COD	Possibility to fully replace commercial coagulant in the clariflocculation process	Cost saving during wastewater treatment
Chemical (alum/ferric) sludge from coagulation/flocculation	Observed removal of COD and TSS only when treating raw wastewater in primary settlers	-	Benefits are related to application in primary settlers
Pyrolized hydrochar for adsorption process	Activation methods for hydrochar at pilot/full scale are not available yet to produce an alternative adsorbent material from sewage sludge	-	The investigated technology is not ready for the market and for full-scale implementation
Fluorescence sensors to monitor organic micropollutants during quaternary treatments (e.g., adsorption and AOP technologies)	Observed important correlations between fluorescence removal and micropollutants removal during quaternary treatments	Availability of a digital tool to monitor performance of quaternary treatments	Extended reuse possibilities by monitoring continuously compliance with new EU regulations

The results of this case study are also summarised using the ULTIMATE KPI's in **Error! Reference source not found.**.

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Table 14. Overview of the ULTIMATE KPIs for material recovery for case study 3.

KPIs specified in GA	**How it will be measured/determined?**	**Achievable targets – Pilot scale scale**
Material recovery (>10%)	Possibility to replace entirely or partially commercial product for clariflocculation process by using industrial by-products	Recovered industrial by product: - Soda Solvay light, out of specification for the market, has the potential to replace commercial coagulant for clariflocculation process - 100% replacement
Innovative Technologies and Digital WSIS support tools deployed (n. 2)	Number of innovative technologies deployed to support WSIS	Deployed digital technology: - Fluorescence sensors for micropollutants and water quality monitoring - Mach-making tool and sewage system model (discussed in Deliverable D1.3) - sewage system model and Early Warning System (discussed in Deliverable D1.3)

Best practices and recommendations for technology implementation

In this deliverable are reported results related to the investigation of the use of industrial by-products as alternative material for wastewater treatment with the aims to reinforce the public-private symbiosis cluster already existing in the industrial area of Rosignano (Livorno, Italy). Indeed, Aretusa public-private-partnership (PPP) is a good example of industrial symbiosis practices, where urban wastewater management and the chemical industrial sector complement to each other to improve circularity in water.

In this study, hydrochar produced by hydrothermal carbonization of sewage sludge was tested as alternative adsorbent for wastewater treatment. However, a chemical/physical activation is needed before utilizing this material as adsorbent. Even though activation procedure is possible at laboratory scale, its implementation at pilot/full scale is hampered by some technological issues. Simple pyrolysis of the material eliminates the leaching of organic material, but it is not enough to activate the material as adsorbent material. Hence, it was concluded that the investigated technology is not ready yet for its implementation at full scale.

Other by-products produced during the production industrial cycle at Solvay plant were investigated as alternative coagulants for the clariflocculation process of the municipal wastewater. The by-product Soda light Solvay, which is a product out of specification for the market because of the presence of some impurities, was found to be a suitable coagulant for the process. The following recommendations are suggested when using this product:

- the effectiveness of the process is strongly related to reached pH at the end of the treatment. Hence, a dosage control based on pH reading at the inlet and outlet of the process is suggested for a full-scale implementation
- Successful removal of hardness and COD are obtainable at pH in the range 9 - 9.5. Hence, desired implementations should be compatible with those pH values.
- It is preferable to dose the product in a powder form to reduce costs related to waste/sludge production and cost for the dosage.

Aluminum sludge from drinking water treatment plants was also tested as alternative coagulants. However, its application is limited to coagulation/sedimentation process in primary clarifiers, and this product is not suitable for the treatment of tertiary wastewater effluents.

Innovative spectroscopic sensors based on fluorescence measurements were tested to monitor organic micropollutants removal during quaternary treatments, specifically adsorption processes in filtration media and AOP treatment (i.e., UV/H_2O_2). Successful results were obtained, and fluorescence spectroscopy can be proposed as suitable surrogate parameter for the on-line control of organic micropollutants as required by the proposal of EU directive concerning urban wastewater treatment. The following recommendations are suggested when using fluorescence sensors for wastewater quality monitoring:

- Cleaning of the optics need to be accomplished at least once per week to avoid biofilm formation
- shade cap as it provides a fixed distance for sample measurement is recommended during on-line measurements
- Sensors should be installed in suitable location to avoid light interference with the optical measurements
- Reduction of intensity of excitation light source need to be monitored during the useful life of the sensors.
- Correlations observed with organic micropollutants are independent of water quality. On the contrary, they are dependent on the physical characteristics of the adsorbent media, including adsorption capacity, carbon type, bed high, porosity.

Crucial factors for technology implementation and its optimal performance

- Mandatory requirements for the use of out of specification soda for coagulation process are continuous pH control and dosage in powdered form
- Application of fluorescence sensors for micropollutants monitoring during adsorption processes requires regular cleaning as well as unchanged physical characteristics of the absorbent system (i.e., carbon type, bed high). It is also required sensors installation in place protected by the sunlight to avoid interferences
- Application of fluorescence sensors for micropollutants monitoring during AOP treatment requires regular cleaning as well as installation in place protected by the sunlight to avoid interferences

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2.3. Recovery of high added-value compounds (antioxidants) in Nafplio (EL)

2.3.1. Case study and ULTIMATE concept

The Eastern Peloponnese is one of the most productive regions in Greece in terms of citrus fruits (it is to be highlighted that Greece is the third largest producer of citrus fruit in the EU). Alberta S.A. is a Greek fruit processing industry and specialises in the production of fruit juice concentrates, fruit purees and concentrates, clarified juice concentrates, NFC juices, as well as tailor made products and blends, since 1981. Not only do they produce fruit juices but also by vegetable juices, such as carrots and red beets. The majority of fruit juices come from citrus fruits (oranges, lemons, grapefruits, and mandarins), pome fruits (apples, pears), stone fruits (peaches, apricots), pomegranates, chokeberries, grapes, carrots and red beets.

Particularly in the Argolida area, where Case Study 4 (CS4) (Figure 1) is situated, there is an increasing water demand for irrigation. Most irrigation water comes from wells, often illegal ones. This practice, along with the high-water consumption of the fruit processing industry, is exerting great pressure to the local aquifer. Over-irrigation has led to subsequent intrusion of the seawater into the aquifer, which has reduced the quality of the groundwater aquifer, which exhibits high conductivity values (in the region of 3000 μS/cm). With a view on reducing the overall cost of disposing wastewater to the municipal biological treatment, as well as meet the effluent legal criteria, all sizeable fruit processing plants of the area have constructed and are currently operating individual primary biological plants. Nonetheless, each plant periodically ceases to operate as a result of the seasonality of the production. This practice increases operational costs, as it is necessary to kick start the wastewater treatment plant when it is again needed.

Alberta S.A has a primary biological treatment plant of about 20 m^3/h capacity to meet the effluent criteria, as well as to reduce the cost of disposing wastewater to the municipal WWTP. This process is mainly focused on the removal of organic matter, achieving more than 90% removal (COD concentration in the outlet stream).

The by-products of fruit and vegetable processing sector contain a significant amount of valuable compounds. A certain class of such compounds, polyphenols, are complex organic molecules with significant biological activity and as a result high market price. Their complex structures make their synthesis indeed very challenging leaving nature as the only plausible source. Their price per gram in their purest form ranges from a few euros to hundreds of thousands of euros.

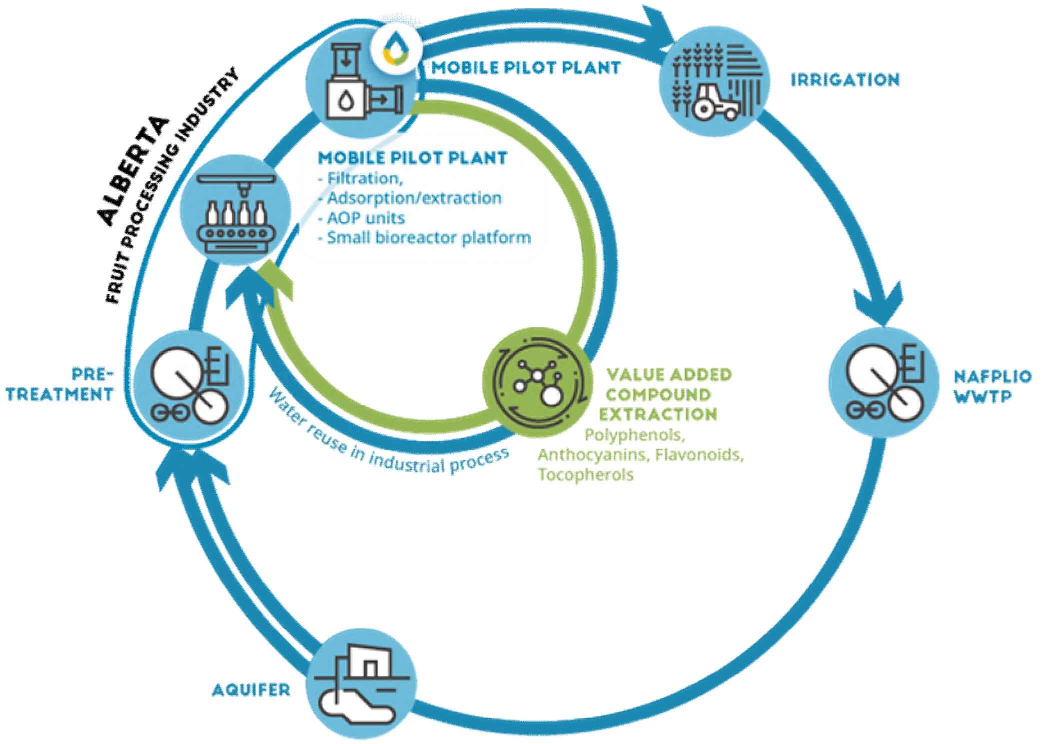

Figure 33 Scheme of Case study 4

Before Ultimate, there was no communication let alone an established symbiotic system among the water stakeholders in the area, which could have enabled water reuse or recovery of any valuable resources.

In the frame of Ultimate, Greener than Green (GtG) Technologies developed VesperX, a mobile unit that treats and recycles water and nutrients present in aqueous industrial by-products (Figure 34).

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Figure 34 Mobile unit (Case study 4)

VesperX combines a number of physicochemical & biological processes to isolate, value-added compounds and treat the remaining water (Figure 35), so the extent that it is rendered suitable for irrigation and/or secondary industrial uses.

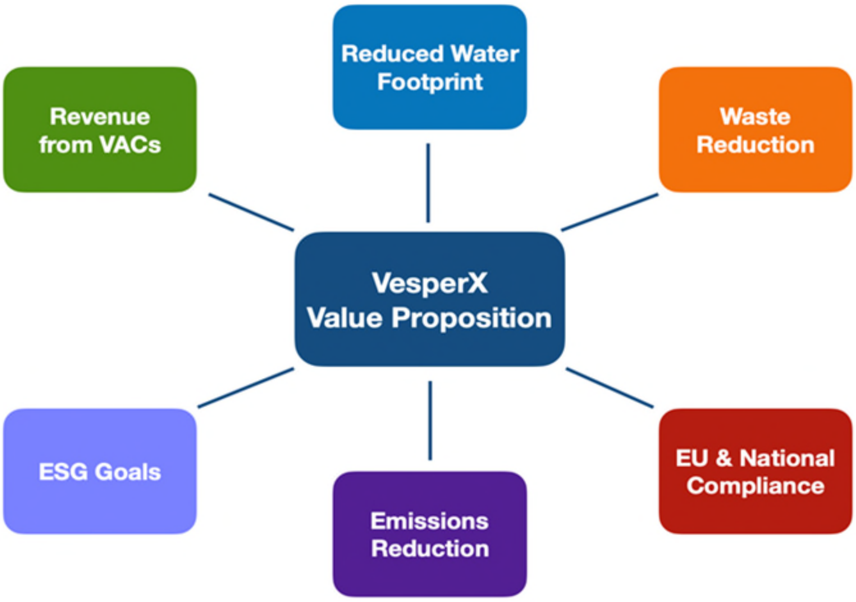

Figure 35 Value proposition

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VesperX is offered as a Product as a Service (PaaS), i.e. the units are not sold to the customer, they are leased for an agreed period. This model perfectly fits with the seasonality of the food processing sector and eliminates the need for extensive capital expenditure. It is needless to say that the revenue generated from the exploitation of Value Added Compounds (VACs) significantly offsets the cost of the treatment unit, thereby self-funding the environmental operations.

VesperX provides an opportunity for symbiosis not only within the water and materials clusters but also extends the notion of symbiosis to the societal aspect as an industry no longer competes for water with the weaker stakeholder: the farmers.

A fully functional VesperX unit is installed at Alberta's production facility. It consists of two 20-foot containers suitably converted into treatment tanks, and an ISOBOX containing the electrical installation, control units and AOP module. The current TRL is estimated to be 6-7. The unit is capable of treating the water by-product of fruits & vegetables such as oranges, carrots, tomatoes and olives.

The processes that are employed were initially developed on a lab scale. The overall process is described by the following layout (Figure 36):

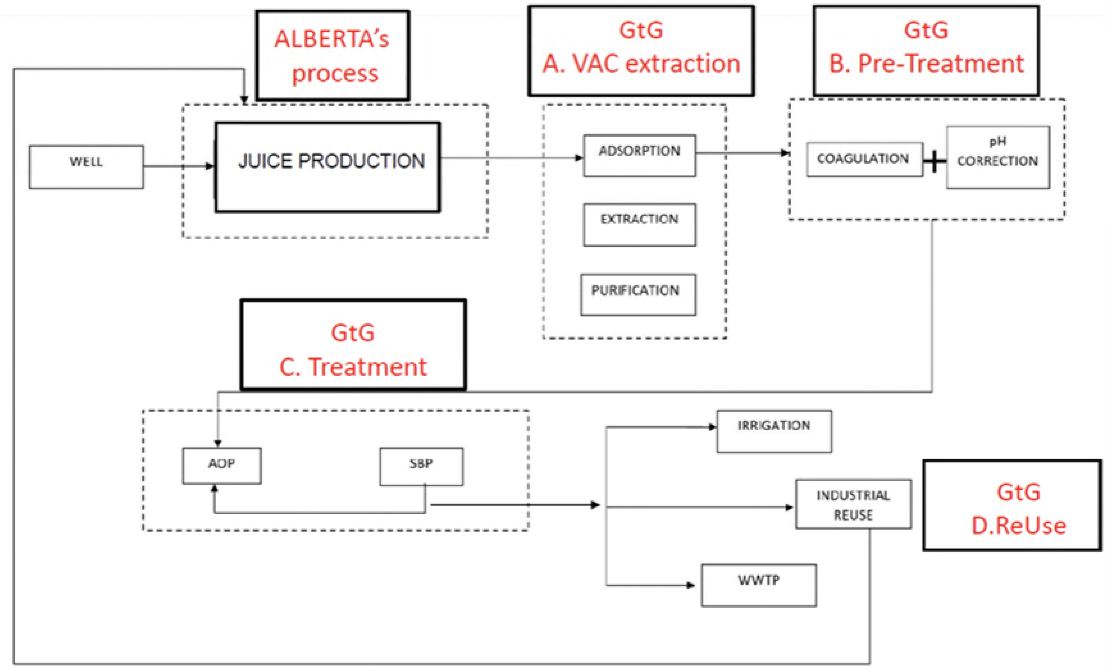

Figure 36 Case study 4 process

- The pilot comprises of the following components:

A. VAC adsorption

In this module VACs are selectively adsorbed on a solid phase material that exhibits high affinity towards phenolic compounds relative to other chemical species. The extraction step deemed to take place prior to any other physical or chemical process. Based on the results of extensive laboratory experiments, the type of sorptive material, contact time and adsorption capacity where selected and called up to fit the described pilot unit (Figure 37).

Figure 3. VAC adsorption process

Figure 4a. VAC adsorption lab-scale unit

Figure 4b. VAC adsorption pilot sub-unit

Figure 37 VAC adsorption process, VAC adsorption laboratory scale unit and VAC adsorption pilot sub-unit.

B. VAC extraction

B1. Conventional extraction

The polyphenols that were adsorbed on the resin were extracted using a liquid solvent. Typical solvents that were used are water methanol and ethanol and also mixtures of water and ethanol and water and methanol in various concentrations. Among this solvents water is cheap and non-toxic but quite inefficient. Methanol has high cost and increased toxicity especially when the extracts are to be consumed. Finally, ethanol has a high cost but lower toxicity. Ultrasound and elevated temperature were utilized to enhance the extraction process.

B2. Subcritical Water extraction (SWE)

Subcritical water is liquid water maintained under pressure at temperatures above its usual boiling point of 100 °C (212 °F), typically within the range of 10 to 20 bar. This method of extraction is known for its efficiency, cost-effectiveness, and environmentally friendly nature. Utilizing subcritical water for extraction processes offers a low-cost and non-hazardous alternative to traditional solvents, making it a green technology suitable for various industrial applications. Methanol as a co-solvent can be used to enhance the extraction yield and extract less polar compounds.

Figure 38 Subcritical/Supercritical Extraction Equipment

B3. Supercritical Fluid Extraction (SFE)

Supercritical carbon dioxide (sCO_2) is a fluid state of carbon dioxide where it is held above its critical temperature and critical pressure, where it can adopt properties midway between a gas and a liquid. CO_2 reaches its critical point at 31 °C and 73.7 bar, at which it behaves like a solvent. This supercritical CO_2 has low toxicity, making it a safer alternative for extraction processes. When the pressure is reduced, the CO_2 reverts to its gaseous state, allowing it to escape easily, leaving behind the extracted compounds.

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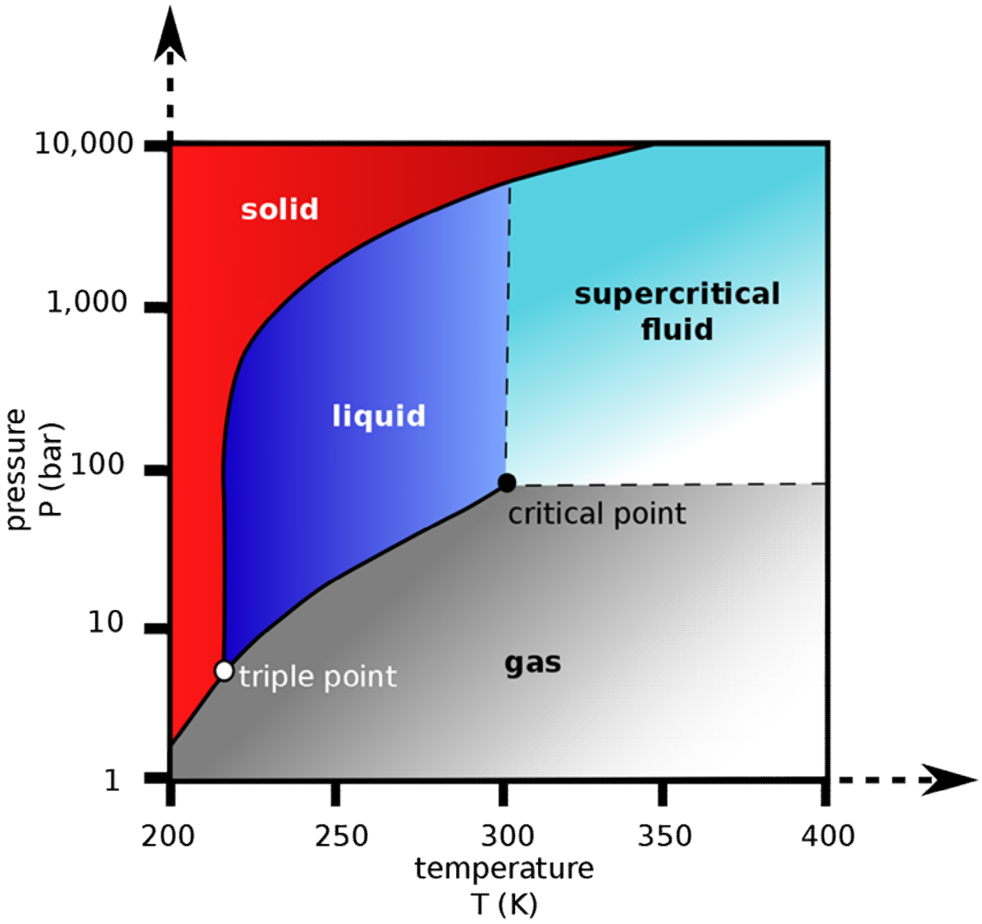

Figure 39 Carbon Dioxide pressure temperature phase diagram

VesperX can operate as a standalone wastewater treatment plant or can be installed as part of an existing treatment facility. There are no extensive site requirements. Some initial testing and planning are required to determine which outflow streams are most suitable for reclaiming VAC, and to determine the remediation needs.

The adsorption of VACs on the resin is taking place on site and then the saturated resin is transferred to our lab where the extraction apparatus is placed.

For the Subcritical Water Extraction

Operational Parameter	Value
Pressure	12 bar
Temperature	120 °C

For the Supercritical CO_2 extraction

Operational Parameter	Value
Pressure	150 bar
Temperature	70 °C

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The apparatus is capable of reaching pressures up to 700 bar. However, when VACs are adsorbed onto resin, such high pressures can damage the resin, thus it cannnot be regenerated and reused.

The workflow for compound identification included the following steps: 1) A number of polyphenols were specifically selected and targeted, due to their abundance and frequent occurrence in citrus by-product water; 2) their molecular formula, exact theoretical *m/z* identification ions, exact experimental detected *m/z* identification ions, Δppm (mass accuracy) and MS/MS fragment *m/z* were calculated (Table 16) in order to be separated chromatographically, and extract the respective ion chromatograms using Full MS Spectrum; 3) For the semi-quantification of targeted compounds, two compounds were spiked to the initial samples at a predefined concentration (quercetin for positive MS and gallic for negative MS).

Semiquantification was carried out using the following approach (Malm *et al.*, 2021; Gutiérrez-Martín *et al.*, 2023):

The response factor (RF) of spiked compounds at known concentrations, namely quercetin (positive ESI) and gallic acid (negative ESI), were calculated and compared to the targeted compound.

$$RF\ spiked\ \frac{peakarea}{concentration}1)$$

$$C\,t\arg e\,t = \frac{peakarea}{RF\ spiked}\text{OBJ}$$

similar to that of the targeted, and therefore, the RF of the similar standard (e.g. quercetin) can be used to estimate the concentration of the unknown.

8. LC-HRMS (MS) analysis

A Dionex UHPLC system (Thermo Scientific, Bremen, Germany) was used for the chromatographic separation. The system consisted of a vacuum degasser, a high-pressure binary pump, an autosampler with a temperature-controlled sample tray set at 7ºC and a column oven set at 30ºC. Chromatographic separation was performed at 30ºC using a Zorbax Eclipse Plus C18 column (100 × 2.1 mm i.d., 1.8 μm particle size; Agilent Technologies). The mobile phase consisted of 5 mM ammonium formate in 0.02% formic acid (solvent A) and a mixture of acetonitrile:water (90:10 v/v) containing 5 mM ammonium formate and 0.02% formic acid (solvent B). A gradient elution program was employed at a constant flow rate of 0.2 mL/min with solvent B starting at 5% for 3 min, initially increasing to 30% in 4 min, then increasing to 90% in 11 min and finally, set back to 5% in 11.5 min. Post-run equilibrium time was 3.5 min. The injection volume was 20 μL. Diverter valve was programed to send LC eluent in waste for the first 4 min.

A Q Exactive benchtop Orbitrap-based mass spectrometer (Thermo Scientific) operated in the positive polarity mode equipped with a heated ESI (HESI) source. Source parameters were: sheath gas (nitrogen) flow rate, auxiliary gas (nitrogen) flow rate and sweep gas flow rate: 40, 10 and 1 AU, respectively, capillary temperature: 250ºC, ESI heater temperature: 20ºC, spray voltage: +4.0 kV (positive polarity). The instrument operated in full scan mode from *m/z* 100-1000 at 17,500 resolving power and injection time of 100 ms and in MS/MS mode from *m/z* 100-1000 at 17,500 resolving power and injection time of 62 ms (product ion mode). The automatic gain control (AGC) was set at 10^6 ions. Mass calibration of the Orbitrap instrument was evaluated in both positive and negative modes weekly and external calibration was performed prior to use following the manufacturer’s calibration protocol.

2.3.2. Compound identification was achieved by: (a) t_R of compounds, (b) Δppm between theoretical and experimental accurate mass of precursor *m/z* < 10 ppm and (c) the presence of two characteristic precursor/product ion transitions from bibliographic references. Results of new approaches

In Table 15 are reported target KPI for case study 4, where recovery of material is related to recovery of phenolic compounds (antioxidants).

Table 15. Overview of the ULTIMATE KPIs for material recovery for case study 4.

KPIs as specified in GA	Achievable targets - Full scale
Reduction in fresh water use by wastewater reuse (90%)	90% recovery of water (compared to the water present in industrial by-product)
Material recovery (60%)	75% total phenolic content recovered (as of total phenolics present in industrial by-product)

Recovery of high-added-value compounds (antioxidants) in Nafplio

Adsorption

On average 80% of the polyphenols present in industrial by-product are adsorbed on the resin. This step is crucial both for the recovery of the polyphenols and for the further water treatment as it offers significant TOC reduction of around 20-25%. In the case of orange by-product each kg of resin can adsorb 4,7 g of polyphenols. This is quite lower than the olive wastewater where each kg of resin can adsorb 23,7 g of polyphenols present in olive oil mill wastewater. This difference is believed to arise from the presence of sugars in orange water by-product, which also have a relatively high affinity for the sorptive material surface and compete for the adsorption sites.

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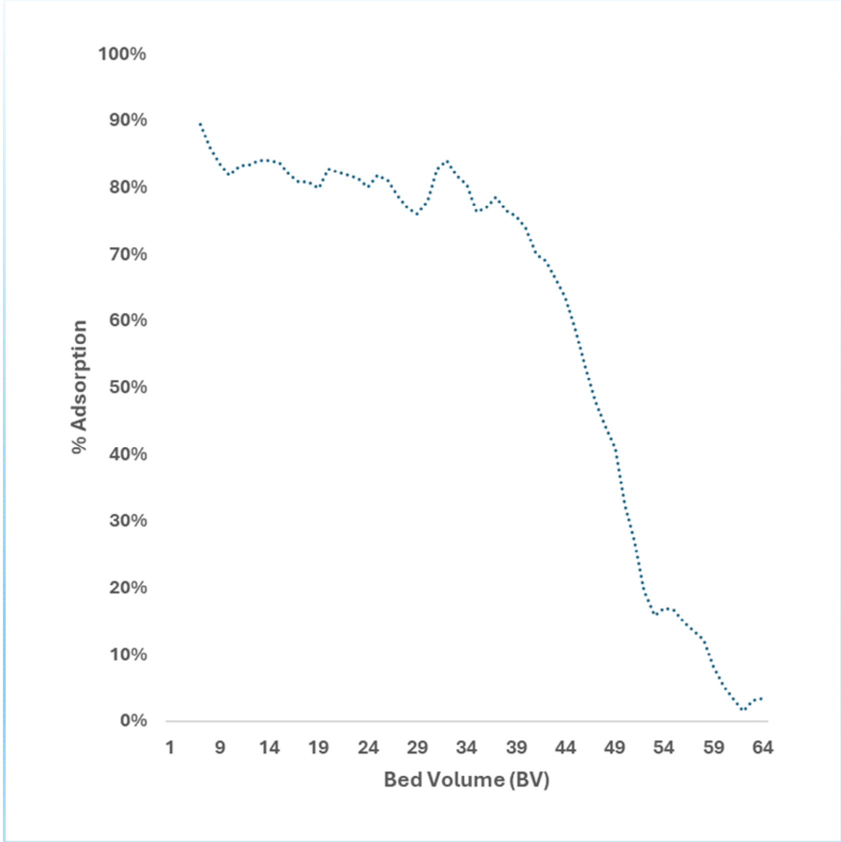

Figure 40 Adsorption on the resin

Conventional Extraction

The comparison of different eluent compositions for the extraction of polyphenol from the resin reveals notable differences in efficiency. Pure water (100 % H_2O) exhibited the lowest extraction efficiency, 5.2%. At 100% concentration, ethanol (EtOH) did not perform significantly better, maintaining at 8% extraction, while methanol (MeOH) remained highly efficient at 26%. At 50% concentration both MeOH and EtOH led to the highest extraction, EtOH showed significant improvement, achieving around 27% extraction efficiency, whereas MeOH demonstrated the highest efficiency observed, nearing 70%. In any other composition the efficiency ranged from 5 to 20%. At 5% concentration, EtOH achieved a low extraction percentage of 7%, while MeOH performed slightly better at 18%. At 10%, 10% EtOH showed similar efficiency to 5% EtOH, at 7%, while 10% MeOH achieved 8 % extraction. Increasing the concentration to 20% concentration, EtOH saw some improvement, reaching 8%, while MeOH remained at 9%. In general, methanol (MeOH) outperformed ethanol (EtOH) in extracting polyphenols across all concentrations. The most efficient eluent composition was 50% MeOH, achieving an extraction percentage close to 70%. Ethanol showed moderate efficiency at 50% concentration but did not perform as well as methanol at any concentration. Pure water was the least effective eluent for polyphenol extraction.

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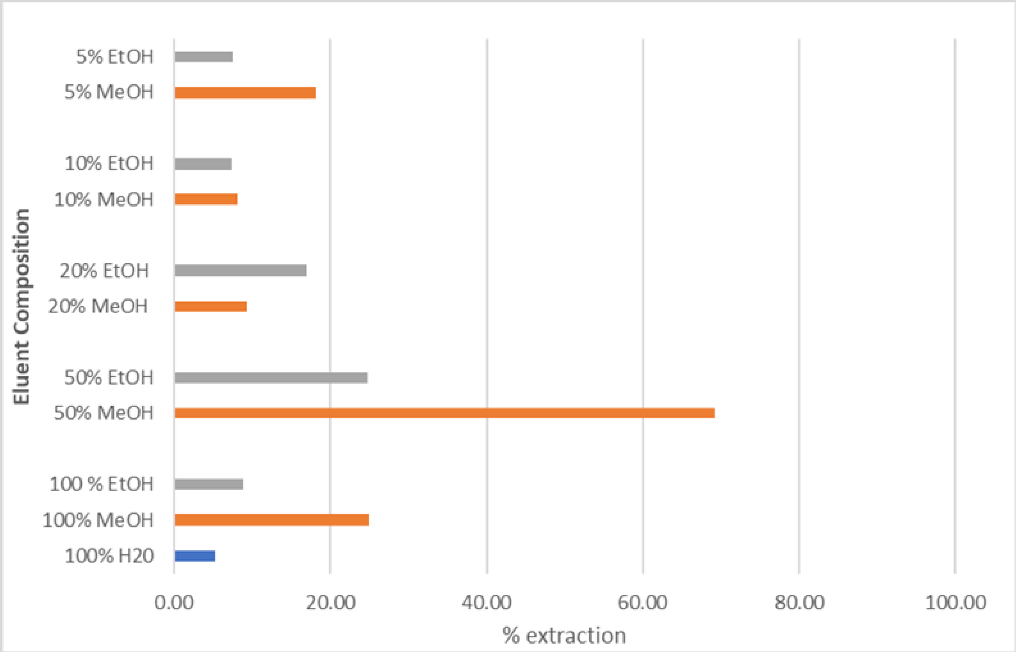

Figure 41 Conventional Extraction Results

Subcritical Water extraction

Subcritical water extraction enhanced the extraction process five-fold achieving 25% recovery of polyphenols while the use of solvent, water in this case, was five time less than in conventional extraction with pure water (
Figure *42*).

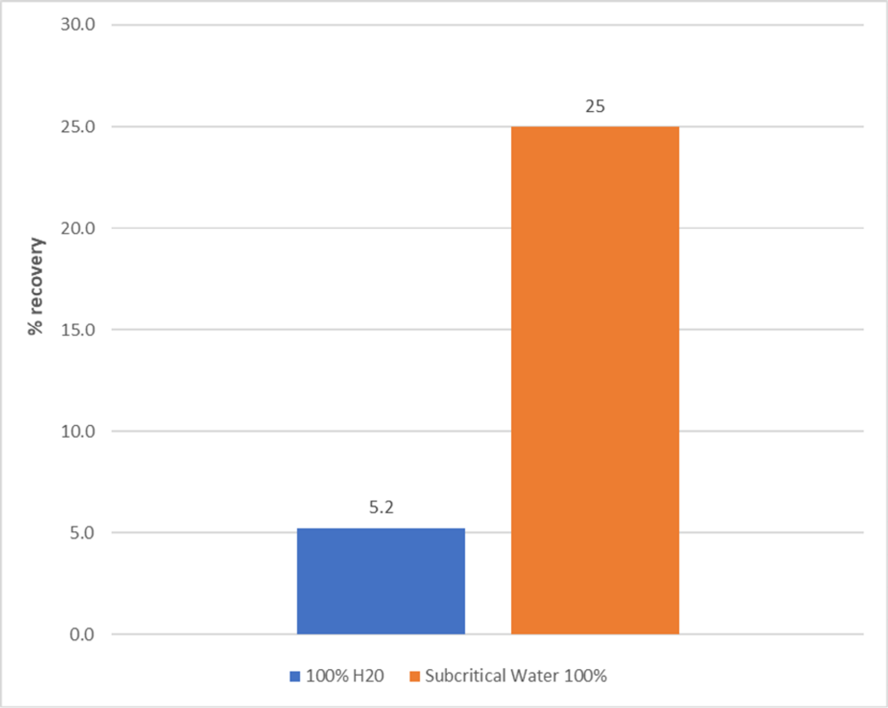

Figure 42 Comparison of Conventional Extraction with Subcritical Water Extraction

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When 20% methanol was added as a co-solvent the extraction yield was 33% (Figure 43).

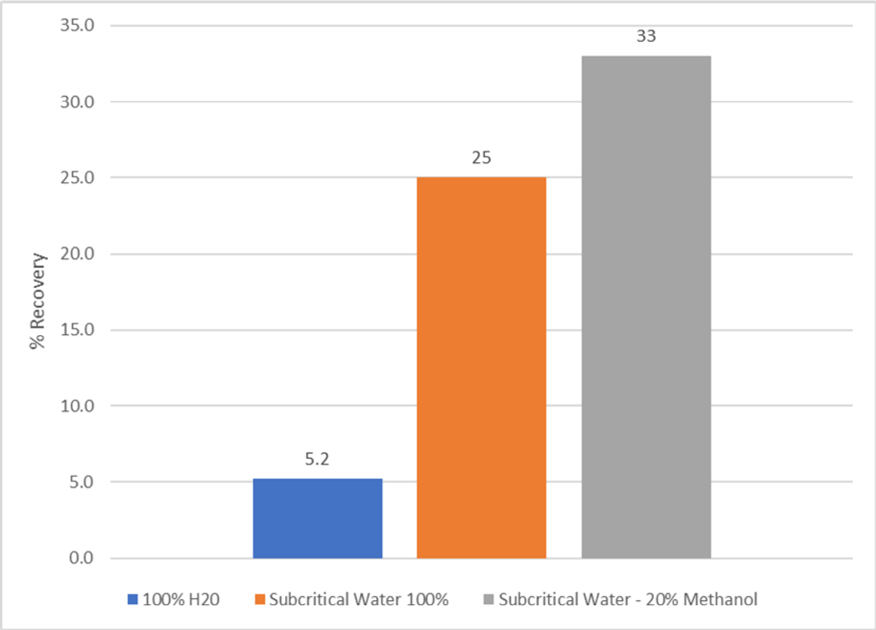

Figure 43 Comparison of Conventional Extraction with Subcritical Water Extraction and Subcritical Water Extraction with 20% MeOH

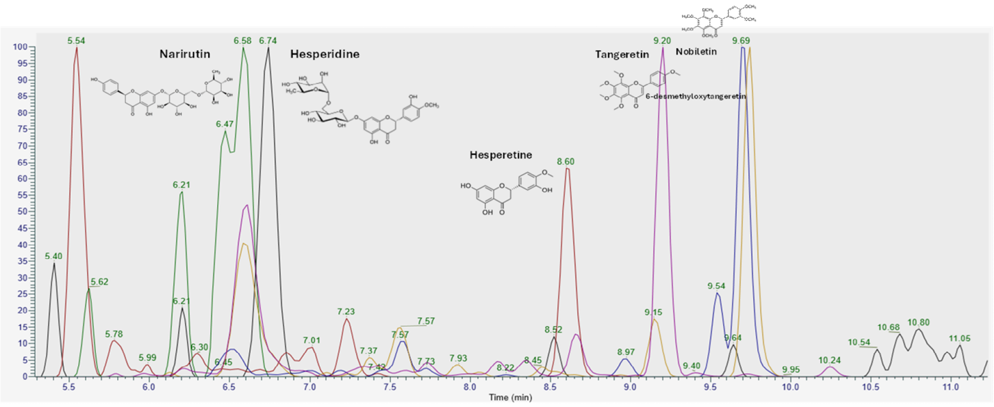

Figure 44 Chromatogram of compounds extracted with Subcritical Water Extraction

Also, the addition of methanol enabled the extraction of polyphenols that were not extracted with pure water, such as 3-desmethyloxytangeretin, and also enhanced the extraction of other polyphenols like hesperetine (

Figure *45*).

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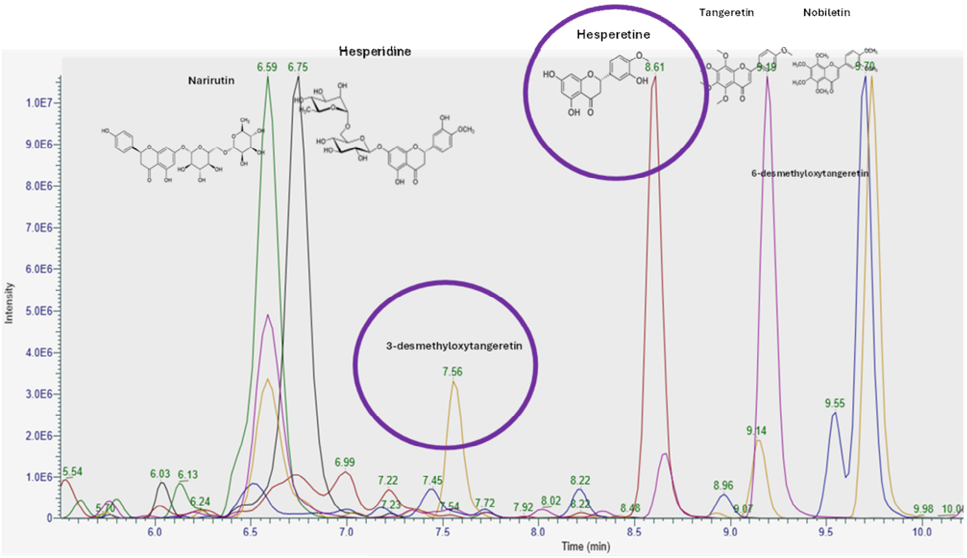


Figure 45 Chromatogram of compounds extracted with Subcritical Water Extraction and 20% MeOH

Supercritical CO_2 extraction

Supercritical CO_2 extraction doubled the extraction yield, reaching 75% recovery without using any additional co-solvent. After the extraction, when pressure decreases, CO_2 escapes as gas so the extracts are solvent free. In our case where we extract the polyphenols from the saturated resin we cannot increase the extraction pressure as the resin is destroyed and cannot be regenerated and reused.

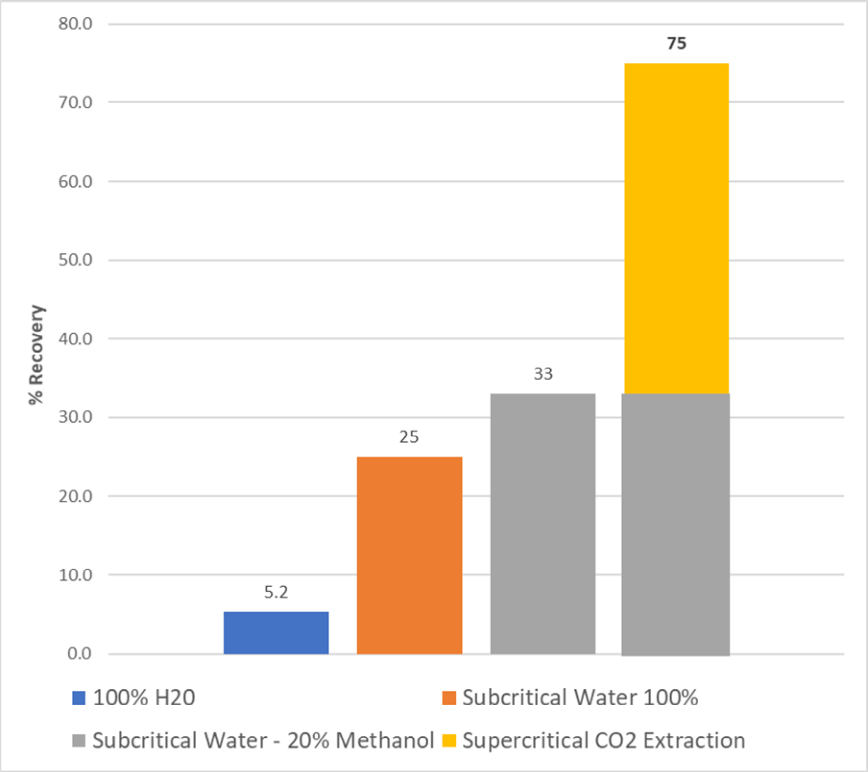


Figure 46 Comparison of Conventional Extraction with Subcritical Water Extraction and Subcritical Water Extraction with 20% MeOH and Supercritical CO2 Extraction

Chemical profile of polyphenol extracts

The analytical method targeted 37 polyphenolic substances with adequate mass accuracy, which are presented in Table 16. A representative Extracted Ion Chromatogram (EIC) of the class of Flavonones is presented in Figure 47, along with the mass spectrum of selected compounds.

Table 16. Targeted compounds with chemical formulae, m/z values, retention time (RT) and mass accuracy

			mol. formula	M-H theor	M-H exp	M+H theor	M+H exp	Δ (ppm)	RT (min)	ms2
Flavanones	1	Hesperidin	$C_{28}H_{34}O_{15}$			611.1953	611.1961	1.4	6.85	518.3528 / 509.1278 /375.1429 / 326.1380
	2	Hesperetin	$C_{16}H_{14}O_6$			303.0855	303.0861	2.1	8.71	237.1846 / 155.1065
	3	Naringin	$C_{27}H_{32}O_{14}$			581.1848	581.1860	2.1	6.69	227.0909 / 207.1377
	4	Naringenin	$C_{15}H_{12}O_5$			273.0750	273.0752	0.6	8.52	237.1847 / 219.1742
	5	Nobiletin	$C_{21}H_{22}O_8$			403.1374	403.1376	0.4	9.85	343.1170
	6	Narirutin	$C_{27}H_{32}O_{14}$			581.1848	581.1857	1.5	6.69	548.3630 / 430.3007 / 227.0909
	7	Tangeretin	$C_{20}H_{20}O_7$			373.1286	373.1274	-3.1	9.30	207.0648 / 151.1116

	8	Hexamethylquercetagetin	$C_{21}H_{22}O_8$			403.1374	403.1381	1.6	9.65	369.0965/ 355.0803/ 341.1014/ 327.0864
	9	Diosmetin	$C_{16}H_{12}O_6$			301.0707	301.0703	-1.3	8.60	286.0465/ 272.0641
Flavonols	10	Rutin	$C_{27}H_{30}O_{16}$			611.1607	611.1585	-3.6	5.62	303.0499/ 145.0495/ 129.0546
	11	Quercetin	$C_{15}H_{10}O_7$			303.0499	303.0492	-2.3	8.01	284.1070/ 177.0543/ 153.0183/ 111.4206
	12	Kaempferol 3-neohesperidoside	$C_{27}H_{30}O_{15}$			595.1642	595.1649	1.1	5.83	287.0544/ 271.0595/ 242.1168
	13	Diosmin	$C_{28}H_{32}O_{15}$			609.1814	609.1796	-3.0	6.39	463.1223/ 301.0699/ 129.0542
	14	Chrysoerial-7-O-neohesperidoside	$C_{28}H_{32}O_{15}$			609.1814	609.1804	-1.6	6.70	463.1236/ 301.0699
	15	Neodiosmin	$C_{28}H_{32}O_{15}$			609.1814	609.1811	-0.5	7.30	301.0700/ 286.0499
	16	Diosmetin	$C_{16}H_{12}O_6$			301.0707	301.0703	-1.3	8.61	286.0465/ 272.0641
Coumarins	17	Ferullic acid	$C_{10}H_{10}O_4$	193.0506	193.0498			-4.1	6.91	151.0390 / 136.0153
	18	sinapinic acid	$C_{11}H_{12}O_5$	223.0612		225.0757	225.0754	-1.3	6.85	165.0546 / 135.0439
	19	p-coumaric acid	$C_9H_8O_3$	163.0401	163.0390	165.0546		-6.7	6.72	119.0490 / 121.0282
	20	4-OH-coumarin	$C_9H_6O_3$			163.0390	163.0387	0.0	8.92	149.0233 / 139.1116
	21	5,7-Dihydroxycoumarin	$C_9H_6O_4$			179.0339	179.0338	-0.6	7.44	164.1069 / 135.1168
	22	5,6,7-Trimethoxycoumarin	$C_{12}H_{12}O_5$			237.0757	237.0754	-1.3	8.42	219.1740
	23	Kaempferol	$C_{15}H_{10}O_6$			287.0550	287.0552	0.7	7.92	209.1531
	24	Umbeliferon (isob 4-OH coumarin)	$C_9H_6O_3$			163.0390	163.0389	-0.6	7.08	152.1067 / 130.1227
Terpenes	25	Limonin	$C_{26}H_{30}O_8$			471.2013	471.2005	-1.7	9.52	373.1274 / 345.0965
	26	(nomillinic acid ms2) / Nomilin	$C_{28}H_{34}O_9$			515.2260	515.2255	-1.0	9.90	403.1381 / 343.1172
	27	Nomillinic acid	$C_{28}H_{36}O_{10}$	531.2236	531.2236	533.2381		0.0	9.30	517.2082 / 329.2330
	28	Obacunonic(MS2) / isoubacunonic (MS2)/ Obacunone	$C_{26}H_{30}O_7$			455.2064	455.2056	-1.8	10.40	
	29	Isolimonic acid	$C_{26}H_{34}O_{10}$	487.1976	487.1971	489.2119		-1.0	8.80	301.0718 / 229.1441
Anthocyanins	30	Cyanidin 3-O-acetylglucoside cation	$C_{23}H_{23}O_{12}$			491.119	491.1185	-1.0	6.53	209.1534 / 180.1018
	31	Delphinidin 3-O-glucoside cation	$C_{21}H_{21}O_{12}$			465.1033	465.1019	-3.0	6.10	402.2690 / 321.1916 / 265.1431
	32	Peonidin 3-O-glucoside cation	$C_{22}H_{23}O_{12}$			463.124	463.1228	-2.6	6.61	386.2744 / 213.1116
	33	Petunidin 3-O-glucoside cation	$C_{22}H_{23}O_{12}$			479.119	479.1173	-3.5	6.82	474.3266
	34	Malvidin 3-O-glucoside	$C_{23}H_{25}ClO_{12}$			493.1336	493.1331	-1.0	6.71	430.3003
	35	gallic acid	$C_7H_6O_5$	169.0142	169.0139			-1.8	2.79	
Various	36	Resveratrol	$C_{14}H_{12}O_3$	227.0714	227.0707	229.0859		-3.1	7.69	201.1131 / 157.0861 / 137.0595
	37	Myricetin	$C_{15}H_{10}O_8$			319.0448	319.0441	-2.2	7.14	167.0702 / 209.0807

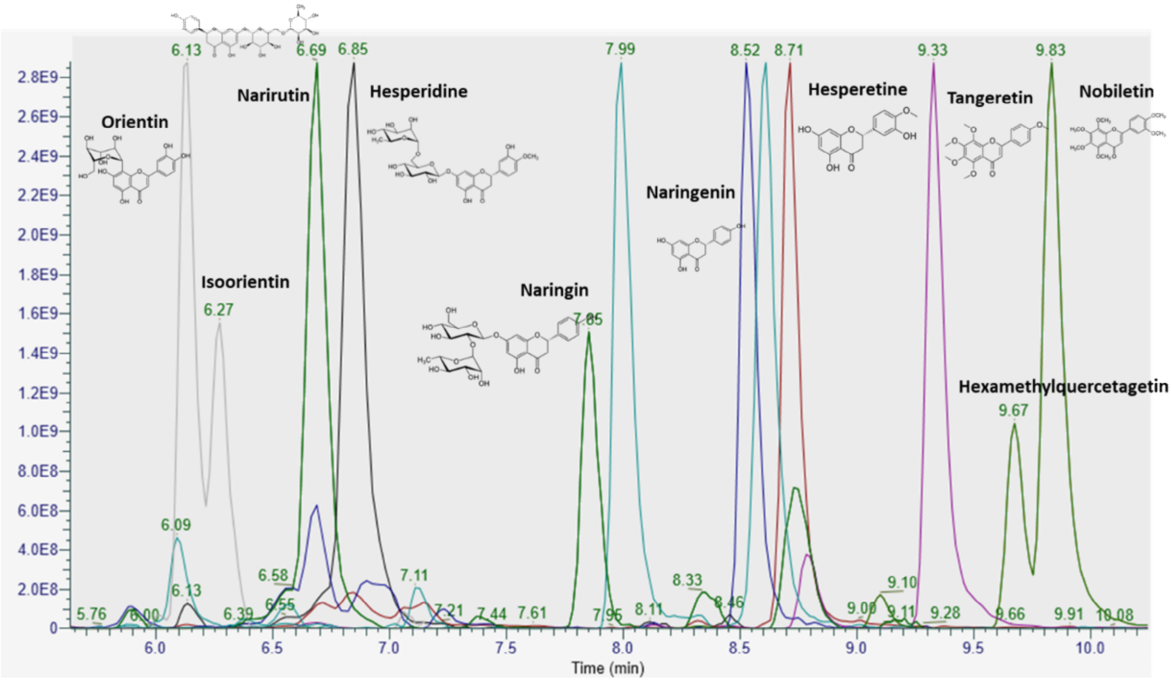
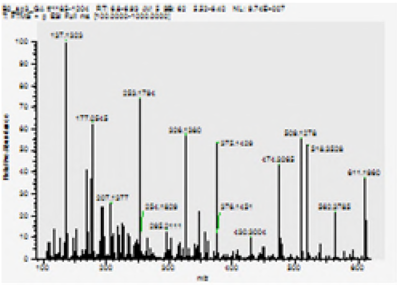
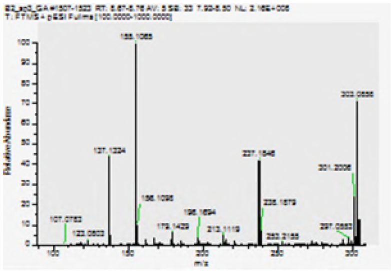


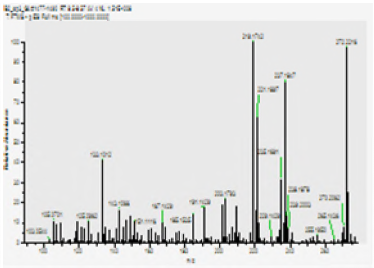
Figure 47 Normalised EIC of flavonones (all peaks reaching 100% pf relative abundance) in sample Supercritical CO2 with mass spectrum of main peaks



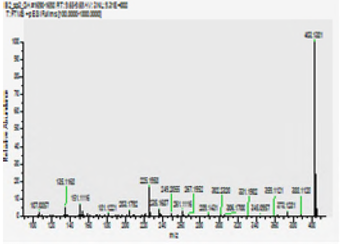
Hesperidin

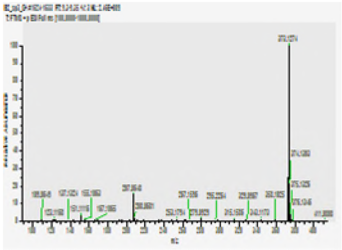


Hesperetin

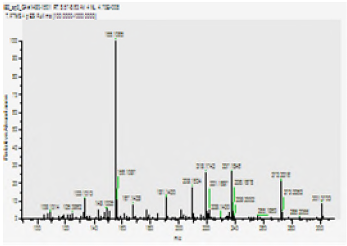


Naringenin





Tangeretin



Diosmetin

Hexamethylquercetagetin

From the wide range of targeted compounds, the most abundant signals and the widest range of compounds were obtained using SFE, with abundances increasing given longer extraction times.

SFE provided several compounds in the class of flavonones, and the most abundant compounds were hesperetine, tangeretin, hexamethylquercetagetin and nobiletin. SWE with 100% water (SubW) provided mainly narirutin, hesperetine, tangeretin and nobiletin and lower concentrations due to the dilution factor of the process method, while using 80/20 Water/MeOH for SWE mainly extracted naringenin narirutin, hesperetin, tangeretin and nobiletin and different ratios than using 100% water. A comparison of the EIC chromatograms is given in Figure 48.

The extraction technique and solvent clearly influence the abundance and profile of compounds extracted from the sample.

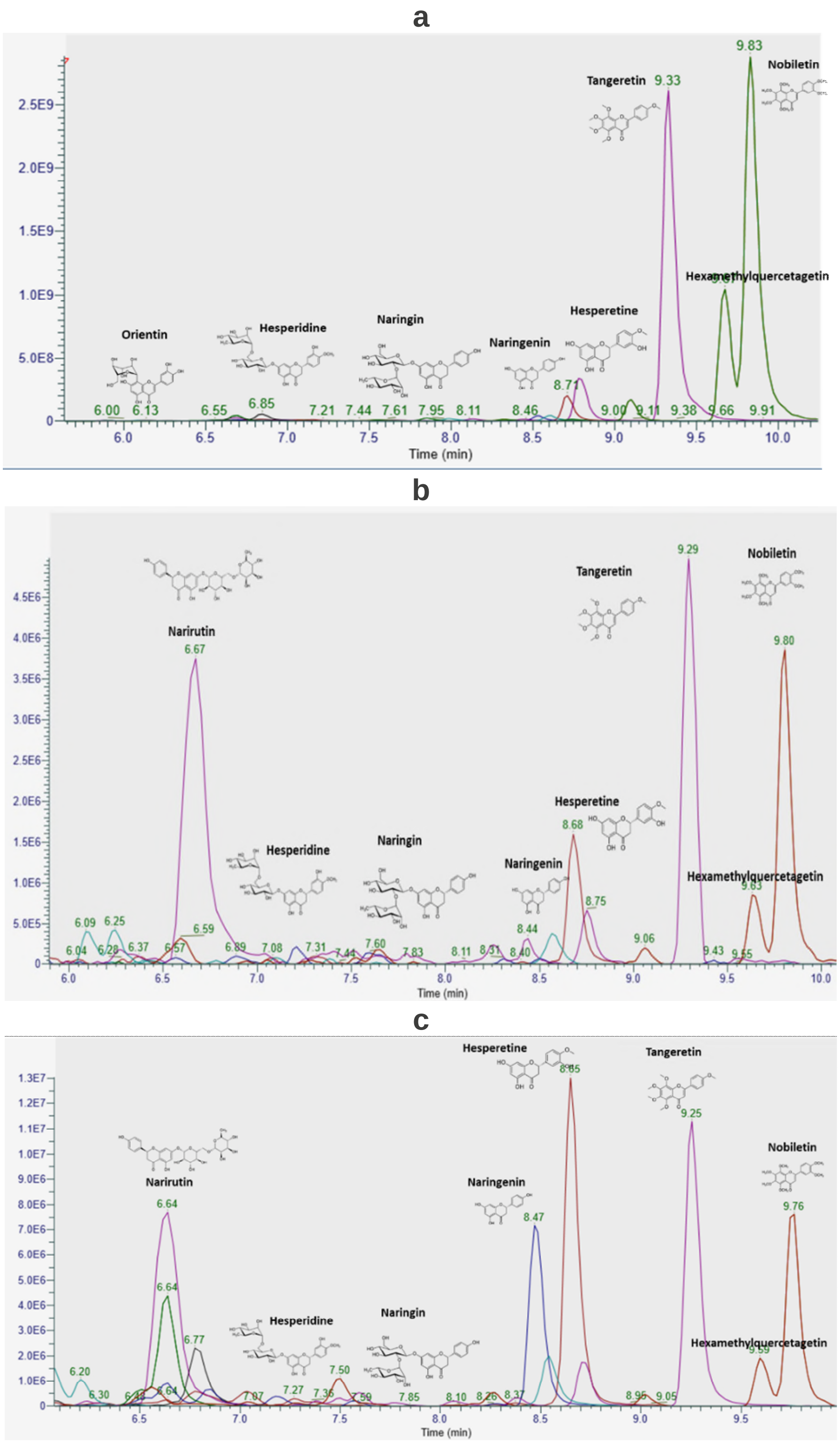


Figure 48 Comparison of EIC chromatograms for flavonones, using a) supercritical extraction Super2, b) subcritical water extraction with 100% water (SubW) and c) subcritical water extraction with 20% MeOH (SubWM)

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In the case of flavanols, the most abundant compounds identified in the sample Super2, were rutin, kempferol, diosmin, diosmetin and iso-kaempferide, while SubW mainly showed mainly kaempferol and SubWM kaempferol and diosmin.

The main coumarins obtained using SFE were p-coumaric acid, sinapinic acid, umbelliferon, 5,7dihydroxycoumarin, 5,6,7trihydroxycoumarin and 4-hydroxycoumarin. On the other hand, far less abundant were the compounds obtained using SubW, providing only p-coumaric acid, sinapinic acid, umbelliferon and 5,7dihydroxycoumarin. SubWM included mainly p-coumaric acid, sinapinic acid, umbelliferon and 5,7dihydroxycoumarin at higher abundances than SubW.

In the case of terpenes, isolimonic acid, nomilinic acid and limonin were mainly identified in Super2 sample, while SubW included the same compounds at far less abundance, while SubWM also included isolimonic acid, nomilinic acid and limonin, as well as resveratrol which was identified only in this sample.

Anthocyanins peonidin, malvidin and petunidin were the main identified members of this class in Super2, while SubW and SubWM contained mainly peonidin, at far less abundance.

4. Semiquantification of polyphenolic compounds

Figure 49 presents the estimation of different extracted compound classes using the four different extraction processes, and the semiquantification method previously described.

The use of SFE provided extracts (SuperA) with significantly higher concentration of the targeted compounds, as was expected by previous studies(Brijesh kumar, Brunton and Brennan, 2013). SubW produced extracts with fewer compounds, mostly water soluble. The SubW extract did not include hesperidin, narirutin, naringin, diosmin, trimethocyxoumarin, nomilin, obacunone or myricetin, while the overall quantity of the extracted compounds only accounted for 1-5% with respect to SuperA. The addition of MeOH in the eluent (SubWM), resulted in the presence of semi-water soluble compounds, and higher compound abundancies (Figure 49a).

For example, the contribution of SubW in the extraction of p-coumaric acid, sinapinic acid and ferulic acid is quite significant, while tangeretin, nobiletin, diosmetin, hexamethylquercetangetin are mainly extracted through SuperA and SuperB (Figure 49b)

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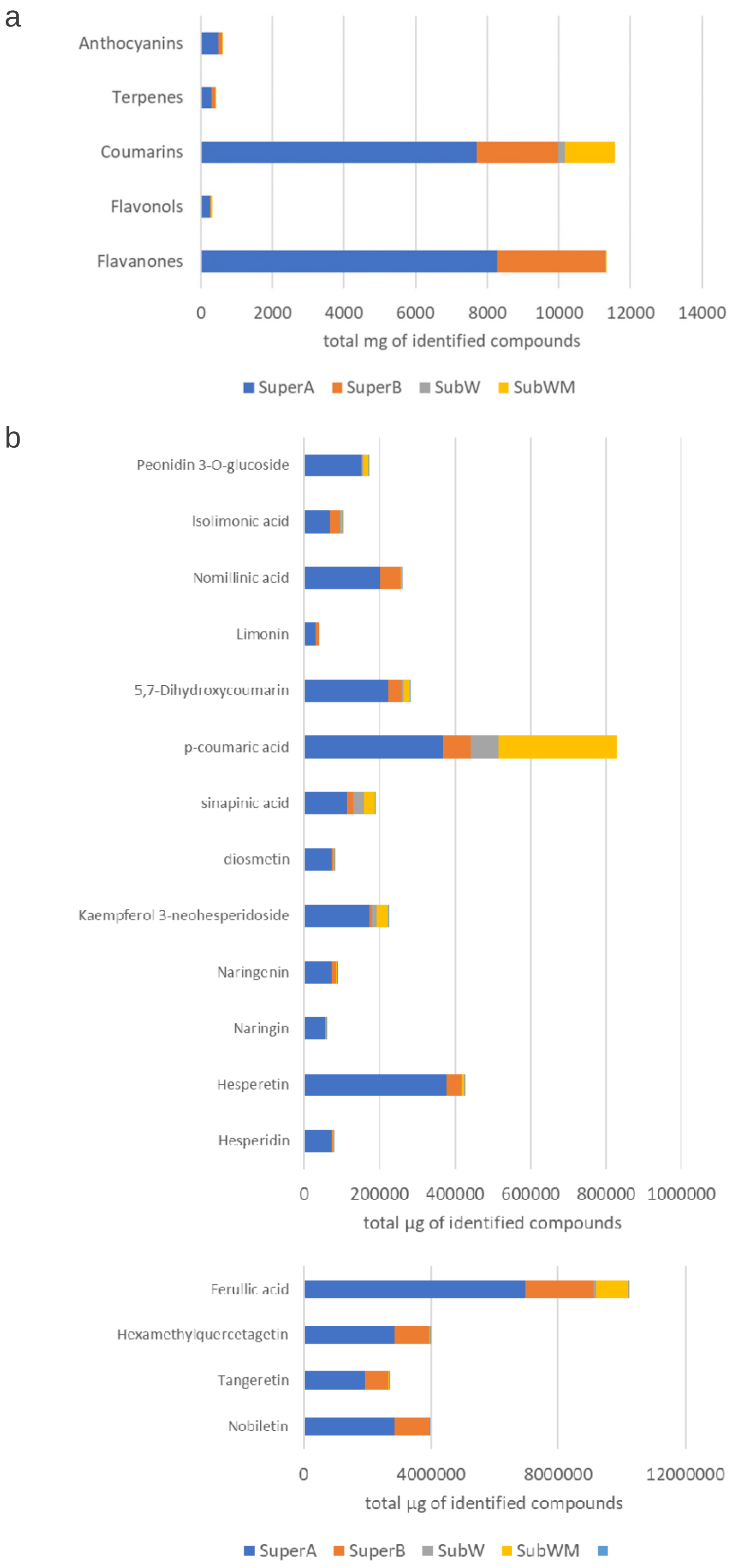

Figure 49 The effect of different extraction processes on the extraction of a) different chemical classes of extracts and b) specific compounds

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The total amount of flavanones extracted from the resin that was used to process 20L orange juice by-product, mostly contained tangeretin, nobiletin and nexamethyl-quercetagetin (Barrales *et al.*, 2018), at values higher than 2500, 3950 and 3900 mg respectively, as shown in Figure 50(a). The calculated concentration of these compounds in the initial processed stream was higher than 130, 200 and 190 mg L^{-1}, respectively.

Kaempferol and diosmetin were the main compounds found in the total extract, exceeding 200 and 70 mg in the resin, or 3 and 11 mg L^{-1} in the initial extract, as shown in Figure 50(b). In the case of coumarins, ferulic acid is the most abundant representative of the class (>10g in the resin, or >500 mg L^{-1} in the processed stream), with p-coumaric acid (> 500 mg) and the hydroxy-derivatives of coumarin at concentrations >40 mg L^{-1} in the processed stream (Figure 50c).

Nomillinic acid, limonin and isolimonic acid were the dominant compounds in the terpene group , at concentration higher than 200, 30 and 100 mg L^{-1}in the processed stream (Figure 50, d).

Anthocyanins were detected at significantly lower concentrations, in agreement with Brito *et al.* (2014), as expected by previous studies, with peonidin found at the highest concentration (> 8.5 mg L^{-1}) (Figure 50e).

In total, the most abundant classes of polyphenols that were extracted from the stream are flavanones and coumarins (Figure 50f). Based on the semiquantitative technique the concentration of polyphenols extracted is 22 g.

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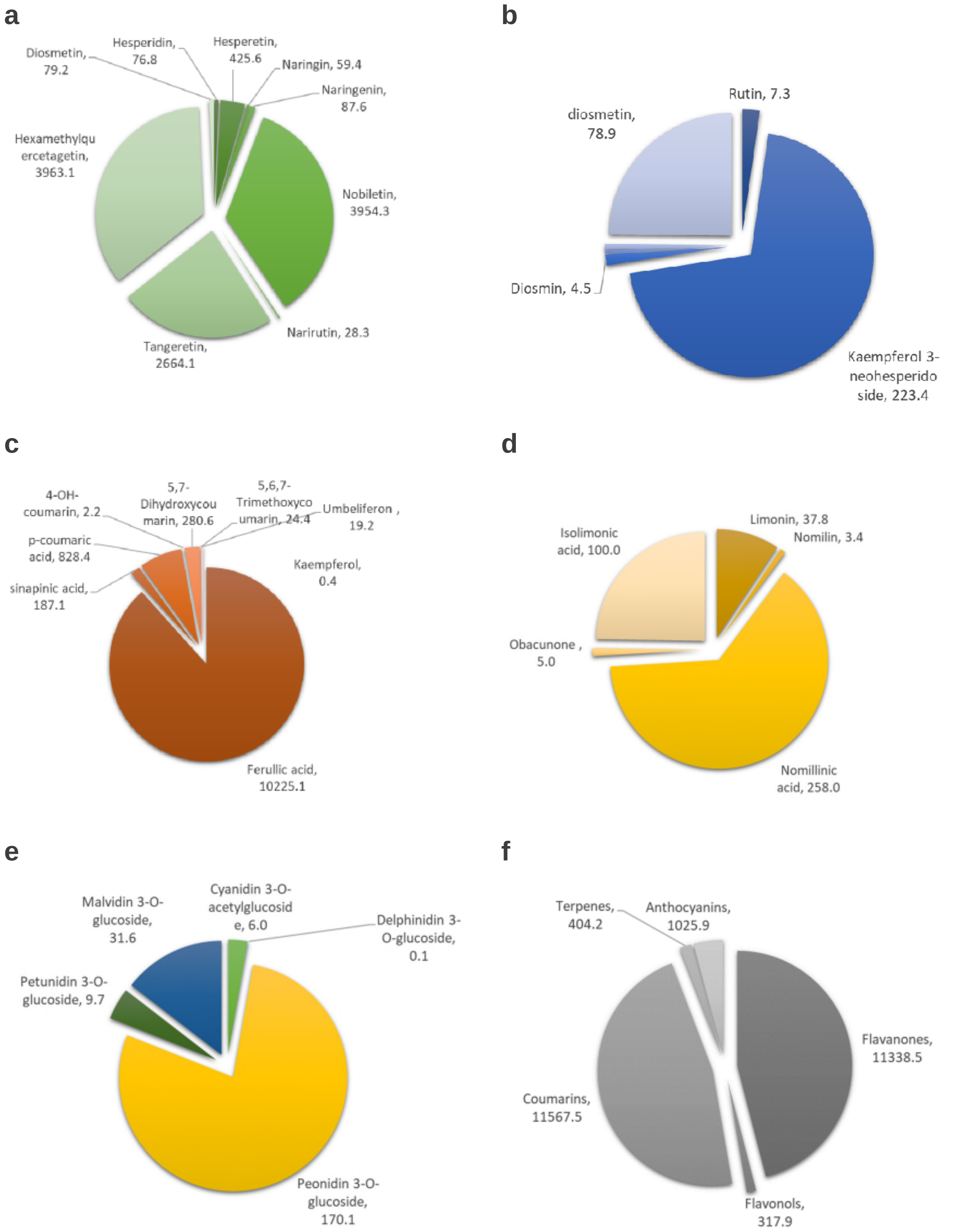

Figure 50 The chemical profile of each individual class of targeted compounds including their semi-quantified total mg in the sum of extracts SuperA, SuperB, SubW, SubWM: a) flavanones, b) flavonols, c) coumarins, d) terpenes, e) anthocyanins, f) presented as classes of compounds.

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2.3.3. Conclusion

Greener than Green Technologies has successfully designed constructed and optimized the VesperX prototype. Operated for several months at the Alberta facilities, in Nafplio, Greece, the functionality of VesperX has been demonstrated in a real environment. It is capable of treating at least 10m^3/d of water by-product originating from various juice production streams. The pilot can successfully remove and reclaim polyphenols for further purification and exploration Regarding our initial design we made a significant change moving the adsorption step prior to any other treatment such as pH-adjustment and addition of coagulant, that irreversibly destroyed the compounds of interest. For future units it is needed to minimize the tank sizes (inventory minimization from the operation management perspective) in order to reduce data lagging. This was our main concern in the SBP case. Furthermore, the cost benefit analysis indicated that SBP should be replaced. It is an expensive solution (0,5 € per capsule/ at least 4000 capsules needed each week) and as the annular reactor achieves partial mineralization maybe a different final step should be selected, membranes or MBR.

Another issue that needs to be addressed to make the process more cost effective is to find alternatives to the extremely high-priced adsorption material. We believe it is imperative to migrate towards more environmentally friendly and circular materials. To address these adsorption issues simultaneously we will look into natural alternatives as well as preparation/production processes. Currently, we are working on the development of a process that treats solid wastes from the same or similar industries to be suitable for adsorption the polyphenols. After one or more uses these materials can be further processed in order to render them suitable as added value animal feed. All these steps offer a new symbiotic relationship that did not exist before, let alone another life opportunity for material considered as waste.

In terms of further product optimization several ideas have been proposed, with the most prominent one being the reduction of the bulk of the unit, that will make it easier to transport between sites, hence both reducing the costs and environmental impact.

Finally, one of the major challenges we are facing is streamlining the process so that it is more cost effective. As we are currently targeting very high-priced value-added compounds this cost, although significant, is acceptable or even negligible. By reducing the operational cost, we can target compounds of lower market price and make their recovery worthwhile. This will increase our addressable market and make our technology/product more attractive to a wider range of industries. Simultaneously, and in conjunction with our proposed business model, we will reduce the environmental footprint of our business, an idea and ideal deeply embedded in the company's vision and culture.

Crucial factors for technology implementation and its optimal performance

- Polyphenols are succesfully adsorbed on the resin
- Extraction can be achieved by conventional extraction, Subcritical Water Extraction & Supercritical CO_2 extraction
- Better Yield was achieved By Supercritical CO_2 Extraction which is also the most environmental friendly of the 3 methods
- The prices that polyplenols can be sold make the cost of extraction irrelevant

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2.4. Recovery of nutrients from brewery digestates in Lleida (ES)

2.4.1. Case study and ULTIMATE concept

A concept study has been conducted, where two materials (struvite ($MgNH_4PO_4 \cdot 6H_2O$) and hydrochar) are proposed as candidates for being recovered from municipal and industrial streams. Two respective solutions are proposed for the recovery of both: Aquavite(R) for struvite and hydrothermal carbonization (HTC) for hydrochar.

Struvite would be recovered from the side-stream (i.e. the liquid phase generated after the dewatering of anaerobically stabilized sludge) in the municipal WWTP. On the other hand, hydrochar would be produced:

- from the brewer's spent grain (BSGs) of a brewery.
- from the digested sludge of the municipal WWTP of Lleida.

Both technologies can be considered mature as several solution providers and references can be found in the current European water market.
Aquavite(R) is based on the patented technology (EP3112320A1).

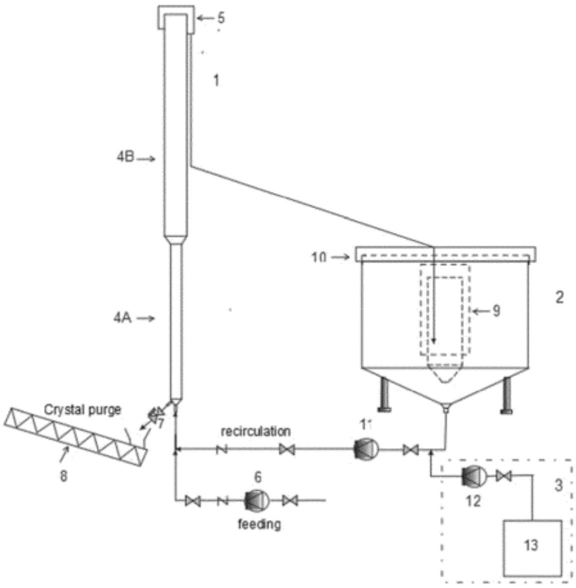

Figure 51 Aquavite process

According to Annex II of the Regulation 2019/1009 ("fertilizer regulation"), struvite recovered from wastewater is allowed in EU fertilizers. This definitely opens the door to the recovery of the P content of wastewaters. Since 2019, fertilizer companies can accept recovered P products as they bring some economic benefits to their business. Precipitating phosphorus and nitrogen from side-streams can:

- save chemicals and/or energy to be put on the mainstream water line in the WWTP for nutrient removal.

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- save maintenance costs due to undesired struvite precipitation in pipelines.
- generate incomes thanks to struvite sells (a high-value, slow-release, efficient fertilizer).
- substitute an essential, strategic and non-renewable resource (P rock)

HTC is a hydrothermal process that aims to concentrate the carbon in a given biomass, occurring in water at temperatures in the range of 160–280 ºC, above saturated vapor pressure, where water's dielectric constant decreases so drastically that it catalyses the carbonization of biomass while acting as an organic solvent. Due to exothermic nature of the reaction, heat is released. As such, the process can be driven auto-thermally. The carbonaceous materials obtained in the process show a reduction in mass while at the same time exhibiting an increase in net calorific value. HTC proceeds via a series of mechanisms, including hydrolysis, dehydration, decarboxylation, decarbonylation, and demethanation.

<u>HTC in municipal WWTP</u>:
The use of HTC as post-treatment of the digestate from anaerobic digestion of sewage sludge can:

- save energy, since the thermal energy required by HTC can be applied to a stream more concentrated in solids obtained after thickening;
- reduce the digestate volume, since hydrochar is formed, thus reducing sludge management and disposal costs; and
- improve biogas yield, by recycling the HTC liquor and possibly hydrochar back to the anaerobic digestion.

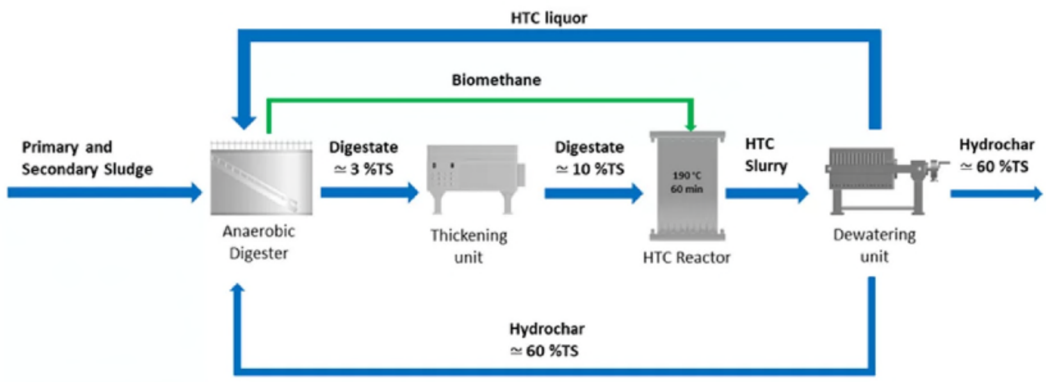

Figure 52 Scheme of the integration of the AD with the HTC process: AD–HTC scenario. The green biomethane stream represents a heat input to HTC. Indicative total solid (TS) content is also reported. Extracted from Ferrentino et al. (2020)

<u>HTC in Brewery</u>:
The specific energy intensity of brewing processes is about 150 MJ/hL beer produced, while the energy recovery from spent grains by HTC could reach 36 MJ/hL beer produced. The composition of the liquid phase generated after HTC has been described previously (Weber et al., 2013), and includes acetic acid as the most

prevalent compound. The high organic content is well suited for further anaerobic treatments and thus the energy potential is increased.

The struvite crystallization takes place with high concentrations of ammonium and phosphorous under alkaline conditions (pH ≈ 8 - 10). The higher the pH, the higher the nutrient concentration on the sidestream, the easier the crystallization and the less reagent will have to be added to increase the pH. Generally, struvite is considered as suitable for sidestream, since pH meets the abovementioned requirements. Additionally, the suspended matter content is low (compared), allowing the obtention of a clean struvite crystal.

HTC is performed in 80–95 vol% water, making it an ideal processing pathway for wet biomasses such as sewage sludge or BGS.

2.4.2. Results of new approaches

In the municipal WWTP of Lleida, the current sidestream P content is about 80 mg TP/L and a total flow of side-stream of 200 m3/d is produced daily. That means a potential of ca. 6 T TP/year. A realistic approach of 80% removal, means obtaining daily ca. 100 kg struvite, or 37 T/year.

Hydrochar would be produced:

- from the brewer’s spent grain (BSGs) of the brewery. Assuming that for 1 hL of beer produced, 20 kg of wet BSG is left over, and that the brewery produced 2 M hl of beer annually, the potential BGS production is 40.000 T BGS/annually.
- from the digested sludge of the municipal WWTP of Lleida. An amount of 5 T dry matter gets out daily from the digesters. Since the HTC process generates a 70% solids yield, a 28% liquid yield and a 2% gas yield, and the hydrochar is dewatered to 60% dry matter, the mass balance indicates 3,5 ton/day of 60% TS hydrochar to be generated.

2.4.3. Conclusion

Although regulation has become favorable for struvite profit, and although struvite crystallization is feasible from a technical point of view, struvite recovery with the proposed solution is not economical, and is limited for scenarios with higher P fluxes.

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2.5. Recovery of high-value products from olive mill wastewater in Karmiel (IL)

2.5.1. Case study and ULTIMATE concept

The Symbiosis interconnects 2 SMEs from the agro-food sector with a public wastewater utility, linking industrial WWTP with municipal WWTP. The agro-industrial sector includes agriculture, food industry, olive oil mills and water treatment. Partners involved are AGROBICS LTD (AGB), Galilee Society Institute of Applied Research (GSR), Mekorot company (MEK), and Greener Than Green Technologies AE (GtG). The symbiosis enabled to protect the current WWTP of Karmiel and similar system that are usually exposed to any sudden shocks of strong and problematic agro-industrial wastewater (i.e, OMW, Slaughterhouse, winery). Also, the additional produced biogas will be an added value to generate power as renewable energy within the context of circular economy.

Figure 53 Representation of the Case Study in Karmiel (IL)

Recovery of high value-added compounds from olive mill wastewater (OMW) was done by the adsorption system that Greener than Green Technologies (GtG) developed as pre-treatment of OMW before the anaerobic system – AAT, which was developed by the AgRobics Ltd.d. and Galilee Society. The adsorption system enables resource recovery and improve the performance of downstream systems by removing upstream to the treatment, inhibitory compounds, namely polyphenols. The polyphenols adsorption on the resin was followed by extraction of high value-added compounds as a crude extract. The production of a crude phenolic extract was done by a simple, low-cost extraction employing hot water and methanol.

Resin is packed in the containers (~ 20 L each). In each container (4 in total) (Figure 54), a metallic filter disc was added to the bottom. Then filled with a small amount of water (approximately 3L) to assist the packing. A sponge was placed at the top of the resin to retain large particles and prevent the resin from escaping. The unit is designed to operate with 2 containers each time, so daily treatment can be achieved. A pump with flow rate of 1 L/min is used to pass the OMW through the resin. Preliminary lab work showed that the desired contact time is 30 min. Once the resin is saturated, it was taken to the lab for extraction.

Figure 54 GtG adsorption system in the front side of the AAT at the Karmiel site.

A step-by-step description of the Standard Operating Procedure (SOP) for polyphenols adsorption on the resin then extraction by employing hot water and methanol then regeneration of the resin was given by GtG. However, due to the different characteristics of the OMW used in GtG lab with the one available in Karmiel (OMW is characterized with 69000 mg/L of COD and high Polyphenols content of 4500 mg/L), which is about 100 times higher in terms of polyphenols concentration than the OMW used by the GtG team), some modifications were made. First, to the SOP to enable working at the pilot demonstration site, and secondly to decrease the methanol consumption and increase its reuse. First, the resin was reused for adoption for 6 runs, each time by applying a new volume (1 L) of OMW to the lab scale adsorption column containing 110 mL of resin. After each run, the resin was washed with distilled water, then the resin was oven dried thereafter an extraction of the polyphenols by the same used methanol volume (1L).

Figure 55 shows the polyphenols concentration of the raw OMW and the OMW after the different adsorption runs. From the figure it is clear that the initial polyphenols concentration of 4300 mg/L was reduced to 2150-2900 mg/L, thus between 1400 to 2150 mg/L of polyphenols were adsorbed on the resin. This corresponds to a reduction of 38% of the polyphenols in average (The COD reduction was 21%, results not shown).

The reuse of methanol for extracting the adsorbed polyphenols on the resin was tested, results are shown in Figure 56. From the results we can use the same solvent 4 times, thus the recommended solvent ratio is 1 liter of methanol per 4 liters of olive mill wastewater (OMW). While each run extracts about 1000 mg/L of polyphenols from around 2000 mg/L adsorbed, getting an average of 50% recovery.

The final step of extraction included placing the methanol in rotary evaporator to condense it and get the crude extract. Each liter of extracted organics in methanol gave 4.2 g crude powder per batch, the crude powder contained 1 g of polyphenols in average.

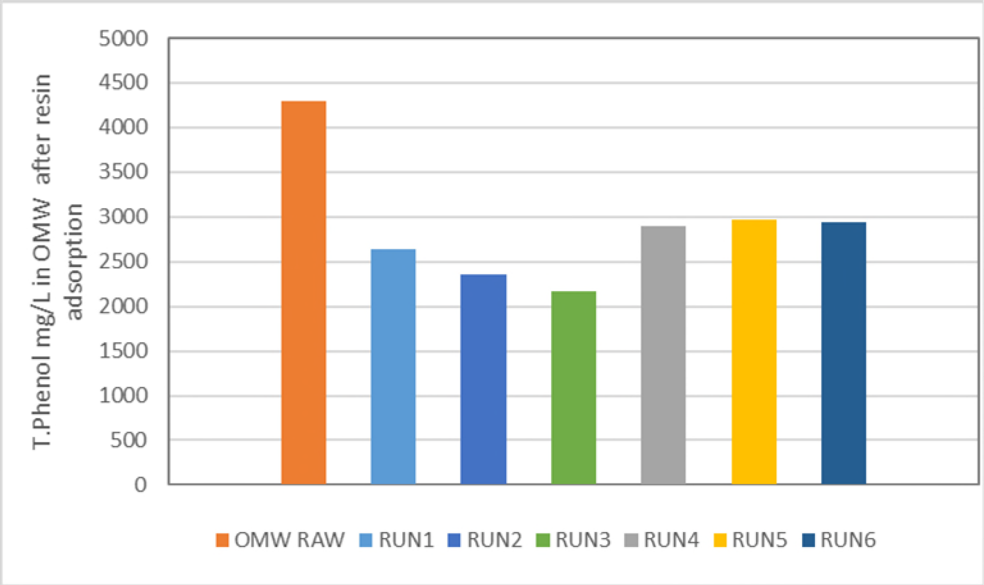

Figure 55 Polyphenols concentration of the raw OMW and the OMW after the different adsorption runs

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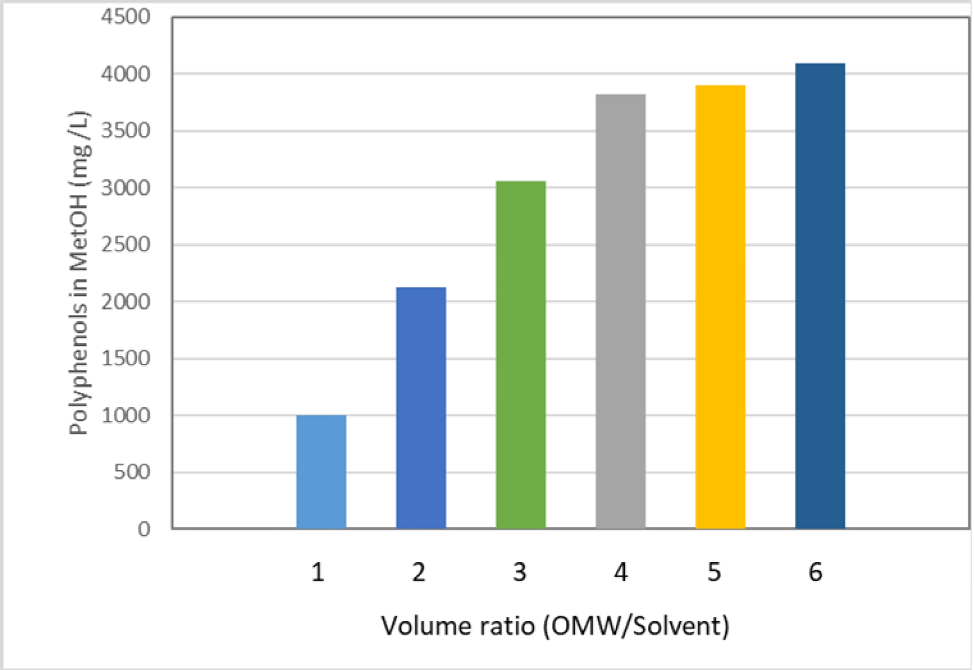

Figure 56 The reuse of methanol for extracting the adsorbed polyphenols on the resin for six successive runs.

The next step was testing the effect of the adsorption on the anaerobic digestion. Two 440-mL lab scale bioreactors containing 150 g of granular sludge were operated and stabilized using a synthetic medium. Thereafter, 2.5% of OMW was added into the inlet. Results of the soluble COD inlet and outlet from the system can be seen in Figure 57, in which Figure 6.4 A corresponds to mixing 2.5% of OMW with synthetic wastewater, and B corresponds to the same ratio of OMW (2.5%) but after treatment (extraction) by the resin bed.

After 17 days, due to a reduction in the inlet COD of the treated OMW, the percentage of the treated OMW was increased to 3% to achieve a similar OLR to the untreated inlet. In this second period of operation similar reduction in COD was achieved, indicating that the anaerobic digestion reactor was able to remove both types of inlets successfully.

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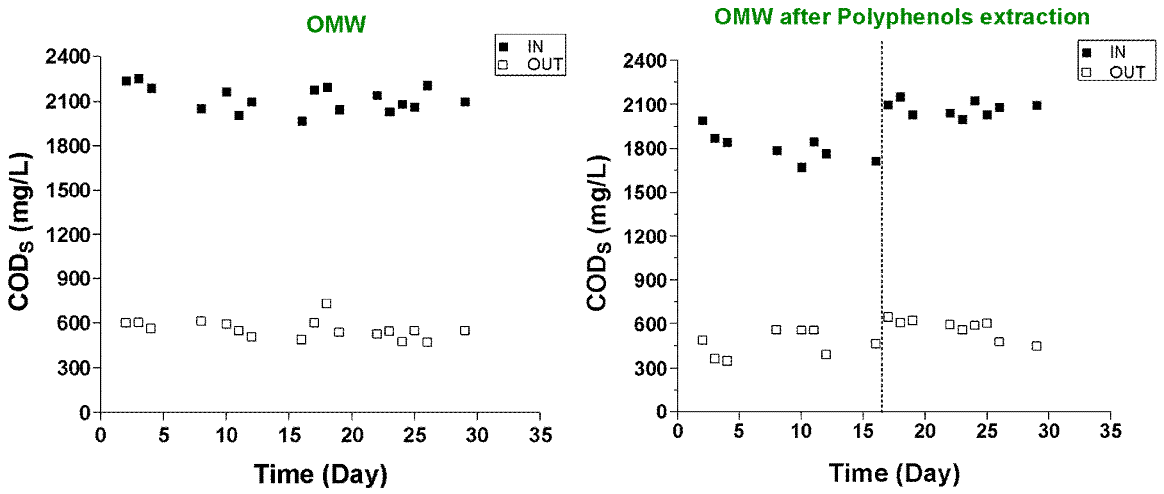

Figure 57 (A) corresponds to the system with 2.5% of OMW mixed with synthetic wastewater, and on (B) corresponds to 2.5% of treated OMW by the resin bed.

Focusing on the second period of operation, when the OLR was similar, we can see from Figure 58a that the methane yield was also similar (a bit lower for the treated OMW). This indicates that the AD could biodegrade the OMW, with possibility of degrading even part of adsorbed COD on the resin. In terms of polyphenols removal, the differences are clearer (see Figure 58b), in which the inlet was around 120 mg/L and 40% of polyphenols removal was achieved in the AD treating synthetic WW with OMW, while for the WW and OMW after the resin bed extraction the AD could remove less polyphenols.

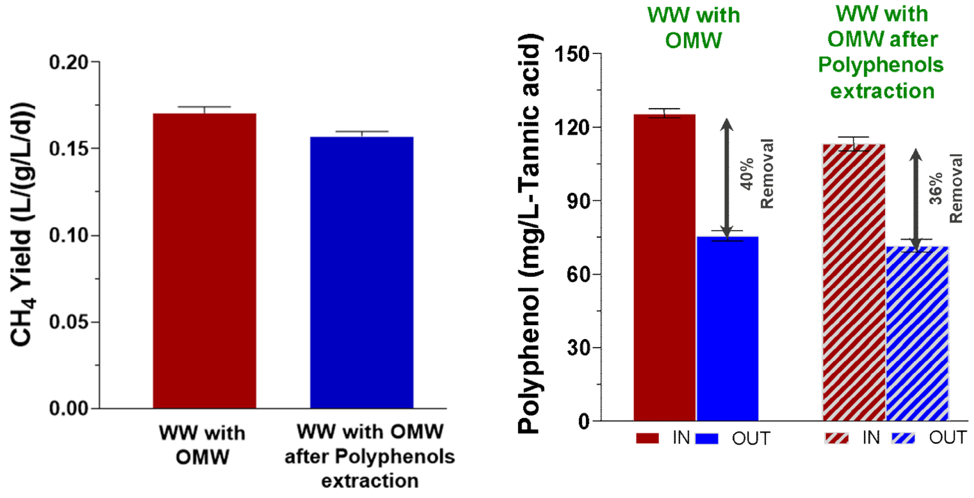

Figure 58 a) the effect of extraction of polyphenol from OMW othe methane yield of the the mixed OMW with domestic WW. (b) the effect of polyphenol extraction on its removal by the anaerobic biodegradation.

The extraction of polyphenols by the modified procedure was also conducted at the Karmiel's demonstration pilot and the results are shown in Figure 6.6. At the beginning a volume of 5 m3 of OMW was extracted by the GtG system, then the treated OMW (extracted) mixed with the domestic wastewater and entered the pilot system of Karmiel (0.5 m3 of treated OMW were mixed with 99.5 m3 of WW per day).

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From Figure 59 and Figure 60, it is clear that there was a reduction in the total COD of the feed after the extraction process of the OMW by the resin, leading to a slight reduction of the total COD of the effluent.

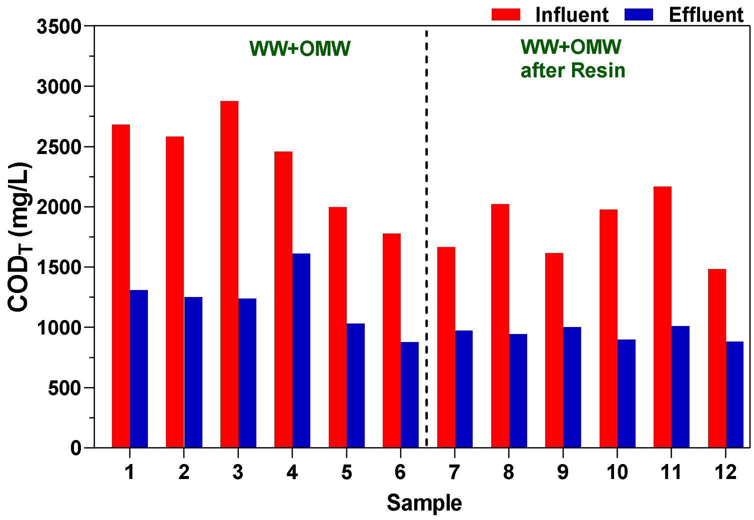

Figure 59 Total COD of in and out of the AAT as a result of the extraction process of polyphenol by the resin.

The soluble COD is presented in Figure 6.7, Similarly to Figure 6.6, also the soluble COD of the feed was reduced after extraction, however the soluble COD of effluent was not stable.

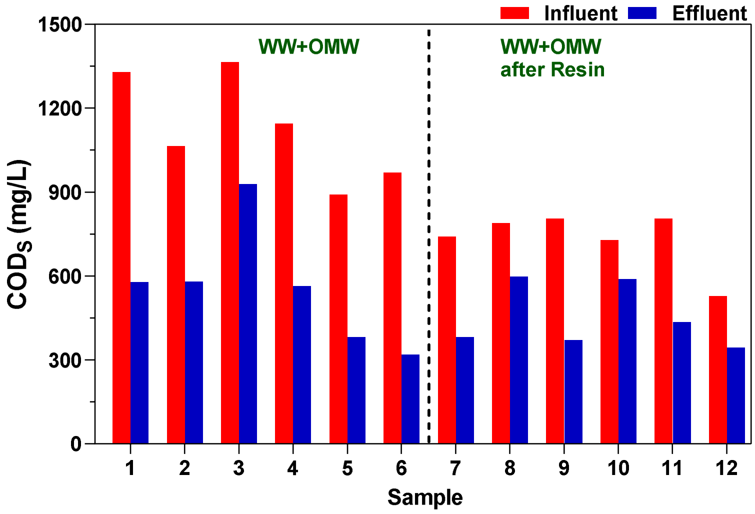

Figure 60 Soluble COD of in and out of the AAT as a result of the extraction process of polyphenol by the resin.

In terms of polyphenols concentration, there was a significant reduction in the concentration of polyphenols in the feed after passing the OMW trough the adsorption resin, and the effluent had a stable concentration of around 28 mg/L (Figure 61).

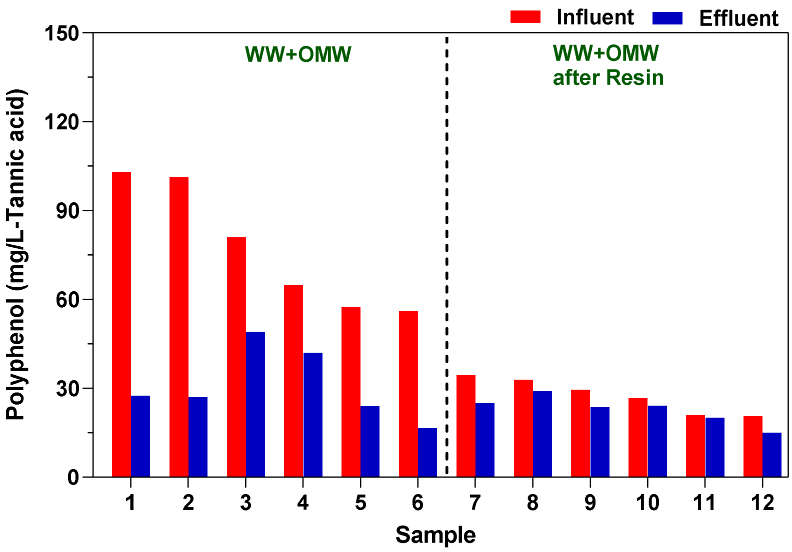

Figure 61 The effect of polyphenol extraction on the removal of polyphenol after the anaerobic (AAT) treatment

The biogas produced as a function of OMW sample and temperature is presented in Figure 62 bellow, where a similar range of biogas produced was achieved for the two periods of operation. An average of the biogas produced can be seen in Figure 63, where there were no notable differences between the biogas produced from both inlets, apparently the addition of treated OMW in 0.5% did not affect biogas production, relatively to the untreated OMW.

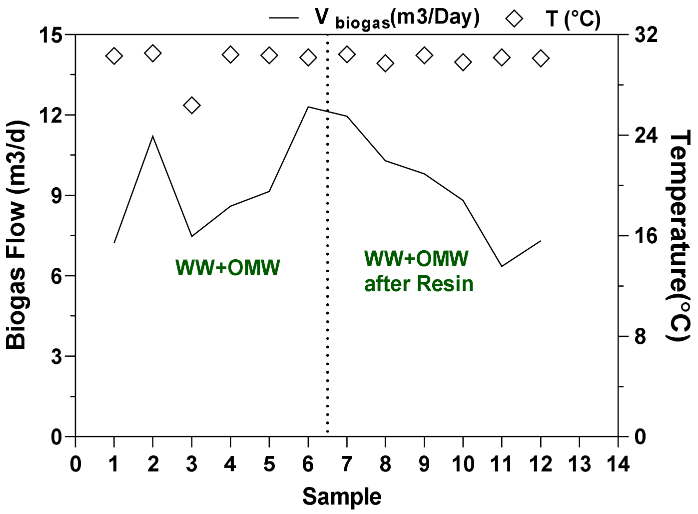

Figure 62 The effect of polyphenol extraction on the biogas rate

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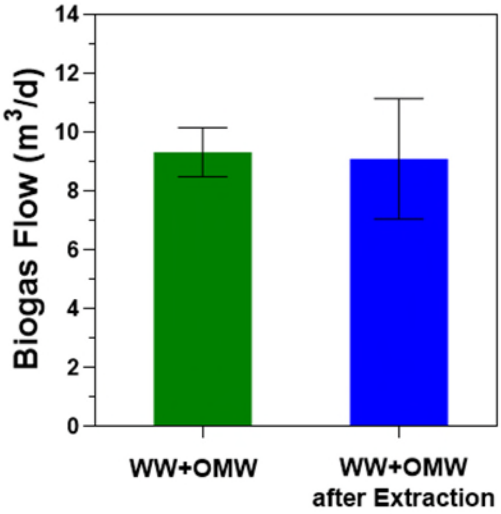

Figure 63 The effect of polyphenol extraction on the average biogas production rate.

2.5.2. Conclusion

GtG has successfully built and tested an innovative extraction unit for recovering valuable polyphenols from Olive Mill Wastewater (OMW). This achievement marks a significant step forward in addressing the environmental challenges posed by OMW while simultaneously creating value from this waste stream.

The extraction unit has demonstrated its capability to effectively produce crude extracts of polyphenols using conventional methods. This success validates the core concept and provides a solid foundation for further refinement and optimization. The project team has successfully constructed and operated the unit, proving the viability of the concept and showcasing the potential for value creation through effective recovery of crude polyphenol extracts from OMW.

Throughout the process, GtG has identified opportunities for process optimization, particularly in areas such as automation and operational efficiency. These insights are driving the next phase of development, where the focus will be on enhancing the technology's performance and economic viability.

Looking ahead, GtG is exploring several promising avenues for improvement. The team is investigating cost-effective alternatives for high-CapEx components, particularly the resin, to enhance economic feasibility. Advanced extraction methods, such as supercritical and subcritical techniques, are being considered for their potential to increase efficiency and yield. Additionally, the development of automated systems is a priority to streamline operations, especially considering the seasonal nature of OMW production. Refining separation and purification processes to upgrade the crude extracts into higher-value products is another key area of focus.

While the initial capital expenditure (CapEx) is considerable, particularly given the seasonal operation, this investment has provided invaluable insights and a platform for future innovations. The project team is actively working on strategies to optimize costs and expand the unit's applicability.

These lessons learned and identified areas for improvement position GtG at the forefront of OMW valorization technology. The company is well-equipped to lead the next phase of development, potentially revolutionizing how the olive oil industry manages its waste streams and recovers valuable compounds. With a solid foundation in place and a clear vision for future enhancements, GtG is poised to make significant strides in sustainable waste management and resource recovery in the olive oil industry.

Crucial factors for technology implementation and its optimal performance

- Optimization of capital expenditure (CapEx), particularly focusing on cost-effective alternatives for high-cost components like resin, is essential for improving the economic viability of the extraction unit.

- Exploration of advanced extraction methods, such as supercritical and subcritical techniques, holds potential for enhancing efficiency and yield, which could significantly improve the process's overall effectiveness

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2.6. Recovery of nutrients from distillery wastewater after AnMBR treatment in Tain (UK)

2.6.1. Case study and ULTIMATE concept

Case Study 7 is the Glenmorangie whisky distillery located in Tain, in the north-east of Scotland. The current effluent treatment plant, at the start of the symbiosis between the distillery, the water sector and farmers, was designed and installed by Aquabio, partner in the Ultimate project, and consists of screens followed by an anaerobic membrane bioreactor (AnMBR) to treat the wastewater generated during the whisky making processes. The treated effluent is then discharged in the local estuary, the Dornoch Firth. The main target for the current treatment train is to remove the organic content, achieving over 98% removal of the 10.7 t/d COD load. In the AnMBR, the COD is biodegraded and converted to a methane rich biogas which is processed in a boiler to produce heat currently used for heating the stills in the distillery. Overall, this reduces the dependence in fossil fuels of the distillery by 15%. In addition, the excess sludge produced in the AnMBR is provided to the local farmers for application to the fields as soil enhancer.

It should however be noted that the effluent for discharge still contains concentrations of ammonium and phosphorus of about 700 mgN/L and 250 mgP/L, respectively, offering potential for recovery as fertiliser for example. Also, the AnMBR is operated in the mesophilic range; thus, its effluent has a temperature between 35 and 40°C which provides an opportunity for residual heat utilisation within the treatment facilities, reducing the overall energy demands of the additional technologies being considered. Finally, the effluent can be further treated to produce high quality water that can then be reused at the distillery for cleaning or cooling purposes. This would then lead to a significant reduction in tap water demand for these uses. As part of the Ultimate project, Aquabio and Cranfield University (partners in the project) are collaborating with the Glenmorangie distillery and Alpheus, the current operator of the treatment site, to evaluate options to expand the circular economy approach at distilleries with residual heat utilisation, nutrients recovery and water recycling.

As stated above, the current AnMBR effluent contains high levels of both nitrogen and phosphorus, it was then decided to apply a two-step approach for the recovery of these nutrients. The effluent was first processed through a precipitation system for the formation of struvite ($NH4MgPO4·6H2O$). As the ammonia is in excess, this step will be focused on maximising the removal of the phosphorus. The effluent from the struvite reactor will be further treated in an ammonia stripping unit for the removal and recovery of the remaining ammonia present. In this case, the ammonia will be recovered in the form of an ammonium sulphate ($(NH4)2SO4$) solution. Both products recovered can be used as fertilisers by the local farmers.

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As part of this project, the two-step approach with struvite precipitation followed by ammonia stripping was tested at demonstration scale (Figure 64). Struvite precipitation requires the presence of phosphate (PO43-), ammonium (NH4+) and magnesium (Mg2+) in the water to be treated. In anaerobically treated distillery wastewater, ammonium is in excess (~700 mgN/L) and magnesium (~50 mg/L) is the limiting compound. For the reaction to occur, struvite crystals to form and ultimately to maximise the removal and recovery of phosphorus, it is critical to obtain suitable super saturation conditions which will be influenced by the compounds' concentrations and the pH. The AnMBR effluent was then supplemented with magnesium by dosing magnesium chloride (MgCl2) and the pH was adjusted with caustic dosing. The water was fed at the bottom of the reactor (0.5 m3/h) and due to its design with 4 zones with increasing width from bottom to top (Figure 64a), provided a gradient of velocities from high in the narrower zone at the bottom to very low in the larger zone at the top, also controlled through a recirculation loop (7 m3/h). The struvite crystals formed are then fluidised allowing for aggregation into larger particles through collisions in the reactor. As the aggregates grow bigger, due to their density, they settle in the narrower zone with higher velocity at the bottom of the reactor, from where they are harvested at regular intervals (weekly). The treated effluent overflowed at the top of the reactor into a clarifier to remove any remaining fines before the water is pumped to stripping unit.

For the stripping, the ammonium present in the water has first to be converted to ammonia, which is volatile. This can be achieved by increasing the pH (caustic dosing) and/or the temperature of the water. The water is pumped (0.5 m3/h) at the top of a packed stripping column and flows down while an air blower sends air (2500 m3 air/h) upwards in the column (Figure 64a). The packing media in the column provides increased surface area for a better mass transfer of the ammonia from the liquid to the gas. The treated effluent flows out at the bottom of the column and the ammonia rich air is sent into a scrubber, where it comes into contact with a sulphuric acid solution. The ammonia is then transferred from the air to the water producing an ammonium sulphate solution (liquor).

The integrated system with struvite precipitation and ammonia stripping allowed to remove the nutrients from the AnMBR effluent, leading to the discharge of an effluent with lower eutrophication potential. Although, this is not currently a requirement for the case study site, implementation of such approach will be critical for other sites when discharging in other locations at sea or in fresh water receiving water such as rivers and lakes. In doing so, the systems recovered two products: struvite, a slow-release fertiliser, and an ammonium sulphate solution which can be used as fertiliser or can also be used for other applications such as the production of proteins. This would allow to further expand the current symbiosis between the distillery and the local farmers or possibly develop new symbioses with other industries. The technologies evaluated here are already commercially available but their application for distillery wastewater had, to our knowledge, not yet been done with also no reports of their integration for such industrial applications. Based on this, the systems were at a TRL of 5 at the start of the project and through the demonstration of the technologies at large scale in real conditions that increased to TRLs of 7 respectively.

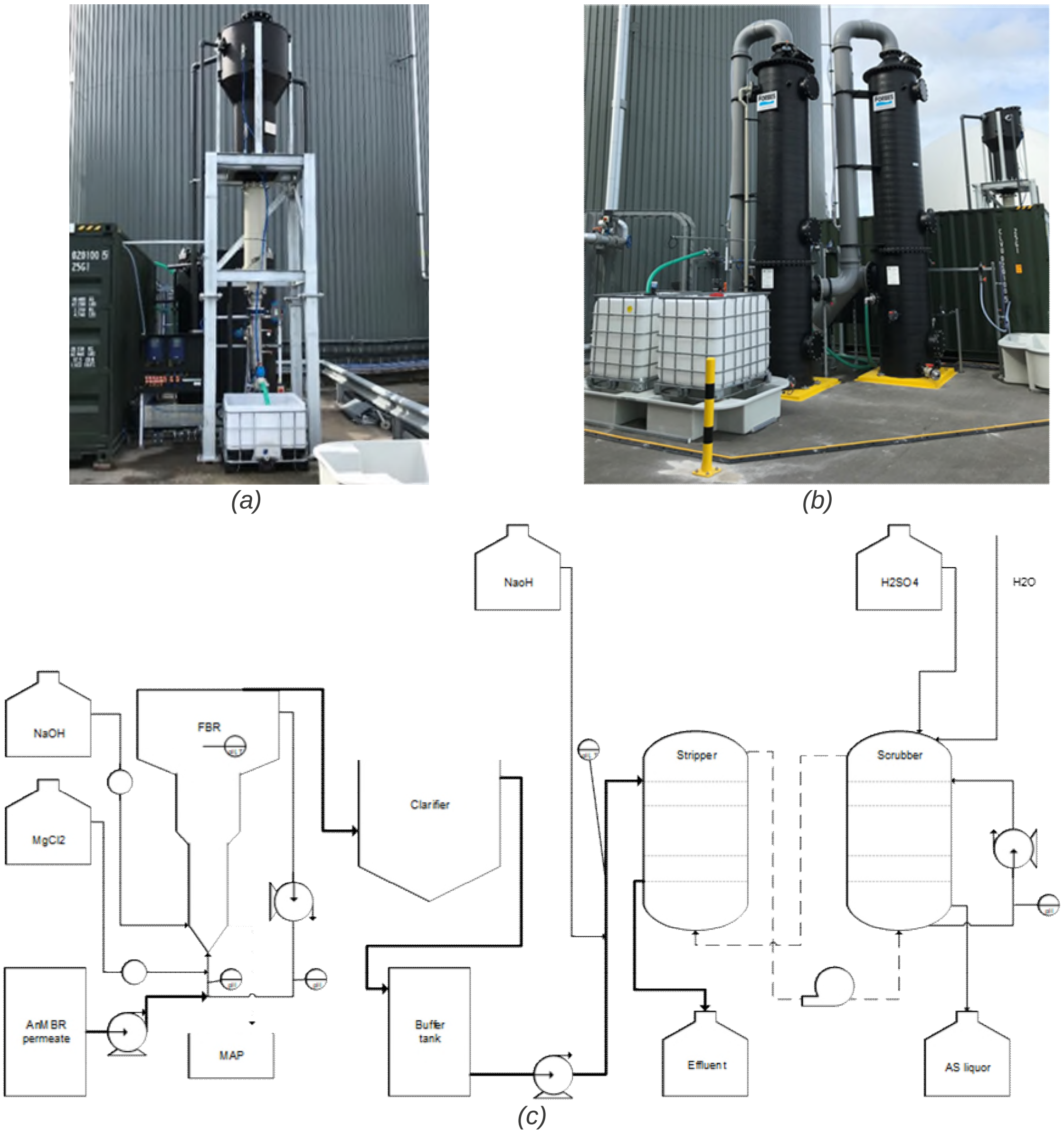

Figure 64 Photos of the (a) struvite reactor and (b) ammonia striping units and (c) flow diagram of the integrated systems.

2.6.2. Results of new approaches

As the systems were operated continuously, some of the operational conditions were changed to evaluate the performance of technologies evaluated here. As stated above, pH is a critical parameter for the struvite crystallization process and an increase in pH was found to lead to an increase in phosphorus removal (Figure 65). Indeed, the highest phosphorus removal efficiency of about 80% was observed for pHs above 8.9,

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corresponding to a residual phosphate concentration of just under 50 mgP/L in the effluent of the reactor. Due to the high initial concentration in ammonium, nitrogen removal remained low between 5 and 20%. The higher nitrogen removal efficiencies were found at the higher pH tested. This could be explained by the fact that at those pHs, a higher proportion of the ammonium was converted to ammonia, some of which then left the reactor by volatilization. This is confirmed by the balance of elements (PO43-, NH4+ and Mg2+) contributing to the formation of struvite as indeed, more ammonium was proportionally removed than the other compounds.

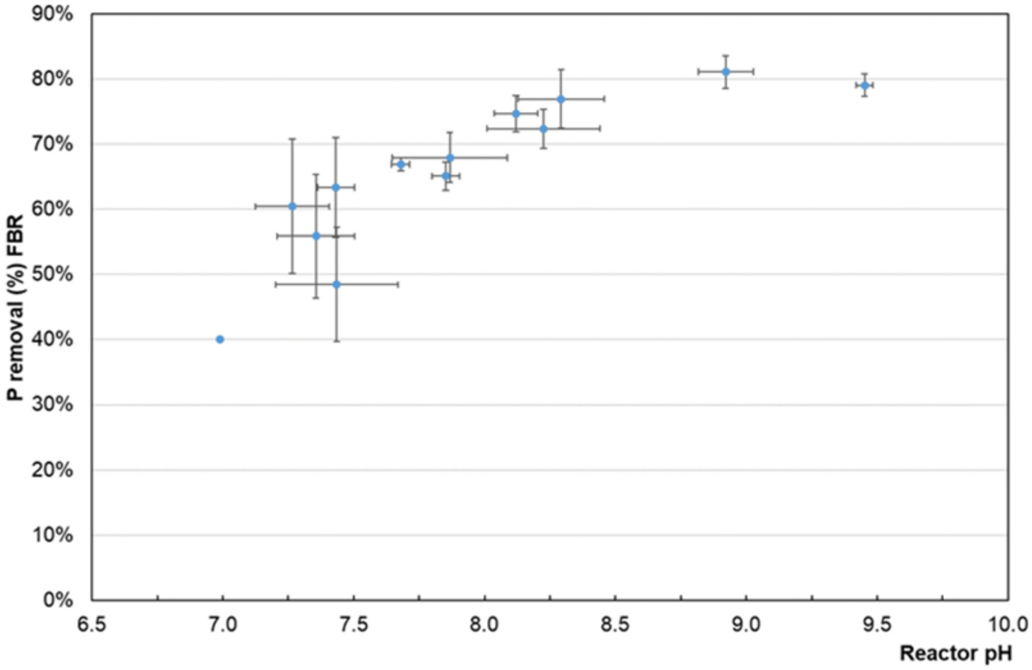

Figure 65 Impact of pH on phosphorus removal by struvite precipitation in distillery wastewater.

Samples collected from the struvite reactor during operation with different pH conditions (Figure 66) demonstrate the stratification expected in the different zones. At the lower pH of 7.4, the majority of the particles were found in the so-called core and middle zones of the reactor, with no visible particles at the top of the reactor and few but very large particles in the bottom zone. As the pH was increased, more, smaller particles were found throughout the reactor with also very fine particles present at the top of the reactor as indicated by the cloudiness of the samples. In these conditions, carry over of the fines in the clarifier was observed but the effluent samples collected after the clarifier were found to be clear. This demonstrates the efficiency of the clarifier in removing those fine particles and eliminating the risk of carryover and possible clogging in the subsequent stage.

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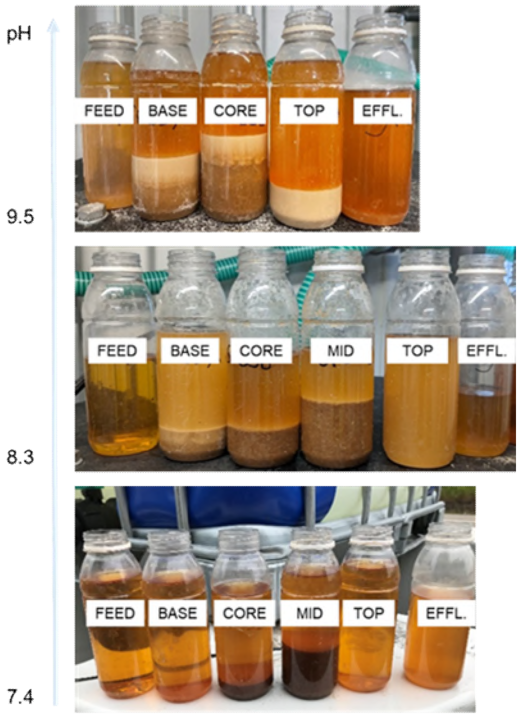

Figure 66 Precipitates levels in samples collected in the different zones of the reactor from bottom to top (base, core middle and top) during trials with different pH conditions.

The product collected during the trials was found to change with the different conditions tested (Figure 67). To illustrate, at a pH 7.4 the product recovered mostly small beads and flakes of 1 to 5 mm in size. At a pH of 7.7, the product mostly contained beads of about 5 mm in size. As the pH was further increased to 7.9 and 8.1, the product was a mixture of the beads and fine particles. As the pH was increased 8.9 and above, only fine particles were then recovered. As the pH was increased between 7.4 and 9.5, the supersaturation ratio was increased between 2.5 and 16.3. It has been previously reported that higher supersaturation ratios favour a faster nucleation which produces smaller crystals also limiting aggregation. Alternatively, at lower pHs, with slower nucleation, crystal growth and aggregation were increased, leading to the larger beads observed. This highlights that the physical characteristics of the product recovered can be tuned by changing the operational conditions in the system. Further analysis of the products recovered, with in particular imaging under a microscope, highlighted the structure of the crystals and beads recovered (Figure 68). It can be seen that flake-like crystals of a few hundred microns were generally formed and then aggregated to form large particles. With continued aggregation and due to movement in the fluidised reactor, the particles ultimately shaped into beads. The products recovered were also analysed by X-ray diffraction (XRD) to identify the type of material formed (Figure 69). All XRD spectra obtained for all conditions tested confirmed that the product recovered was struvite. It should be noted that struvite in its pure form is white but it can clearly be seen here (Figure 65 Figure 66 and Figure 67) that the products recovered are brown. This shows that although it has been identified as struvite there can be some contamination with other compounds being trapped in the particles. The brown colour observed is expected to be organic matter. COD removal in the water was found to be low and to fluctuate significantly so no clear pattern could be identified. However, the products recovered were dissolved in acid and the liquid phase was analysed for contaminants such as organics (as COD) and metals (Table 17). These analyses first showed that consistently 4 to 7% of the products' mass was organic matter. Alternatively, all metals analysed were found in extremely low levels or not detected. There were concerns that some metals could be present in the products due to their high concentrations in the wastewater with, in particular, copper coming from the construction material of the stills in the distillery process. These results combined to the quantitative chemical risk assessment carried out as part of the activities in WP2 demonstrated that the products recovered are of high quality and would not provide a risk to the soil and environment is used as fertiliser. It has been reported in the literature (González-Morales et al., 2021) that higher supersaturation ratios lead to higher purity of the struvite formed; however, in our case no clear differences could be observed in terms of the quality of the products recovered for the different conditions tested (Figure 65-Figure 67).

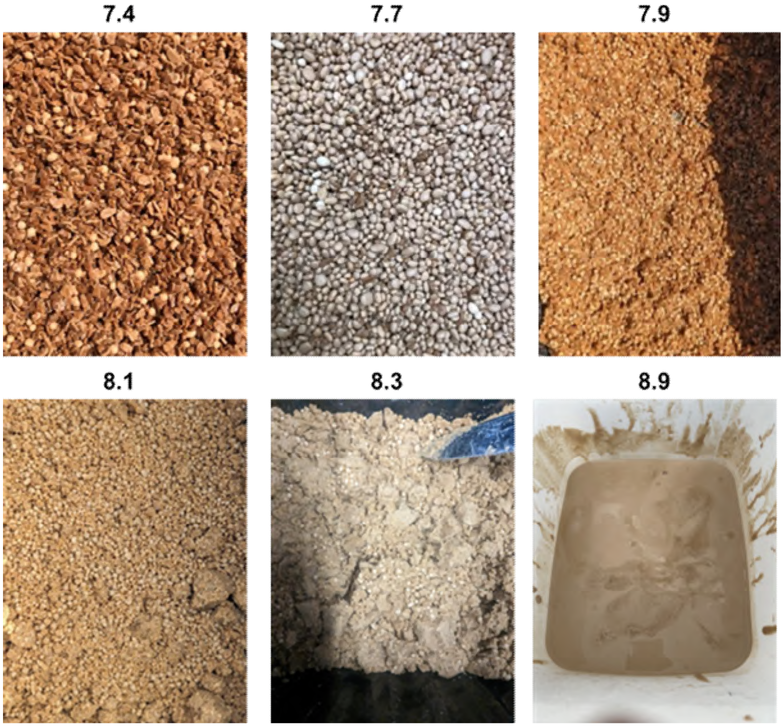

Figure 67 Photos of the products recovered from the struvite reactor.

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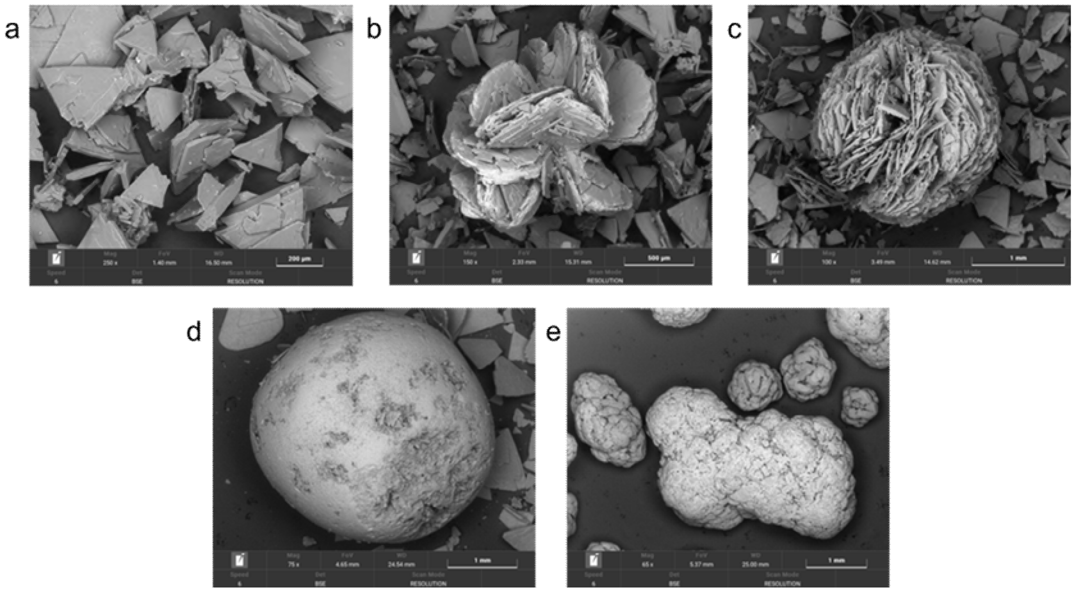
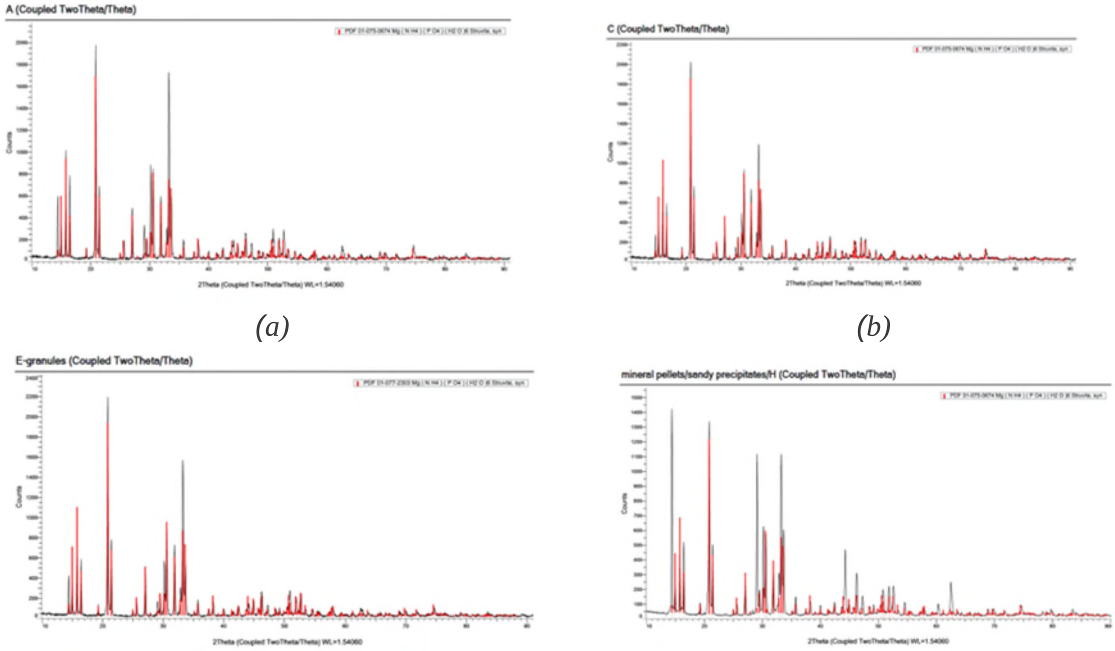


Figure 68 Scanning electron microscope images of crystals and aggregates in different conditions tested with (a), (b) and (c) from the trials at pH 7.3 ± 0.1, (d) at pH 8.1 ± 0.1 and (e) at pH 8.25 ± 0.2.



(a) (b)

(c) (d)

Figure 69 Examples of X-ray diffraction spectra of the products recovered at pHs of (a) 7.4, (b) 7.7, (c) 8.1 and (d) 8.9.

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Table 17 Metals and COD content of the products recovered at different pHs as % mass.

pH	B	Si	K	Ca	Mn	Fe	Ni	Cu	Zn	Sr	Ba	COD
7.3	0.00%	0.00%	0.19%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	7%
7.4	0.00%	0.00%	0.21%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	5%
7.7	0.00%	0.00%	0.19%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	6%
7.9	0.00%	0.00%	0.15%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	5%
8.1	0.00%	0.00%	0.12%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	4%
8.3	0.00%	0.00%	0.14%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	5%
8.9	0.00%	0.00%	0.23%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	4%
9.5	0.00%	0.00%	0.15%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	4%

As the effluent from the struvite reactor was then fed to the ammonia stripping unit, the impact of pH was also evaluated on the stripping performance. In this case, as pH is known to influence the conversion of ammonium to ammonia, expected results with higher ammonia removal observed at higher pHs, were obtained (Figure 70). Based on the conditions tested in the system, a maximum nitrogen removal of 70% was achieved, corresponding to an ammonium residual of about 170 mgN/L. The results generally followed the trend of free ammonia formed based on operational conditions of temperature and pH; however, some points, especially at the higher pHs show some deviation. This highlights that some limitation during the trials with for example a reduced transfer surface due to scaling, ammonia binding to other species in the liquid phase affecting its volatilization or saturated recycling air phase (less driving force). Trials with synthetic waters and the distillery wastewater were also carried out at lab scale (in a vacuum thermal stripping unit) in parallel to evaluate any impacts on the stripping process that could explain those variations. Transition metals are known to react with ammonia and form complexes. As mentioned above, the concentration of some metals can be high in distillery waster and may have influenced the performance of the system. The lab-scale trials confirmed the impact of metals such zinc, nickel and copper on ammonia stripping (Figure 71). The results obtained showed that ammonia removal by stripping could be reduced by up to 30% with high N/Metal ratio in the

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water. The tests showed that zinc affected the process more than nickel and copper and the ratio observed to affect the process significantly were much higher than the ones measured in the distillery wastewater. Overall, this shows that ammonia/metal complexation was unlikely to be the cause of the variations observed. Other tests did not provide a clear explanation for these and additional analyses would be required to further assess this but the complexity and variability of the wastewater matrix is expected to influence the system's performance. Interestingly, the lab-scale trials with the distillery wastewater showed that ammonia removals of over 90% are if the pH (11) or the temperature (60°C) were increased to higher values. No phosphorus removal was observed during the stripping process but some COD removal was observed. This can be explained by the fact that some of the organics present in the wastewater will be volatile and would then follow the same pathways during the stripping and scrubbing processes. As it will be highlighted later, organic matter was measured in the recovered product.

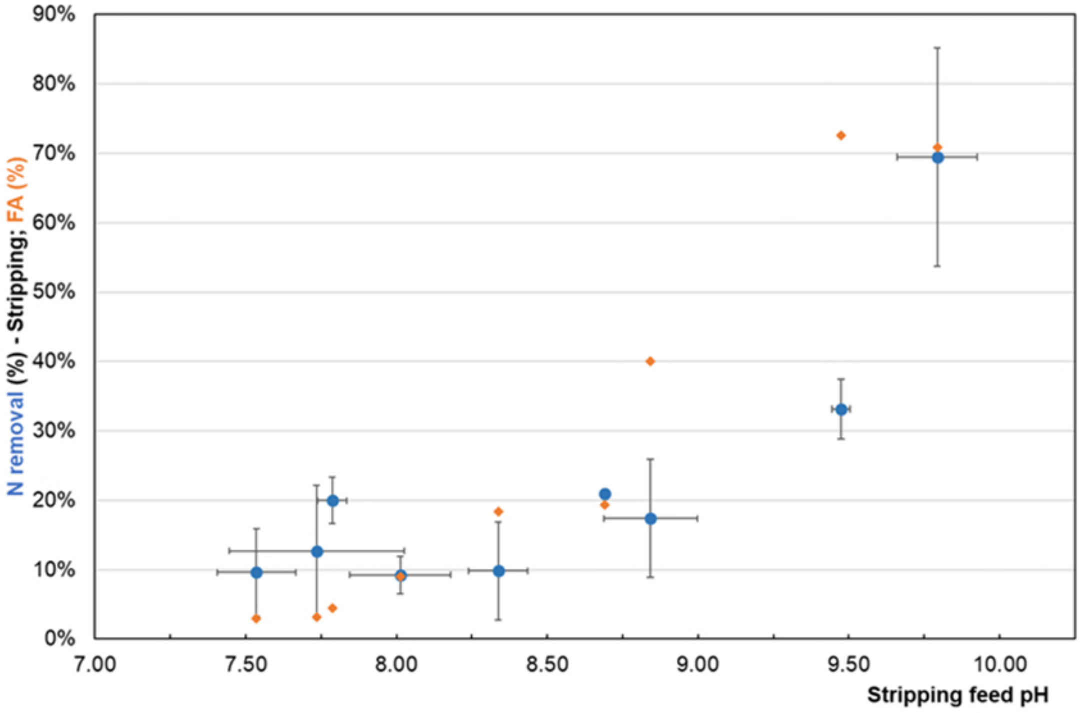

Figure 70 Impact of pH on the performance of the ammonia stripping unit.

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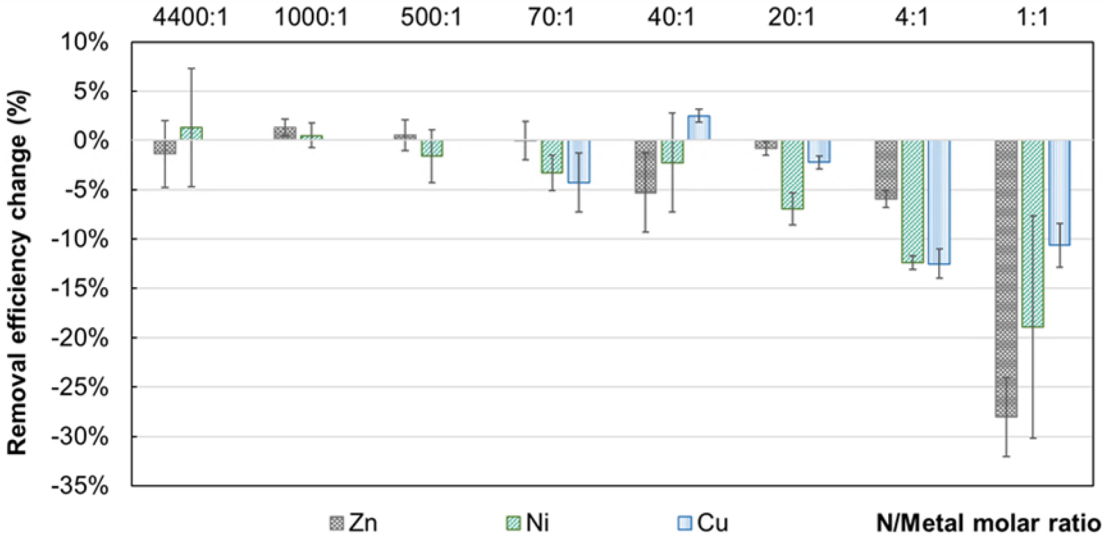

Figure 71 Impact of N/metal ratio on ammonia stripping efficiency (lab-scale trials with synthetic solutions)

Interestingly, the mass balance on the system showed that there was very little losses with 99% of ammonia stripped recovered in the product and hence only about 1% of the nitrogen was lost, most probably vented out. As the ammonia was captured in the acid solution in the scrubber, an ammonium sulphate solution was recovered. The scrubber unit started with a batch of concentrated acid at an initial pH of below 2. As the ammonia is captured over time, its concentration increases in the solution and the pH of the batch will also increase (Figure 72). The batch was then replaced when the pH reached a set value of 5.5. At the end of the batch, the nitrogen concentration was found to vary between 10 and 20 gN/L providing a clear high concentration solution that can be used as a fertiliser or as base for other applications (Figure 73). A higher pH or temperature in the feed water to be treated would increase the transfer rate of the ammonia which would then reduce the acid batch life but would lead to higher concentrations in the recovered solution. Decisions on the operation of the systems will be based on trade-offs between the cost of replacement of the acid solution and the cost of transport and possible processing of the ammonium sulphate solution recovered. Analysis of the ammonium solutions recovered highlighted the presence of organic matter as contaminant. As sated before, some of the organics present in the wastewater can be expected to be volatile and would follow the same process as ammonia in the system hence ending up in the recovered solution with generally concentrations of about 300 to 400mg/L as COD. This is however not expected to create any problem for the use of the recovered products.

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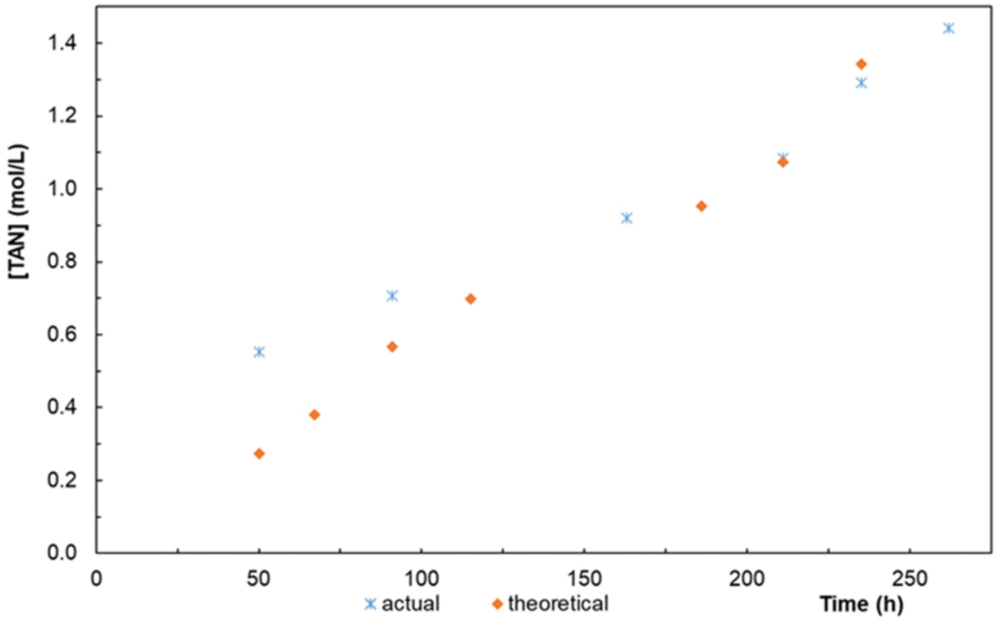

Figure 72 Evolution of the ammonia concentration over time for an example of a single batch of the acid solution in the scrubber.

Figure 73 Photos of samples of the ammonium sulphate solution recovered from the scrubber.

As part of the project the KPI for nutrients removal and recovery was 50%. The trials carried out with the two-stage approach of recovery with struvite and ammonium sulphate as the products led a total nitrogen removal and recovery of 80% across the two systems while the removal and recovery of the phosphorus was also 80% achieved in the struvite step alone. Considering that current practice for distillery wastewater treatment is only focused on the organics removal with anaerobic biological systems before discharge, the new development demonstrated here provide a very significant reduction in the nutrients being discharged in the environment and hence reducing the potential for eutrophication in the receiving waters. Also, the products recovered in the processes applied can be used locally by the farmers further extending the symbiosis of such a case.

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2.6.3. Conclusion

The work carried out as part of this case study clearly demonstrated the potential of the technologies, individually and in combination, to remove and recover nutrients from anaerobically digested distillery wastewater. As such, the results highlight the potential of these technologies to be applied for the treatment of high strength wastewaters such as industrial effluents and so could be applied to other sectors. It should also be noted that the lab-scale tests of the two technologies delivered in parallel to the demonstration system showed that even better removals of over 90% of phosphorus in a struvite reactor and ammonia by stripping could be achieved. This shows that further improvements can still be made to make the approach even more sustainable and more widely applicable. An assessment of the characteristics of the wastewater to be treated could also allow to ascertain if both systems are required. For example, any waters with balanced levels of phosphorus and ammonia could use only the struvite reactor while a water with high levels of ammonia combined to a low phosphorus concentration could only use the stripping process.

The operation of the systems was not without its challenges, in particular for the struvite reactor, but these ultimately helped improve operation and performance. Indeed, as all 3 components of struvite, phosphate, ammonium and magnesium, are already present in the wastewater, the AnMBR effluent was already very reactive and spontaneous precipitation of struvite occurred in the feed pipe, tank and pumps leading to clogging problems. This was then exacerbated by the dosing applied to enhance the reaction. It is critical to ensure close proximity of the systems to avoid long pipes and avoid intermediate tanks wherever possible (it would most probably the case in a full-scale unit as opposed to a demonstration unit). To avoid uncontrolled struvite precipitation before the reactor, the effluent may be slightly acidified (pH < 7). To guarantee controlled struvite precipitation within the reactor, changes to design and more specifically the dosing points were made to allow for optimum dosing and mixing at the base of the reactor. As mentioned, although the struvite reactor delivered excellent removal based on phosphorus, it can still be improved. During operation at the higher pHs (>9) some fine particles could be seen in the top section of the reactor which were them carried over into the clarifier. The clarifier worked efficiently to separate the fines from the treated effluent. Adding a recirculation of the fines collected at the bottom of the clarifier into the feed of the struvite reactor would provide seeding materials to maximize the reaction and aggregation of the particles and would ultimately improve the total recovery of product as well as the performance of the system.

For the stripping unit, precipitation and clogging problems were also encountered when testing the struvite system at lower pHs (7-8) and further increasing the pH for stripping to higher values (e.g. 10). This showed that, as evidenced by the lower removals observed in the struvite reactor, reactive material was still present in the effluent and precipitation occurred when the pH was raised just before the stripping column. This highlighted that operating the struvite reactor at higher pH not only improved the removal efficiencies but also acted as a protection for the stripping unit. This would have to be considered in cases where the stripping technology is used individually. As stated above, for waters with high ammonia and low phosphorus, it would be sensible to apply only the stripping step but the water may still contain high levels of inorganics such as calcium or magnesium which would contribute to the formation of scaling when the pH is increased. In this case a pre-precipitation reactor may still be needed to optimize the operation of the stripping unit. Also, in the current case, the initial step of the treatment train was an AnMBR, fitted with ultrafiltration membranes for separation which delivered a solids free effluent to the subsequent stage tested as part of this work. This is beneficial, limiting the impact of any solids on the nutrient recovery technologies. During the trials, a carryover of water/condensation from the stripping to the scrubber was observed, with an increase in the volume of the acid solution over time. Although the air loop was fitted with a demister which is expected to be 99% efficient, the difference in temperature between the water (30-35°C) and the outside air as well as the general humidity locally may have contributed to this. This also possibly impacted the air blower's performance and may have affected the overall performance of the stripper. This would need to be further considered when installing such systems in locations with colder, more humid climates such as Scotland. As mentioned previously, the performance of the stripping unit can be expected to improve if operated at even higher pHs (~11) and/or temperatures (~60ºC). The increase in pH with caustic dosing is associated with a significant cost in chemicals. In cases such as the one studied here, where an anaerobic biological process is implemented producing a biogas which is then converted to heat, an increased temperature is the more sustainable approach and it would also be the case for any site with waste heat available.

The products recovered, struvite and ammonium sulphate, were shown to be of high quality and hence suitable for use as fertiliser. This would then help further extend the existing symbiosis between the distillery industry and the farmers. More remains to be determined, including the relevant end-of-waste processing, if the products could be sold for a profit or even given away to avoid disposal costs. Ammonium sulphate has a broader range of applications in energy and production of proteins or feed which would potentially lead to greater revenues and expansion of the symbiosis to other sectors.

Crucial factors for the implementation of integrated nutrients recovery

- High strength water in terms of either phosphorus or ammonia is required
- A membrane filtered feed is beneficial to avoid any impact of solids on the nutrient recovery technologies applied
- Waste heat or heat production from biogas onsite is beneficial to control the temperature in the stripping process and improve performance
- pH control of the feed to the nutrients recovery systems may be required to avoid uncontrolled precipitation leading to clogging problems

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2.7. Recovery of sulphur at the Chemical Platform Roussillon (FR)

2.7.1. Case study and ULTIMATE concept

Description of the demo site

The Roches-Roussillon chemical platform exists since 1915 and brings together 19 companies specialized in the chemical industry on the same site, including several giants of the sector such as Seqens, BASF, Adisseo and Elkem. SUEZ RR IWS Chemicals (SUEZ RR) operate on this platform two hazardous waste incinerators (Aqueris) that treat a significant proportion of the chemical platform waste and a biomass recovery unit (ROBIN) that provides 15% of the chemical platform steam requirement. On Roches-Roussillon site, SUEZ RR activity focuses on three areas:

- Aqueris: Two high temperature incineration of industrial liquid hazardous waste (aqueous and organic), named L4000 and L5000 and specialized in:
    - Aqueous waste with strong salt content
    - Sulphurous waste (mercaptan type)
    - Very dangerous waste (cyanide, acetonitrile, etc.)
- Aqueris: evapo-incineration, for waste with a low pollutant load
- Robin: hazardous and non-hazardous biomass valorisation, with steam production distributed to the platform industrials.

Among these, the Ultimate project concerns Aqueris unit. Over the past five years, the site has developed the ranges of waste received with the treatment of high-sulphur waste. This has resulted in an increase in the amount of sulphates collected in the washing water and then sent without recovery to the treatment plant. Due to environmental constraints (discharge of sulphate in the Rhône must be below 26 g/L and 24 t/d and sulphur dioxide content in the fumes must be lower than 120 mg/Nm^3/30min and 30mg/Nm^3/d), but above all due to the will of SUEZ to convert Aqueris into a material recovery unit, a project is being studied by the Industrial Department of SUEZ RR for the recovery of sulphur.

The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869318

A schematic diagram of the process is shown in Figure 74 below.

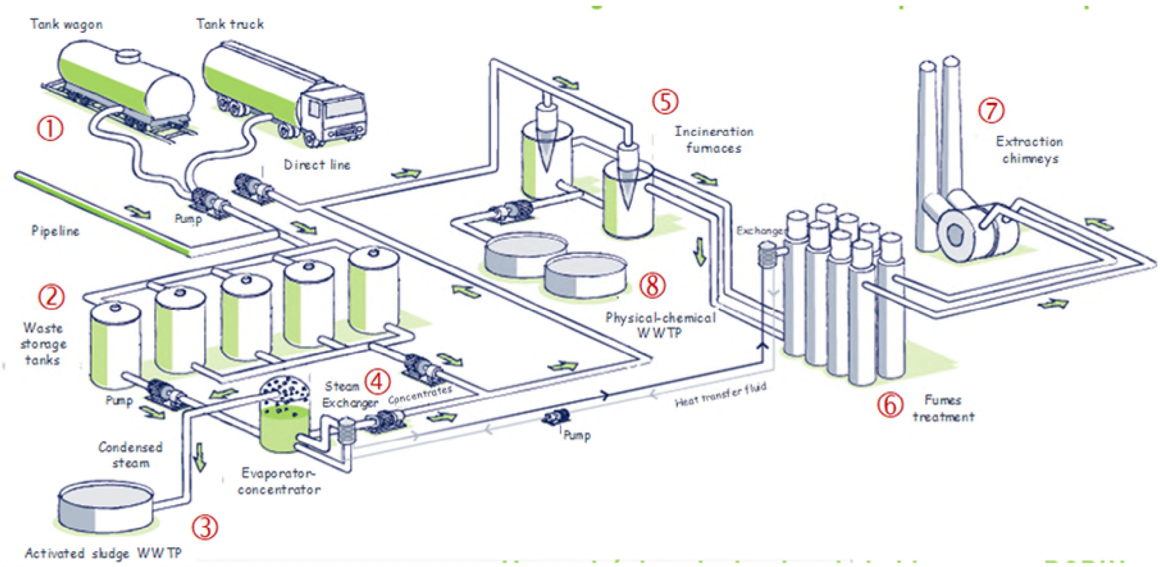

Figure 74: Simplified diagram of the incineration plant of the chemical platform of Roussillon

The objective of the process developed is to produce sodium bisulfite ($NaHSO_3$) solution from SO_2 contained in flue gas of the hazardous incineration plant. Sulphur dioxide is a strong acid gas which forms bisulfite ion (HSO_3^-) in aqueous solutions at a pKa level of 1.9, and sulfite ion (SO_3^{2-}) at a pKa level of 7.2. The pH level will therefore be an essential parameter to obtain the target product. Sodium bisulphite has many commercial uses such as disinfectant, bleaching agent and as mild reducing agent for removal of small amounts of chlorine, bromine, iodine, hypochlorite salts and oxygen (i.e. an oxygen scavenger agent).

The operating principle is shown in the diagram below (Figure 75) and consists in the following steps. The flue gas enters a tubular PVDF heat exchanger, which cools the flue gas and condenses part of the water. Once cooled, the flue gas passes through two absorption columns in series, a packed column and a spray column, whose positions can be inverted. The first column is regulated at acid pH and its role is to form the sodium bisulfite solution of interest by absorbing part of the SO_2 (1), while the second column is regulated at basic pH and absorbs the excess SO_2 to form the sodium sulfite absorption solution (2).

$$SO_2 + SO_3^{2-} + H_2O \rightarrow 2HSO_3^- \tag{1}$$

$$SO_2 + 2OH^- \rightarrow SO_3^{2-} + H_2O \tag{2}$$

Both columns are equipped with immersion heaters to control reaction temperature and limit condensation. The liquid phase of the second column, regulated at basic pH, can feed into the first column, regulated at acid pH. Sodium hydroxide can be added to both columns, but is used in particular for the second, basic pH column. The liquid phase from the first column can be drawn off into a recovery tank. Finally, the flue gases are sent to the unit's flue gas treatment system by means of a fan (approx. 500 Nm³/h). All pH, level and temperature controls are managed by a control system.

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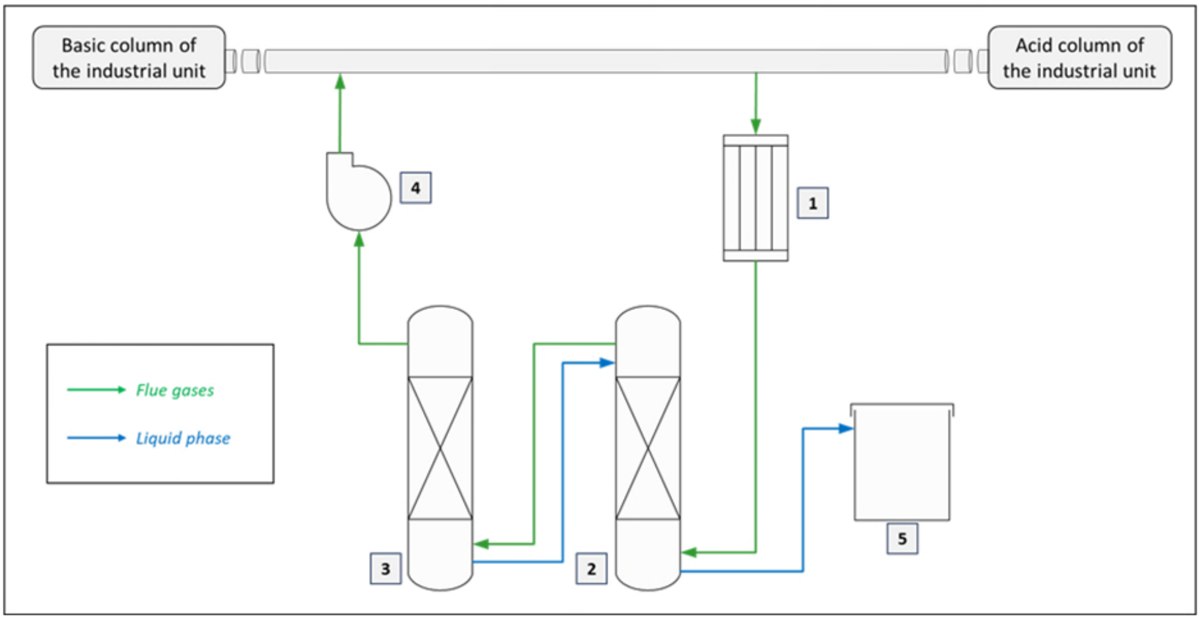

Figure 75: Diagram process of the sulphur recovery system.

1: Heat exchanger; 2: Packed column; 3: Spray column; 4: Fan; 5: Tank for sodium bisulfite solution

Few photos of the demonstration pilot in its industrial environment can be seen in Figure 76.

Figure 76: Pictures of the sulfur recovery system.

Operating conditions

Today, sulphur-containing waste for which recovery is sought is treated directly, i.e. without passing through a storage facility. The tank's contents are sent directly to the furnace. This operation takes usually between one and three consecutive days. This solution makes it easier both to control the odour risk and sulphur dioxide treatment.

The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869318

On the other hand, for recovery tests, it has the disadvantage that tests cannot be carried out continuously. As a result, the pilot plant can only be operated during periods when sulphur-containing waste is burnt.

A summary of the tests carried out is given in Table 18 to improve pilot performance, the following modifications were made:

- Reduction of washing water volume in scrubbers (from the 2nd test)
- Temperature maintained in scrubbers to avoid condensation
- Continuous operation during sulphur waste incineration (from the 7th test)
- Connections between pilot and incinerator modified to reduce turbulence and improve flow gas measurement (from the 12th test)
- Regular bleeding of bottom points to avoid water accumulation.

Table 18: Testing conditions

Custome r	Sulfur concentration range	Number of pilot tests	Period of tests	Test duration
A	12 - 25%	5	12/2023 to 01/2024	21 to 28 h
B	29 - 44%	6	01/2024 to 07/2024	25 to 78 h
C	42 - 49%	3	02/2024 to 04/2024	30 to 52 h
D	23%	1	05/2024	23 h

The number of tests carried out since the start-up of the pilot has been limited essentially by the lack of waste deliveries to the site in 2024, linked to the economic difficulties encountered by the chemical industry. Some customers did not deliver the quantities initially planned during contractual exchanges, and the business had to adapt, losing flexibility in carrying out sulphur recovery tests.

Typical ranges for operating parameters during the pilot tests are described in

Table *19*.

Table 19: Typical ranges for operating parameters during the pilot tests

Parameter	Min	Max
% SO_2 in flue gas	0.1%	0.5%
pH	3	9
Temperature	60°C	80°C

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Oxygen content in flue gas	3.5%	9%

2.7.2. Results of the new approaches

Sulfur recovery from flue gas

Key performance indicators
Material recovery target:

- 80% of organic sulfur waste

Quality target (concentration and purity) of the sodium bisulfite solution:

- 38% NaHSO3
- Na2SO3 < 10 g/L
- Na2SO4 < 30 g/L
- Metals (Zn, Cu, Fe) < 150 mg/kg
- Heavy metals (Pb, As, Cd, Cr, Hg) < 10 mg/kg

Industrial pilot results
First, the demonstration pilot confirms, as expected, that the process is efficient for SO_2 abatement, with overall efficiencies exceeding 99%. Figure 77 details an example of the evolution of SO_2 content between each operation unit of the pilot. The main variations observed between the tests are in the 1st column, whose abatement depends on the pH regulation, as illustrated on the second figure. The second column, regulated at basic pH, systematically captures the remaining SO_2 and guarantees discharge quality.

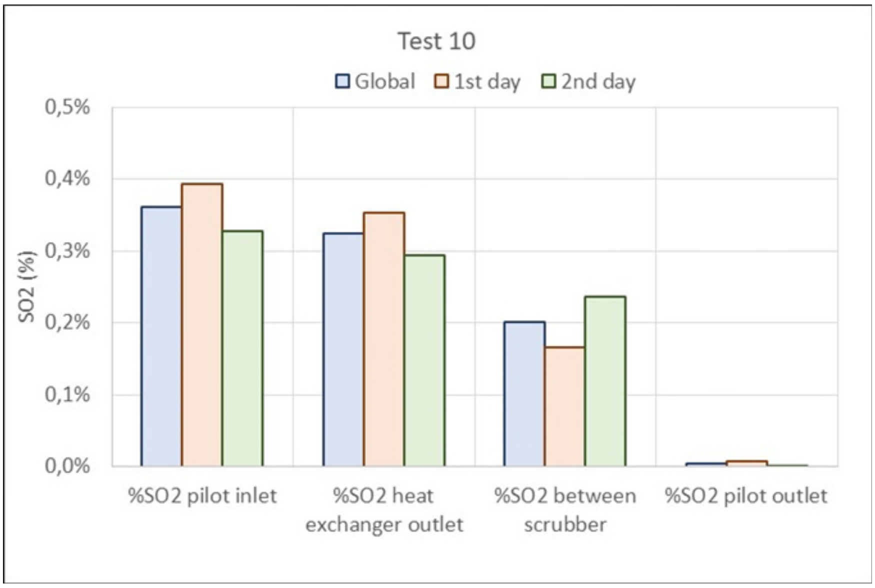

Figure 77: Results obtained in Test 10

A study of the overall yield of the sulfur recovery operation in terms of the quantity of recoverable sulfur introduced into the furnace and considered as recoverable (i.e. forming sulfur dioxide) highlights that a significant proportion (about 40%) of the sulfur dioxide is captured by the flue gas washing process before entering the pilot plant. The modifications required to reduce this adsorption and increase the sulfur recovery rate have been identified:

- Removing basic waste from the furnace inlet increases the SO2 content at the pilot inlet (the effectiveness of this solution has been tested).
- Reducing the operating pH of the quench and first scrubber should also significantly increase the SO2 content at the pilot inlet. Unfortunately, this solution cannot be tested with the materials currently in place on the unit.

In Table 20, the best results obtained on the industrial pilot have been grouped together. It appears that the target set for sodium bisulphite content in the final solution (based on the concentrations of technical solutions available on the market) has not been reached. What is generally observed is that the duration of the tests is insufficient. Often, the concentration in the basic column, in which the sulphite solution feeding the first column is formed, has just enough time to reach saturation. To overcome this difficulty, it was decided to keep the solutions between two tests, to start each test with the solutions obtained during the previous test. Unfortunately, the delays between 2 experiments, directly linked to the receipt of waste, led to significant oxidation of the sulphur solutions. The results obtained from tests with oxidized solutions confirm, as mentioned in the literature, that the oxidation phenomenon is accentuated in the presence of sulphates. No logistical solution could be found to organize series tests on the pilot, to avoid oxidation of the solution.

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Table 20: Best results obtained in the pilot.

Test number	pH	$[NaHSO_3]$ $(g.L^{-1})$	$[Na_2SO_3]$ $(g.L^{-1})$	$[Na_2SO_4]$ $(g.L^{-1})$	Oxidized sulphur rate (%)
7	5.1	106	1.0	0.4	0.3 %
8	5.7	216	8.3	0.9	0.3 %
10	3.4	83	0.1	2.4	2.1 %
13	5.8	154	7.4	3.3	1.5 %
Target	**3.5 – 4.5**	**510**	**< 10**	**< 30**	**~ 4%**

Concerning the other target compositions (sulphite and sulphate contents), the results are rather encouraging. Sulphite content is directly linked to pH, some values of which are higher than the target, but could be adjusted by regulation.

The sulphate concentrations obtained in the bisulphite solution and the associated oxidation rates are in line with expectations. The confirmation of these positive results at higher sodium bisulphite concentrations is still to be confirmed.

Other parameters are also key to validate the solution quality obtained: the content of various metals and of chlorine.

Regarding metals concentration, industrial pilot tests are promising (Figure 78). For both “current” metals (iron, copper or zinc), and for heavy metals, values obtained are below maximum target, indicated by continuous red line on figures below. A second limit, represented by the dotted red line, represents the ideal target. Some pilot tests show results above this ideal target, but measurements have been made on batch sample, and are therefore not fully representative of what could be obtained with continuous operation and grouping solutions obtained. In the way of an industrial solution, the composition of waste treated in parallel with sulphured waste will have to be strictly monitored to ensure the quality of the sodium bisulphite produced.

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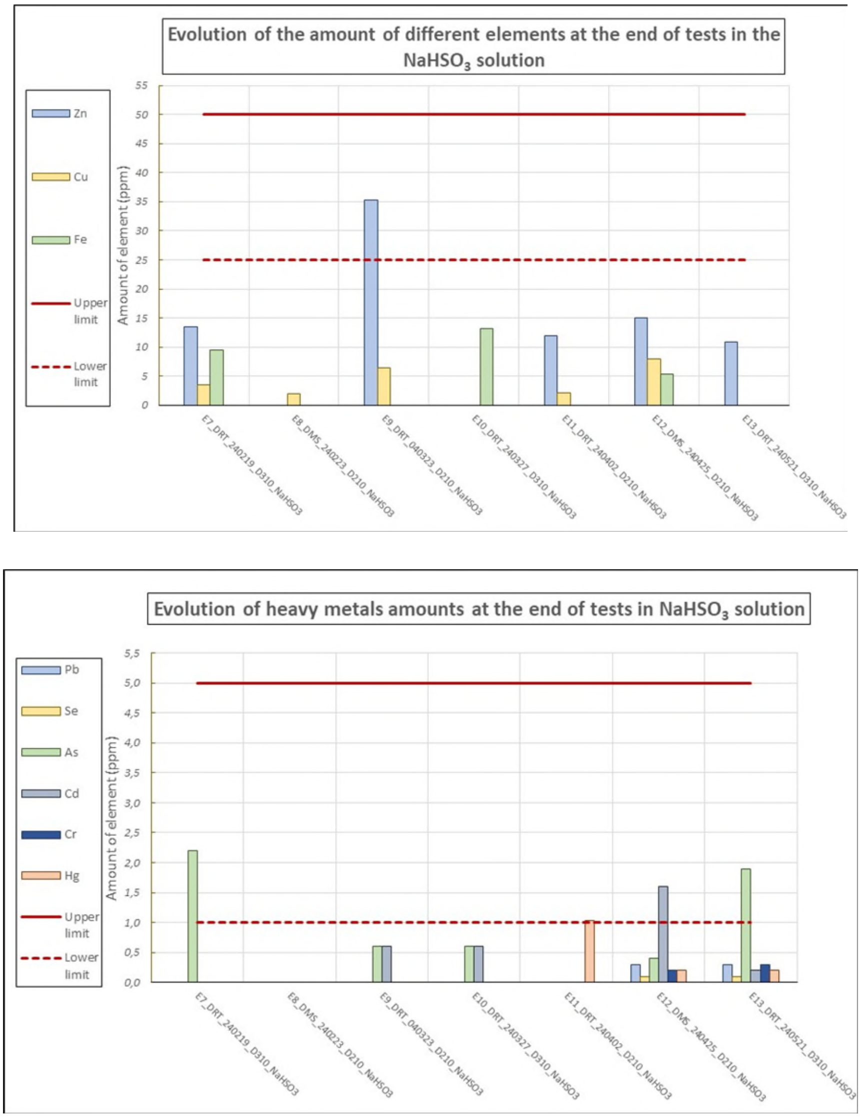

Figure 78: Evolution of metals in the NaHSO$_3$ solution

Concerning chlorine concentration (Figure 79), values obtained are very high. A market study currently in progress should provide us with further information on the importance of this parameters for potential users of sodium bisulfite solution. It however seems that salts treatment must be improved upstream the recovery process, for example by an additional packed column, ensuring that the pH stays acid so that SO_2 is not captured.

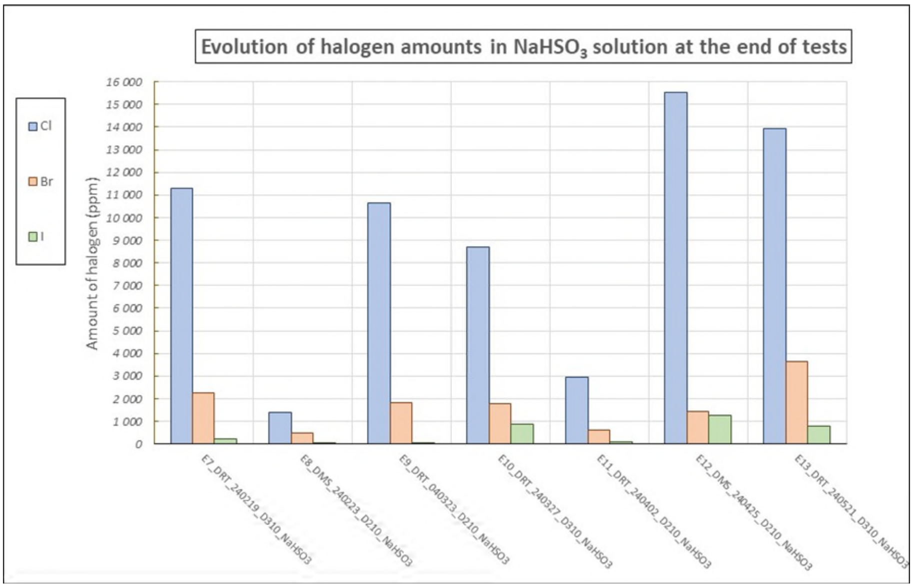

Figure 79: Evolution of halogens in the $NaHSO_3$ solution

Another important observation from the tests was that the adsorption efficiency of the first column, in the target pH range for sodium bisulfite, was lower than expected from the laboratory tests carried out previously, whose results can be seen in Figure 80.

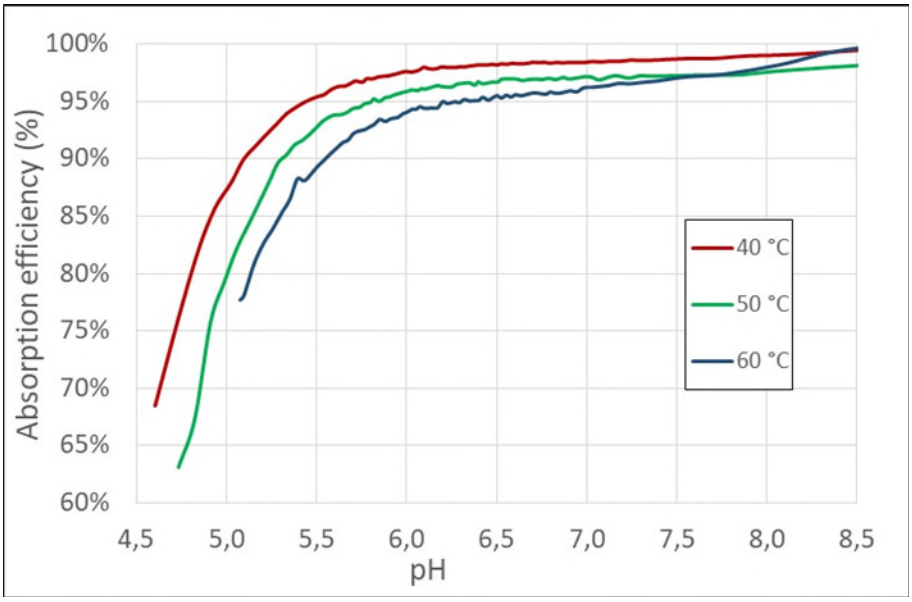

Figure 80: Adsorption efficiency obtained during lab tests at different temperatures

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To further evaluate and improve the process, tests were carried out to measure the adsorption efficiency of the two scrubbers with the pH. The results are shown in Figure 81.

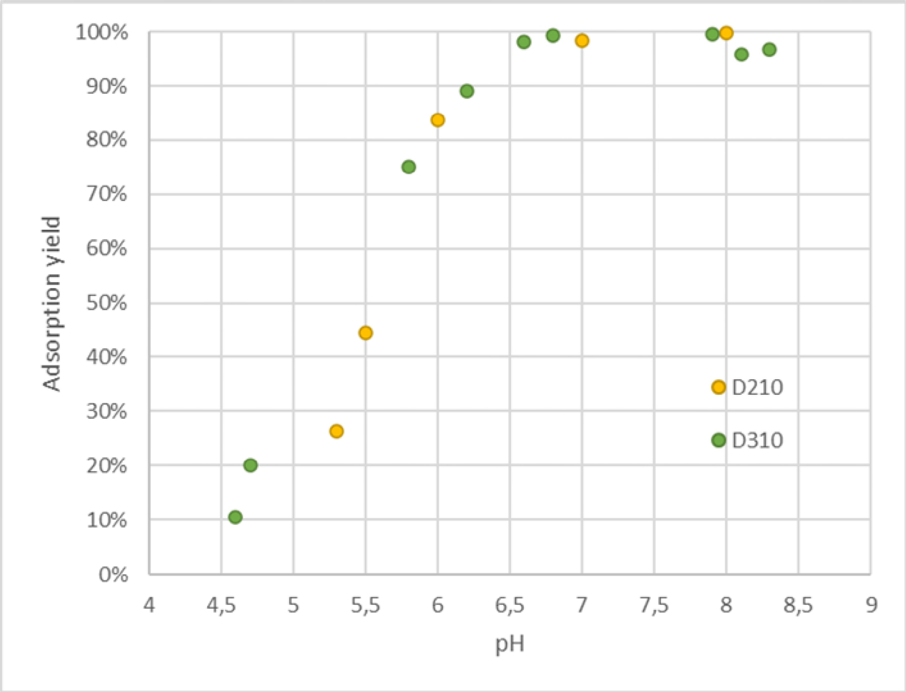

Figure 81: Adsorption efficiency of the pilot at different pH

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Laboratory tests had highlighted the significant influence of temperature on the sulfur dioxide adsorption rate. For this reason, a heat exchanger was designed to cool the flue gas to a temperature of 50°C at the pilot inlet. Unfortunately, the exchanger installed did not deliver the expected efficiency, and the condensation phenomena observed in the columns during certain tests required keeping the columns at temperature to avoid diluting the bisulphite solution by the condensation of the flue gases. To assess the modifications required on an industrial plant to improve these efficiencies, the two columns were modelled, and the results are presented in Figure 82.

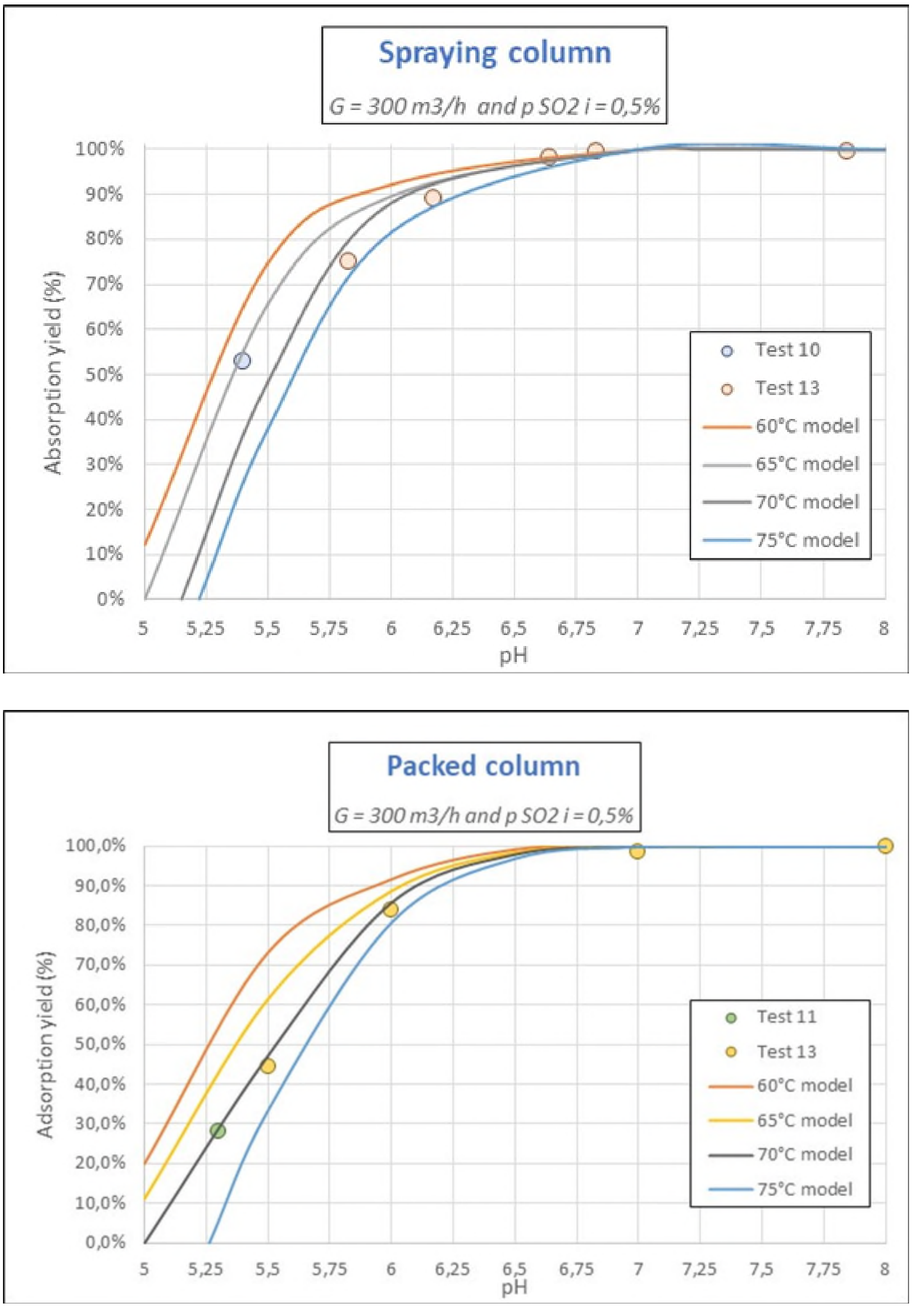

Figure 82: Adsorption yield results of the pilot modelling, comparison with experimental results

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According to scrubber modelling, adsorption yield on the first column can be significantly improved by reducing the flue gas temperature.

However, the sulfur dioxide absorption yield expected for the targeted pH range of the sodium bisulfite solution is too low for the process to be efficient. It is probable that an industrial solution will involve adding a third column to the process. Tests should be continued with the pilot in this way, testing configurations representing the 2 last columns and then the 2 first columns of the projected process.

Design, IT development, configuration and test of a monitoring and control application (ULTIMATE IT application)

a. Stakes

SUEZ Smart Solutions (3S) is a subsidiary of the SUEZ Group, providing expertise in data collection, processing and the design of innovative digital applications for the environmental performance of cities and users. 3S develops numerous software products for the water sector (e.g. the AQUADVANCED® software range) and for the waste sector (e.g. the WasteAdvanced® software).

As part of the ULTIMATE project, 3S is a partner of SUEZ RR on the CS8 case study. Its role was to design, develop, configure and integrate a **single IT application** for the following two studies of CS8, located on the Roches-Roussillon chemical platform:

- **Sulphur recovery** (see section 2.7 of this deliverable D1.5)
- **Heat recovery** (see section 2.7 of deliverable D1.4)

The ULTIMATE application was configured using WasteAdvanced®, a market software product developed by 3S. WasteAdvanced® is a digital solution for optimising the performance of waste-to-energy plants.

Three stakes guided SUEZ Smart Solution's contribution:

1. **Meet** the contractual requirements of the Grant Agreement by deploying the ULTIMATE IT application for the two CS8 studies mentioned above.
2. **Identify** the suitability and technical potential of WasteAdvanced® to meet the business requirements of SUEZ RR, and to develop any missing functionalities, thus enriching the functional spectrum of this software product beyond the initial functionalities dedicated to optimising the performance of waste-to-energy plants.
3. **Evaluate** the opportunity to build, in the future, a technical-commercial offer, based on the expertise of SUEZ RR and the WasteAdvanced® software product; this issue is outside the scope of the ULTIMATE project.

b. Objectives

Three technical objectives were associated with the ULTIMATE IT application:

1. **Collect** measurements from various information sources on the site
2. **Create** and **configure** business indicators based on these measurements and the business calculation formulas supplied by SUEZ RR
3. **Create** and **configure** widgets to display the measurements collected and the indicators calculated, in accordance with the display requirements expressed by SUEZ RR

c. Collect measurements

Table 21 shows the four sources of measurements that feed the ULTIMATE application.

Table 21: Number of measurements configured in the ULTIMATE application by type of data source

Type of data source	Measurements device	Measurements source	Number of measurements
Aqueris process (see subsection “Description of the demo site” of section 2.7.1)	Sensors	Foxboro SCADA (publisher: Schneider Electric)	26
ULTIMATE pilot	Sensors	PLC (manufacturer: Siemens - Model: Simatic ET 200SP)	15
ULTIMATE pilot	Laboratory analysis from samples	Data file	7
ULTIMATE pilot	Gas analysers	Data file	15
		TOTAL	63

The first two data sources (Foxboro SCADA and the pilot's PLC) provide **real-time data**, while the last two (laboratory analyses and gas analysers) provide **off-line measurements**.

For cybersecurity reasons specific to the SUEZ RR site, no IT communication is possible between their industrial network and the SUEZ office network, and vice versa.

In practice, SUEZ RR users manually retrieve the measurements available on their industrial network on a USB key and then manually transfer them to the office network.

As part of the ULTIMATE project, this technical impossibility meant that it was not possible to automatically collect measurements from the two sources of real-time information at the SUEZ RR site: those from the existing Aqueris process and those from the ULTIMATE pilot.

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Figure 83 illustrates the alternative technical solution proposed by 3S to SUEZ RR, based on the manual transfer of data files.

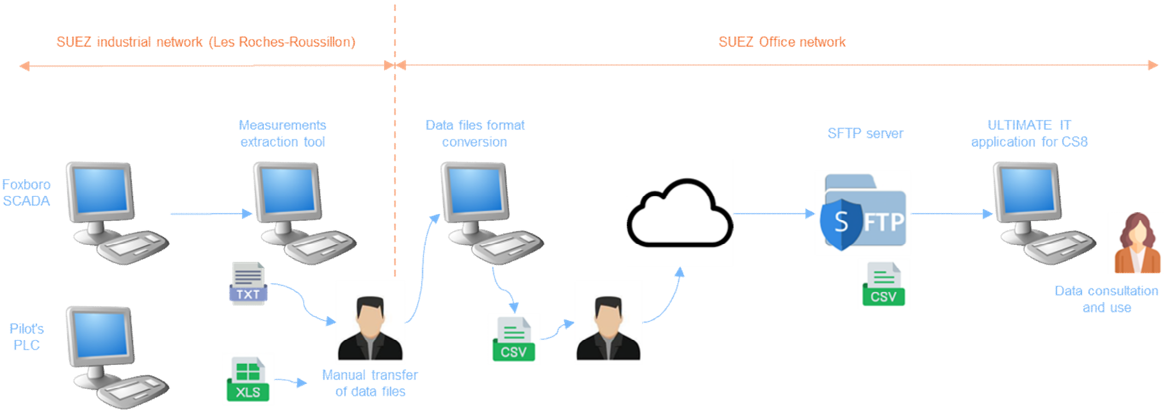

Figure 83: IT architecture for CS08

Process – Acquisition of **real-time measurements** until their consultation:

1. The operator manually extracts the real-time measurements of the existing Aqueris process, available in the Foxboro SCADA installed on the industrial network, and stores them in TXT format files on a USB key.
2. The operator manually extracts the real-time measurements of the ULTIMATE driver, available in the PLC installed on the industrial network, and stores them in Excel format files on a USB key.
3. The operator connects the USB key to a computer located on the SUEZ office network, transfers the measurement files to this computer and converts the two types of data file formats (TXT from Foxboro SCADA and Excel from the pilot's PLC) to CSV format.
4. The operator uploads these CSV files manually on a secure SFTP server created and configured by 3S on SUEZ's Microsoft Azure cloud.
5. The ULTIMATE IT application regularly scans this SFTP server, automatically transfers the new measurements and stores them in its database, which are then available for consultation via the application's graphical interface.

For **offline measurements** (laboratory analyses and gas analysers), the file format is Excel, which is then converted to CSV format. These measurement files are then uploaded to the SFTP server (see points 4 and 5 of the process described above for real-time measurements).

d. Create and configure business indicators

Business indicators have been configured in the ULTIMATE application, in accordance with SUEZ RR requirements for the **Sulphur recovery** study.

At 3S' request, SUEZ RR provided the following information required to configure the business indicators in the ULTIMATE application:

- Information (name, unit, calculation formula, etc.) characterising each **business indicator** $\boldsymbol{y}$ (Figure 84).
- Information (name, unit, etc.) characterising each of the **measurements** $\boldsymbol{x_k}$ used as input for the **calculation formula** $\boldsymbol{F(x_1, x_2, \cdots, x_k, \cdots, x_n)}$ for the **business indicator** $\mathbf{y}$ (Subsection c. Collect measurements).

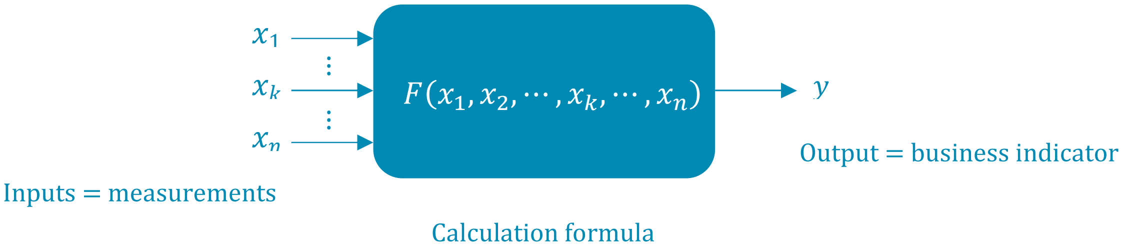

Figure 84: Information characterising each business indicator

A large Excel spreadsheet was edited to store the information associated with CS8. This spreadsheet acted as a specification and exchange document between the CS8 partners, in which numerous revisions were made throughout the ULTIMATE project.

Table 22 Information required by the ULTIMATE application to configure a business indicator

Information required	Comments
Name	Name of the business indicator
Parent	The node in the application tree to which the business indicator is attached
Quantity	Unit of the business indicator (concentration, power, flow, etc.) and associated unit
Expression	Mathematical formula allowing the calculation of the values of the business indicator based on the values of its inputs
Input variables	Inputs required for calculating the business indicator

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Table 23 Information required by the ULTIMATE application to configure an input used in the formula for calculating a business indicator

Information required	Comments
Quantity	Unit of the input (concentration, power, flow, etc) and associated unit
Decimal separator	Comma or dot for instance
Data connector	Name of the connector to the information source. Various types of connector exist in the WasteAdvanced® product: databases, OPC, TXT or CSV files, etc.
Column name	In a text file containing several columns, ID to identify the column to be considered for entry
File name	Name of the file (here for a text file)
Quantity	Unit of the input (concentration, power, flow, etc) and associated unit
Decimal separator	Comma or dot for instance

In the Annex A, screenshots of the application, in which the required information can be entered to configure business indicators (Figure 107, Figure 108, Figure 112 and Figure 113) and their inputs (Figure 109, Figure 110, Figure 114 and Figure 115), are shown.

e. Create and configure widgets

In addition to the site measurements and business indicators, widgets have been configured in the ULTIMATE application, in accordance with SUEZ RR requirements. Two types of information are distinguished:

- Information characterising the **content** of each widget: inputs and/or business indicators to be displayed.
- Information characterising the **display** of the content of each widget: time series, bar chart, pie chart, gauge, etc.

The specifications associated with the widgets have also been added to the Excel spreadsheet for business indicators, mentioned in the previous subsection “d. Create and configure business indicators”.

In the Annex A, screenshots of the application, in which the required information can be entered to configure a widget (Figure 106 and Figure 111), are shown.

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f. Test of the ULTIMATE application

The ULTIMATE IT application is operational and was accessed online by the CS8 users.

Figure 85 shows the authentication page of the ULTIMATE IT application as it is accessible by the case study partners. Examples of the output of the application such as the display of different process parameters are shown in the Annex A, subsection A.1 Results of the feasibility study (complements).

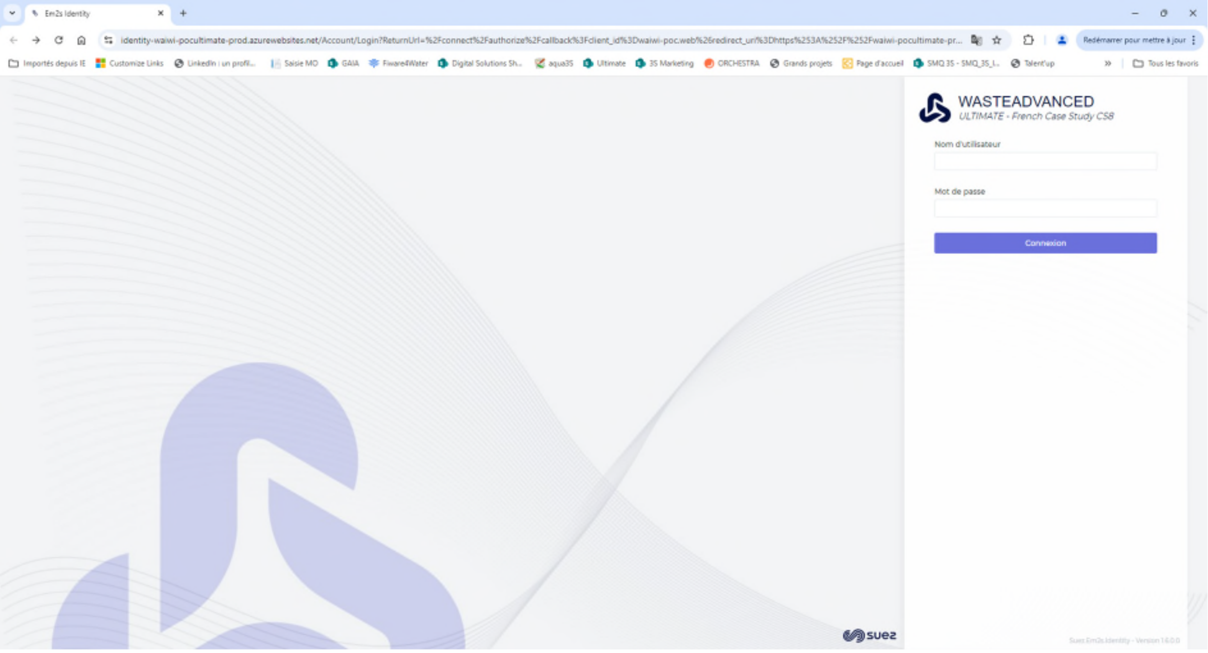

Figure 85 Authentication screen (login and password) to access the ULTIMATE IT application

2.7.3. Conclusion

Industrial pilot tests enabled the production of sodium bisulfite solution, but the concentration obtained is below targeted concentration and further pilot tests have to be carried out to increase the concentration.

The sulfur dioxide adsorption yield observed were lower than expected, but optimization ways have been identified:

- The flue gas treatment process upstream of the recovery process needs to operate at a lower pH, to avoid sulfur dioxide absorption.
- The recovery process must operate at the lowest possible temperature (with the disadvantage of increasing the overall energy consumption of the process, due to the necessity of reheating the flue gas in the subsequent flue gas treatment, for NOx abatement).

The sodium bisulfite solution quality obtained is globally promising. The parameter that really need to be improved is the chlorine content of the final solution. For that, the efficiency of the salt treatment before the recovery process needs to be increased, and

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of course the treatment of chlorinated organic waste in parallel with sulfur-containing organic waste should be avoided.

In parallel with the technical-economic study, conducted by SUEZ RR, the second French partner 3S, also involved in CS8, was responsible for configuring an IT application, based on the WasteAdvanced® software product, developed and marketed by 3S.

A **single IT application** has been designed, configured, integrated and tested to jointly address the following two studies of CS8, located on the Roches-Roussillon chemical platform:

- Sulphur recovery (see section 2.7 of this deliverable D1.5)
- Heat recovery (see section 2.7 of deliverable D1.4)

Three stakes were associated with the ULTIMATE application:

1. **Contractual stake:** meet the contractual requirements of the Grant Agreement.
2. **Technical-industrial stake:** WasteAdvanced® was developed for the business issue "Energy from Waste Plant" (EFW), which is different from that of the **Sulphur recovery** study of CS8. The challenge was to enrich the functional scope of WasteAdvanced® by developing the missing functionalities to meet the requirements of SUEZ RR, associated with the **Sulphur recovery** study.
3. **Commercial stake:** identify a possible joint technical-commercial offer between SUEZ RR and 3S, based on WasteAdvanced® (this third stake is beyond the scope of the ULTIMATE project).

Crucial factors for the implementation of a sulphur recovery system:

- Flue gas treatment (upstream sulphur recovery) ensuring an effective cleaning of dust and salts, and preserving the sulphur dioxide concentration.
- Contractualization of upstream (organic sulphur waste) and downstream (sodium hydrogen sulphite)
- Sufficient economic advantage, as investment grant, to initiate change (from disposal to production)
- Regulations both promoting the development of material recovery projects and not compromise on health, safety and environmental protection

2.8. Recovery of metals at the Chemical Platform of Le Pont-de-Claix (FR)

2.8.1. Case study and ULTIMATE concept

Description of the demo site

The chemical platform of Le Pont de Claix exists since 1928, and brings together 5 companies: Vencorex, SUEZ, Seqens, Solvay and Air Liquid. SUEZ RR IWS Chemicals (SUEZ RR) operate on this platform two hazardous waste incinerators that treat a significant proportion of the chemical platform waste but also waste from other region or countries. This activity of waste incineration produces steam, which is distributed to the platform's network. The plant is specialized in high chlorinated solvent waste, but also treat heat-sensitive waste and compressed or liquefied halogenated gases. This plant also treats a very small proportion of waste directly on the physico-chemical wastewater treatment plant.

The process implemented on the platform is represented in Figure 86.

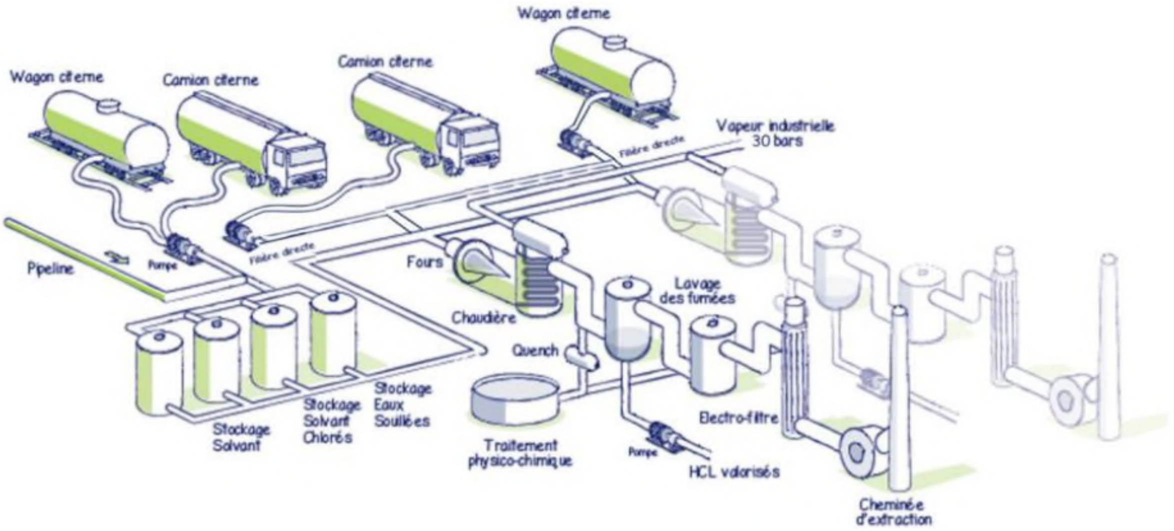

Figure 86: Simplified diagram of the incineration plant of Le Pont-de-Claix

Certain types of waste, because of their heat-sensitive nature or because they contain high levels of certain elements, must be incinerated directly on the furnace (without passing through a storage facility). This particularity has led to the idea of recovering certain metallic elements contained in this type of waste. Indeed, during incineration, the metallic elements are recovered in the flue gas washing water, which is sent for treatment to the physico-chemical WWTP. The feasibility study presented here explains the process studied for molybdenum recovery from flue gas washing waters, and the results obtained.

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Description of the concept

The study consisted in evaluating different ion exchange resins for the recovery of molybdenum from incineration flue gas washing water, characterized by an extremely high HCl content. This study, carried out on a laboratory scale, consisted in assessing the resins' ability to capture molybdenum, as well as their capacity to restore it during the elution stage. Based on the most promising results, the possibility of regenerating the resin and reusing it for a new regeneration step was studied.

Ion exchange resins description

Ion exchange resins are insoluble materials used for the selective exchange of ions in solution. They act as a medium for adsorbing ions from solution and replacing them with ions of the same charge.

These resins are usually in the form of porous microbeads, offering a high specific surface area. These resins also contain functional groups, such as sulfonic acids, carboxylic acids and ammoniums, which can be bonded to the polymer structure, giving them their properties.

Ion exchange resins are usually divided into two categories: cation exchange resins, able to capture cations (1) and anion exchange resins, able to capture anions (2).

$$\text{Resin}^{-} - \text{ex}^{+} + \text{C}^{+} \text{------}\rightarrow \text{Resin-} - \text{C}^{+} + \text{ex}^{+} \qquad (1)$$

$$\text{Resin}^{+} - \text{ex}^{-} + \text{A}^{-} \text{----}\rightarrow \text{Resin}^{+} - \text{A}^{-} + \text{ex}^{-} \qquad (2)$$

Cation exchange resins can be classified into strong cationic resins and weak cationic resins. The exchange capacity of the first one is independent of the pH of the solution, whereas weak cation exchange resins have limited capacity above a pH of 6. Similarly, anion exchange resins can be classified into strong and weak anion resins. Like strong cationic resins, strong anionic resins can be used over the whole pH range.

Ion exchange resins could be regenerable or not. In our study, the priority was given to regenerable ion exchange resins, believing that they could present an economic advantage.

Regenerative ion exchange resin operating cycle

The operating cycle of an ion exchanger, applied during our laboratory tests, consists in 5 phases:

1- Conditioning: this stage introduces into the ion exchange resin the appropriate counterion to capture an ion from the surrounding solution.

2- Saturation: during this operational phase, the solution is in contact with the ion exchanger bed until it is saturated, adsorbing ions from the solution and replacing them with ions of the same charge.

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3- Lifting: this step facilitates the removal of particles that may accumulate on the bed surface, using a flow of water.

4- Regeneration: done by filtering the regenerating solution through the bed. Depending on the type of exchanger and the ions involved, the regeneration process may involve either elution or displacement.

5- Rinsing: During this stage, any excess regenerant in the water is removed at a reduced flow until the resin contains only minimal traces of regenerant, signalling the start of the slow rinse phase. This is followed by a rapid rinse phase, at a higher flow rate, to remove the last traces of regenerant.

Lifetime of ion exchange resin

The lifetime of ion exchange resins is very variable because they are influenced by parameters that are difficult to control. They are particularly sensitive to temperature and oxidants. Regarding their exchange performance, resins generally have an estimated lifetime of several years when used in temperature ranges from 0 C to 40 C. According to manufacturers, some resins can tolerate thermal shock up to 80 C for short periods (1-2 hours), but extended exposure to this temperature can significantly reduce their lifespan.

Washing water from the incineration plant are above the recommended temperature (about 75°C). Lab tests have been conducted on cooled washing water.

Industrial application of ion exchange resin

Ion exchange resins are widely used in the chemical industry for a variety of applications. They are used in water softening and demineralization, essential for many chemical processes. Their high exchange capacity and selectivity for trace contaminants make them valuable tools for purifying chemical compounds. They are also used in specific fields such as production chromatography and taste masking in the pharmaceutical industry.

To our knowledge, the use of ion exchange resins in highly acidic waters with a variable mixture of elements, as it is the case on our incineration plant, has never been studied.

Description of the lab tests

Column tests

The experimental set-up can be seen on Figure 87. It comprises a separating funnel at the top of an inert glass column (2 cm diameter and 15 cm high) and a beaker to collect the treated solution at the output.

A quantity of 15 g of ion exchange resin is introduced in the column, equivalent to filling half the column and the effluent to be treated is introduced in the separating funnel. Then the effluent flows down through the ion exchange resin grains at a flow rate maintained at 250 mL/h. Once the process is complete, the treated solution is analysed by ICP-MS and/or spectrophotometer to quantify metals.

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The aim of this experimental protocol is to check the ion exchange resin behaviour regarding the objective of molybdenum recovery. Further detailed studies proceed with isotherm tests.

Figure 87: Experimental set-up for column tests

Isotherm tests

The objective of the isotherm tests is to evaluate the ion exchange capacity of ion exchange resins at equilibrium. After conditioning (Figure 88), the ion exchange resin is distributed in four separate beakers at an increasing quantity (10g, 20g, 30g and 40g). A fixed volume of effluent (100mL) is then added (Figure 89), and the mixture is agitated for 24h to reach equilibrium (Figure 90). After 24 h agitation, the treated solution is analysed by ICP-MS, to determine its molybdenum concentration.

Figure 88: Conditioning of resins

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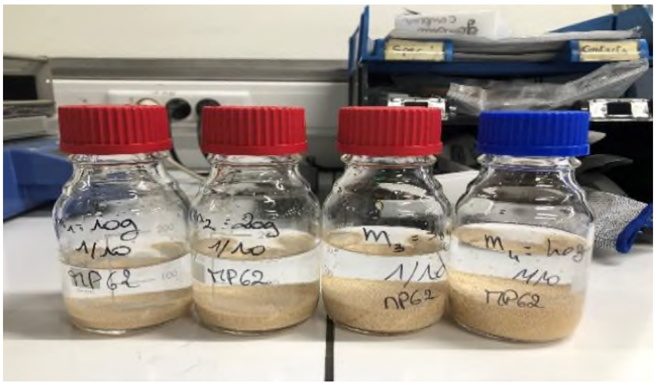

Figure 89: Resin saturation by effluent

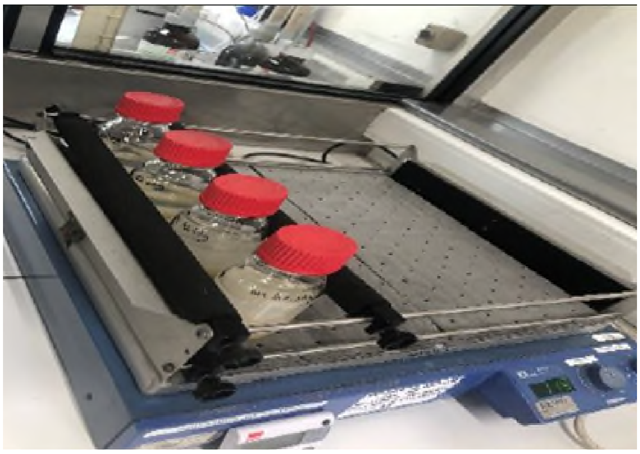

Figure 90: Agitation for 24h

Effluent tested

The effluent used for the lab tests is the washing water obtained at the first step of the flue gas treatment (quench). The solution has a very high content in HCl (>5%) and contains a large quantity of molybdenum in the form of Mo^{2+} (1600 mg/L).

Ion exchange resin tested

The ion exchange resins described in the Table 24 below were tested to recover molybdenum.

Table 24: description of the ion exchange resins tested

Ion exchange resin	Type	Exchange capacity (meq/L)	Regeneration solvent	pH
A	Weak cationic resin	1.3	H_2SO_4 (5%)	1.5 - 14
B	Weak cationic resin		H_2SO_4 (5%)	2 - 3
C	Weak cationic resin	2	H_2SO_4 / HCl	1.5 - 9

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2.8.2. Results of the concept study and modelling

Adsorption tests

The first tests were carried out with conditioning resin, according to the supplier's recommendations. Given that the pH of the effluent to be treated is well below the recommendation (pH<0), the first tests were carried out on diluted effluent and then with diluted and neutralized effluent. In both cases, the dilution factor was 10.

The results obtained are shown in Figure 91 and Table 25.

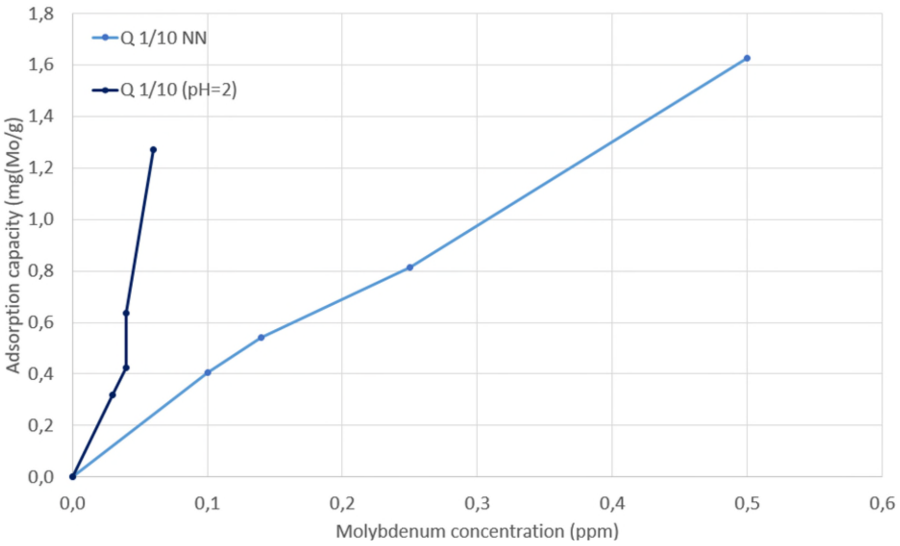

Figure 91: Results on 10-fold diluted effluent for resin A

Even if the resins are not used to their full capacity, almost all the molybdenum is adsorbed on the resins, leading to very low concentrations in the solution to be treated. However, preparation of the solution (dilution by a factor of 10 and neutralization) makes the effluent to be treated significantly different from the initial effluent, and such preparation is not economically feasible. The next lab tests therefore involved testing increasingly concentrated effluents.

Table 25: Results on 10-fold diluted effluent for resin A

Effluent	pH	[Mo]i	[Mo]f	Adsorption capacity max (mg/g)	%Mo adsorbed
Diluted by 10 and neutralised	2	127 ppm	**< 0,1 ppm**	> 1,2 mg/g	**> 99,95 %**
Diluted by 10	0,42	163 ppm	**< 0,5 ppm**	> 1,6 mg/g	**> 99,7 %**

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The results obtained for a dilution of the effluent by a factor of 5 are shown in Figure 92 and Table 26.

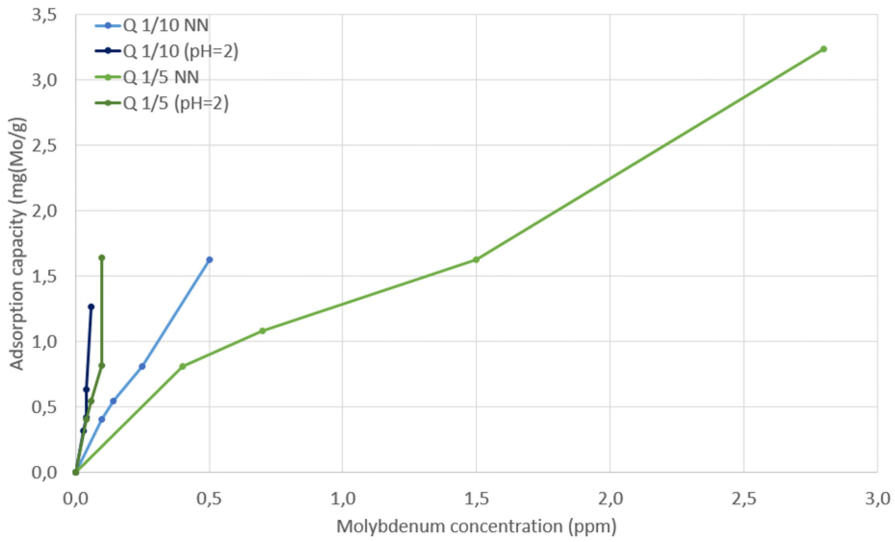

Figure 92: Comparison of results for a 10-fold and 5-fold diluted effluent for resin A

Table 26: Results on 5-fold diluted effluent for resin A

Effluent	pH	[Mo]i	[Mo]f	Adsorption capacity (mg/g)	% Mo adsorbed
Diluted by 5	0,06	326 ppm	**2-3 ppm**	> 3 mg/g	**> 99,1 %**
Diluted by 5 and neutralised	2	164 ppm	**<0,1 ppm**	> 1,6 mg/g	**>99,95%**

For a dilution by 5, the final concentration in molybdenum in the effluent is higher than for a dilution by 10, but this concentration is still acceptable because the effluent contains other impurities which in all cases require additional physico-chemical treatment. And the adsorption yield remains very favourable.

The results also show that the resin supplier's recommendations on the pH range of the effluent to be treated are relevant, but the cost / efficiency ratio is not, in our case, necessarily in favour of adjusting the pH. The next lab tests were therefore carried out by further reducing the dilution ratio of the effluent to be treated, but without further adjusting the pH.

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The results obtained for a dilution of the effluent by a factor of 3 are shown in Figure 93 and Table 27.

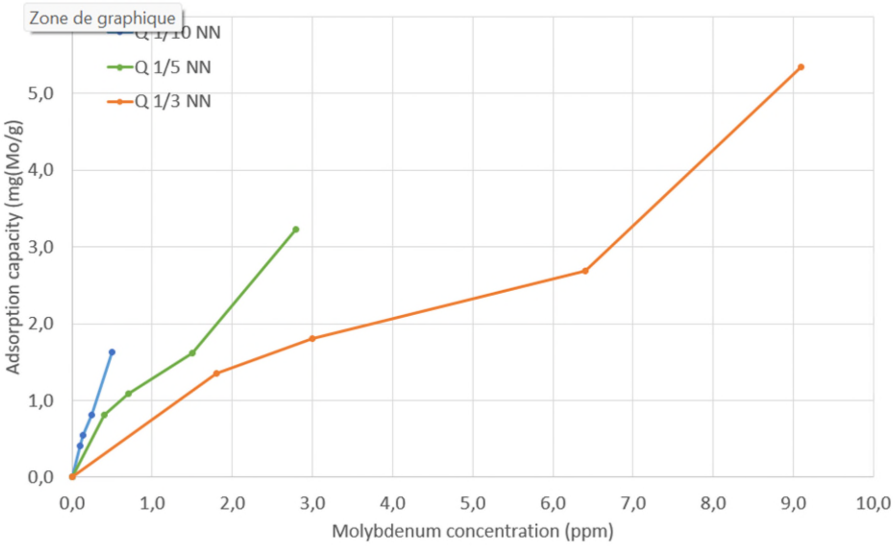

Figure 93: Comparison of results for 10-, 5- and 3-fold diluted effluent for resin A

Table 27: Results on 3-fold diluted effluent for resin A

Effluent	pH	[Mo]i	[Mo]f	Adsorption capacity max (mg/g)	% Molybdenum adsorbed
Diluted by 3	< 0	543 ppm	**< 10 ppm**	> 5 mg/g	**> 98 %**

As in the previous test, a dilution factor of 3 lead to a final concentration in molybdenum higher than for the dilution factor of 5. This concentration is however acceptable regarding the fact that the effluent contains other impurities which in all cases require additional physico-chemical treatment. The adsorption yield remains very favourable. This point is considered a good compromise between the volume increase due to dilution, the molybdenum adsorption efficiency obtained, and the final concentration remaining in the effluent and requiring further treatment before discharge.

A new approach to optimize the solution technically and economically was to test the same resins, but without conditioning.

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Results for an effluent diluted by 5 are given in Figure 94 and Table 28.

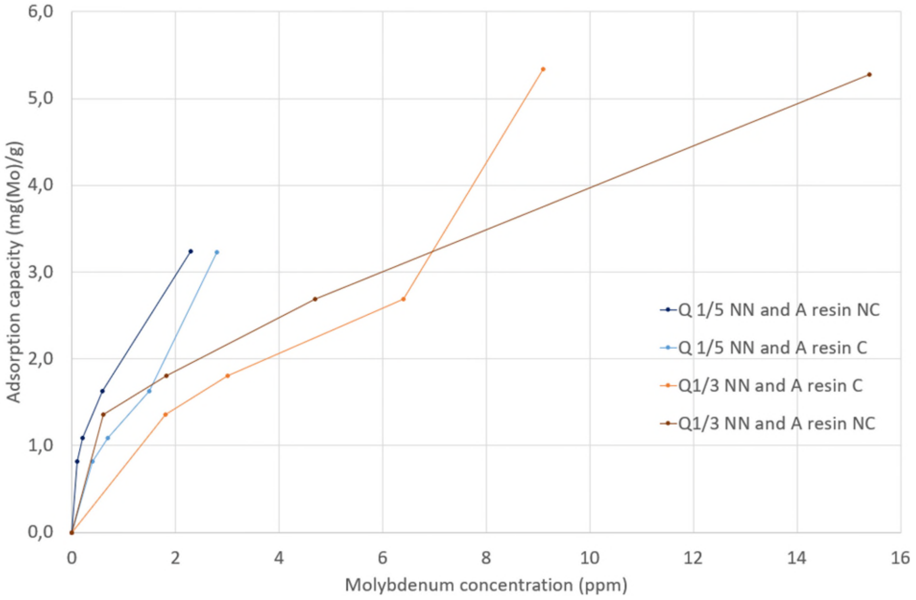

Figure 94: Comparison of results on resin A with and without preconditioning

Table 28: Results with and without conditioning for resin A

Resin	Effluent	[Mo]i	[Mo]f	Adsorption capacity max (mg/g)	% molybdenum adsorbed
Resin A without conditioning	Diluted by 5	326 ppm	**2-3 ppm**	> 3 mg/g	**> 99,3 %**
Resin A with conditioning	Diluted by 5	326 ppm	**2-3 ppm**	> 3 mg/g	**> 99,1 %**
Resin A without conditioning	Diluted by 3	543 ppm	**< 16 ppm**	> 5 mg/g	**> 97 %**
Resin A with conditioning	Diluted by 3	543 ppm	**< 10 ppm**	> 5 mg/g	**> 98 %**

The results show that adsorption isotherms for molybdenum on unconditioned resin are similar to those for conditioned resin. Conditioning does not appear to be of interest in our application.

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To further optimize the molybdenum adsorption step, we tried to reduce the ratio between the quantity of resin and the quantity of effluent to be treated. The results obtained for an effluent diluted by 5 on an unconditioned resin are shown in Figure 95.

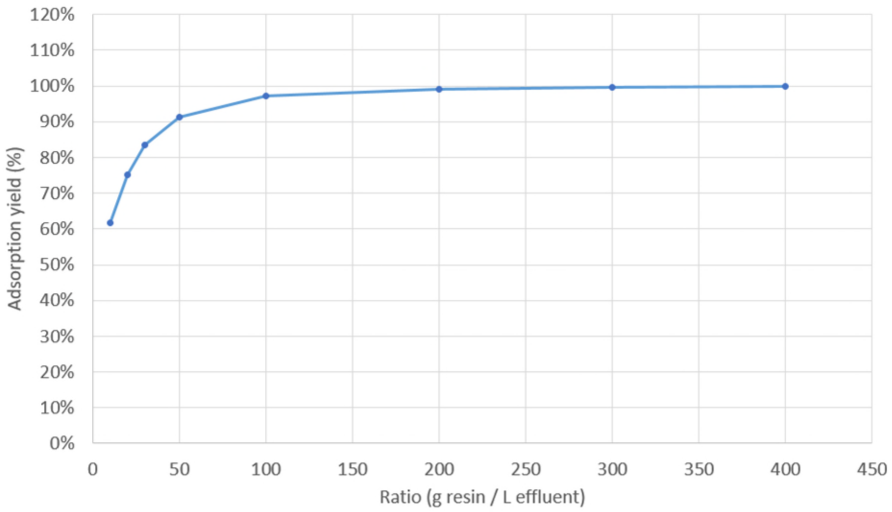

Figure 95: Influence of the resin A quantity / effluent quantity ratio on molybdenum absorption efficiency for 3-fold diluted effluent

Down to a ratio of 100 $g_{resin}/L_{effluent}$ adsorption yield of molybdenum is above 97%. Adsorption yield remain above 90% up to a ratio of 50 $g_{resin}/L_{effluent}$, but then drop significantly.

Once the technical conditions have been optimized for our objective of recovering molybdenum from incineration effluent, i.e.:

- 3- fold dilution of the effluent
- no neutralization of effluent
- start-up without prior resin conditioning

a comparison was made with two other resins. To be more exhaustive, this comparison was made for both conditioned and unconditioned resins.

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The results show that the resin initially chosen for the studies was the most interesting for our case (Figure 96).

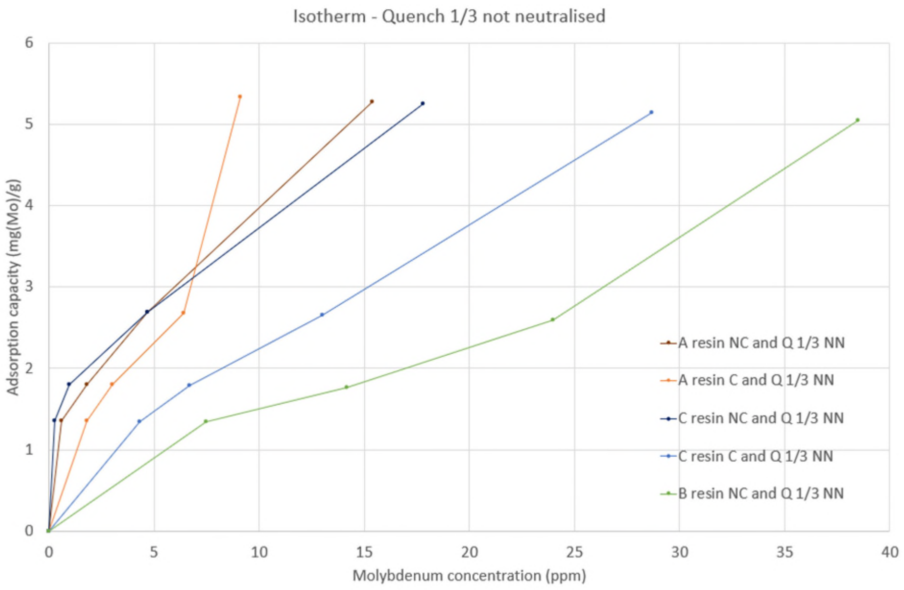

Figure 96: Comparison of results obtained on different resins

<u>Elution tests</u>

As mentioned, the aim of the study was to recover molybdenum from the effluent. To this end, elution tests were carried out to remove the metal from the resin and recover it in the eluate.

Elutions were carried out as follows:

- no prior rinsing of the resins, which would generate a large volume of effluent to be treated and risk the removal of a part of the molybdenum adsorbed on the resin;
- addition of 100 mL of 1N sodium hydroxide solution to the resin samples recovered from 4 series of adsorption isotherms (16 samples) showing interesting results for the adsorption stage;
- agitation for 24 hours, using the same principle applied for the determination of adsorption isotherm.

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Results obtained are in

Table 29.

Table 29: Results of elution lab tests

Resin	Effluent	[Mo] in the effluent (mg/L)	Adsorption yield (%)	Absorption capacity reached (mg/g)	[Mo] in the eluate (mg/L)	Elution yield (%)
Resin A without conditioning	Diluted by 5	326	99.3 %	3.24	283	87 %
			99.8 %	1.63	269	83 %
			99.9 %	1.09	263	81 %
			99.9 %	0.81	244	75 %
Resin A without conditioning	Diluted by 3	543	97.1 %	5.28	423	80 %
			99.1 %	2.69	393	73 %
			99.7 %	1.80	415	77 %
			99.9 %	1.36	360	66 %
Resin C without conditioning	Diluted by 3	543	96.7 %	5.25	403	76 %
			99.1 %	2.69	411	76 %
			99.8 %	1.81	390	72 %
Resin B without conditioning	Diluted by 3	543	92.9 %	5.05	144	28 %
			95.6 %	2.60	194	37 %
			97.4 %	1.76	254	48 %

The results obtained with the first resin are extremely encouraging. In particular, an elution efficiency of 80% for a 3-fold diluted effluent is extremely positive.

Lifetime tests

As the resins studied are regenerative, tests were carried out to assess their lifetime and mechanical resistance under pH conditions that differ from their usual operating conditions.

To this end, adsorption cycles of effluent diluted by 3 were carried out on an unconditioned resin. Between each cycle, the resin was regenerated with H_2SO_4 (5%). The indicator used to qualify the resin for each cycle was its exchange capacity in mg/g of resin.

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The results are shown in

Table *30*.

Table 30: Results of lifetime lab tests

	Cycle 1	**Cycle 2**	**Cycle 3**
Mass of ion exchange resin (g)	**Exchange capacity (mg/g)**	**Exchange capacity (mg/g)**	**Exchange capacity (mg/g)**
2	32.0	30.0	46.8
4	19.5	19.0	23.7
6	14.7	12.0	16.5
10	10.4	8.6	10.4

The results show no particular deterioration of the resins after 3 cycles, although variations are observed between each cycle.

2.8.3. Conclusion

Tests carried out on the effluent of the incineration treatment plant, containing a high concentration in molybdenum, demonstrated the effectiveness of several resin outside of their expected operating range. These tests enabled us to find an acceptable compromise between resin operating conditions and industrial reality. In fact, a 3-fold dilution of the quench effluent could be considered regarding the potential interest of the solution.

The adsorption yields obtained are extremely high, and the elution tests also show positive results, leading to an interesting overall yield of the operation.

In addition, it was found that resin conditioning is not a decisive factor in ensuring its effectiveness. Indeed, our tests comparing conditioned and unconditioned resins with the same effluent gave similar results. This suggests that resin conditioning does not play a significant role in improving its practical exchange capacity.

Increasing the molybdenum concentration in the final solution can only be done at the expense of overall yield. The need to increase this concentration can only be determined by evaluating the potential outlets for this type of solution.

Moreover, since molybdenum is present at a very high concentration in the initial effluent compared with the other metals, no competition was observed during the adsorption stage, and no pollution of the final solution after elution was detected. Nevertheless, other elements could be present, and as before, we would need to know the requirements of the outlets.

Crucial factors for the implementation of metal recovery system

- Identification of the most suitable resin for the metal to be recovered, allowing both effective adsorption from the aqueous effluent and effective elution to produce a recoverable solution.
- Identification of economic optimization opportunities (resin cost, reagent consumption, lifetime...)

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2.9. Concept study for nutrient and/or high-value product recovery in Kalundborg (DK)

The Kalundborg Industrial Symbiosis Association exists since 1972 and interlinks nineteen private and public companies. The local industrial sector includes petrochemical, light building construction material, food, pharma, biotech, energy and bioenergy as well as waste processing. Different circular economy approaches for water, energy and materials are already implemented, e.g. the reuse of cooling water for steam production, the reuse of gypsum from exhaust gas cleaning to produce plasterboards, integrated heat management and the transfer between the industries and the district heating network as well as heat recovery from process water for district heating. Even though the Kalundborg Industrial Symbiosis already recovers and reuses certain materials, water and energy, there are still options to intensify and extend the circular economy related strategies. One aspect is the treatment of wastewaters which is done by two companies: Novozymes and Kalundborg Utility.

2.9.1. Case study and ULTIMATE concept

Case study description

ULTIMATE project focuses on the optimisation of two WWTPs aiming at developing and implementing a joint control system for both plants, the recovery of the WWTP effluent as fit-for-purpose water (Naves 2024) and to explore the potential for the recovery of valuable compounds from the industrial wastewater as well as on identifying options to reuse thermal energy recovered from wastewater (Kleyböcker 2024). Therefore, the symbiotic relationship between Novozymes and Kalundborg utility is extended in the frame of ULTIMATE to create a win-win situation for both.

Site description

The industrial WWTP (iWWTP) pre-treats the wastewater resulting from enzyme, insulin and pharmaceutical protein production processes. The wastewater contains 700-800 mg SS/L, 5’000-6’000 mg COD/L, about 400 mg TN/L, 60 mg TP/L and approximately 200-250 mg S/L.

After a primary clarifier (removing mainly solids and particular phosphorus species) and a pre-acidification tank, the wastewater enters anaerobic internal circulation (IC) tanks (Figure 97). Each IC is realized as expanded granular sludge bed reactor (EGSB), a variation of the up-flow anaerobic sludge blanket (UASB) digestion. Here, soluble organic carbon compounds are biodegraded to biogas with a monthly energy production rate of around 22 GWh. The high Sulphur content in the wastewater results in H_2S formation during the anaerobic treatment decreasing the biogas yield. The H_2S in the biogas is removed via a THIOPAQ system removing the H_2S and CO_2 from the biogas by alkaline scrubbing with caustic soda.

The effluent from the IC tanks undergoes an activated sludge treatment for carbon, nitrogen and phosphate removal. After anaerobic treatment the wastewater contains about 600 mg SS/L, 1’600 mg COD/L, 400 mg TN/L, 40 mg TP/L and 100 mg S/L.

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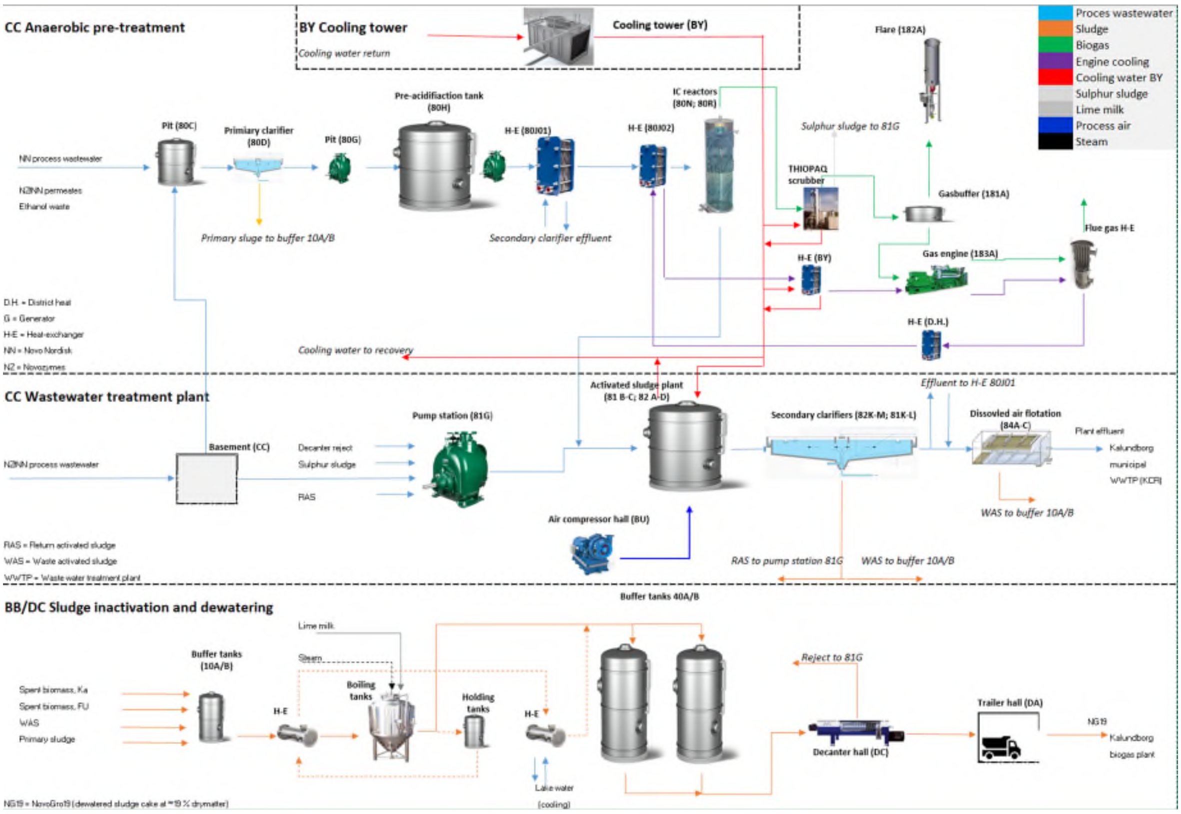

Figure 97: Scheme of the industrial WWTP

The Sulphur sludge from the TIOPAQ treated with the wastewater in the activated sludge treatment. The phosphate precipitates due to the addition of poly aluminium chloride (PAC) and is removed in the secondary clarifiers. If the phosphate concentration is still too high, iron chloride is added to the secondary clarifier effluent in the subsequent dissolved air flotation (DAF) plant. After the aerobic treatment, the wastewater contains around 50 mg SS/L, 150 mg COD/L, 15 mg TN/L and 3 mg TP/L and again about 200-250 mg S/L.

For the inactivation of genetically modified organisms in the sludge, quicklime is used prior to dewatering. Thus, depending on the dosage rate, the concentration of calcium can be so high, that calcium phosphate compounds might precipitate contributing to the phosphorus removal.

Although the influent of the industrial WWTP contain valuable nutrients such as sulphur, phosphorus and nitrogen, but also other compounds such as proteins, they are not worth to be recovered, due to a high degree of dilution. Hence, membrane schemes for water recovery, to reduce freshwater consumption in the enzyme production process had been implemented, corresponding concentrates have severely higher concentrations than the diluted influent of the industrial WWTP. In Ultimate, a screening for suitable compounds is therefore conducted to conceptualize a material recovery scenario.

Description of selected Technologies for nutrient and material recovery

- **Carbon and carbon compounds**

Non-selective Recovery of carbon and carbon compounds is often associated with separation process of solids (as sludge), which gives a mixture of potential valuable and invaluable compounds. Solubilized COD can be recovered into methane for energy production under anaerobic conditions. Selective recovery of carbon compounds ranging from mechanical options (e.g. cellulose recovery) (Remy and Conzelmann 2019), towards biological options (e.g. PHA-rich materials, fertilising products as bio composites or bio stimulants or other higher-grade carbon materials (Remy and Conzelmann 2019)). Such materials may replace fossil-based carbon in refineries in the future circular economy. Process to produce these secondary raw materials are under investigation by researchers. However, the implementation of such technologies is often lacking, due to the cheap availability of fossil-based carbons and the dilution and impurity of secondary carbon resources (e.g. wastewater). Regarding proteins, their saturation can be reduced due to the increase of the salinity of solutions (so called “ammonium sulphate precipitation”) which can be realised with various but not all soluble salts (Hyde, Zultanski et al. 2017). This is practice in industry, however not transferred so far to diluted wastewater streams.

- **Nitrogen**

Nitrogen recovery in form of inorganic nitrogen can be realised via ammonia stripping and scrubbing (air stripping, steam stripping or membrane stripping). These technologies are implemented in ammonium rich, particle poor streams e.g. after anaerobic treatment often in the reject water from the centrifuge. The technology requires for an economic operation an ammonium concentration of at least 1’000 mg NH_4-N/L, a pH value of at least pH 9 and a temperature of at least 50 °C (Wu and Vaneeckhaute 2021). Corresponding product is often ammonium sulphate, due to ammonia gas scrubbing with sulfuric acid.

- **Phosphate**

Phosphorus recovery in form of phosphate recovery can be realised via precipitation and harvesting technologies. Most prominent example is struvite (ammonium magnesium phosphate hexahydrate). Mostly magnesium is the limiting parameter and is dosed via magnesium chloride until phosphate is the limiting parameter. Ammonium is available in excess. The magnesium dosage is realised via a dosing section to avoid supersaturation. In a steering reactor struvite micro crystal are coagulating and macro crystals deposit in a settler. The technology requires for an economic operation a phosphate concentration of at least 100 mg PO_4-P/L and a pH value of 7-8 depending on the ammonium concentration (Stemann, Ewert et al. 2014). In absence of ammonium, with a high concentration of potassium and higher pH values struvite-K (potassium magnesium phosphate hexahydrate) forms. Also, the precipitation of calcium phosphates is possible, such as brushite (calcium hydrogen phosphate dihydrate) or hydroxyapatite.

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- **Other nutrients**

Potentials regarding potassium recovery are limited on K-struvite as described in the chapter on phosphorus. Magnesium and calcium can be recovered with phosphates or in form of calcite, magnesite or dolomite together with carbonate. All these cations are generally not in the spotlight, hence besides potassium, their market value is limited and they do not harm rivers or the wastewater treatment process as such. Valuable products in terms of calcium or magnesium are hydroxides, which can only be precipitated in very concentrated and very alkaline brines.

Sulphur on the other hand is a secondary nutrient which may limit the capacity of an anaerobic treatment scheme due to its different oxidation stage SO_4^{2-}/S^{2-}. Although within aerobic and anaerobic wastewater treatment the majority of sulphur is present in the form of sulphate (SO_4^{2-}), during anaerobic digestion partly hydrogen sulphide (HS^{-}) which lead to H_2S formation in the absence of iron. The toxic and corrosive sulphide species HS^-/H_2S needs to be removed before biogas utilisation. One option is the TIOPAQ system, whereby besides H_2S also CO_2 is removed under alkaline conditions and a Sulphur rich sludge with reduced sulphur is produced. Precipitation of sulphate with calcium in form of gypsum on the other hand, is under normal conditions not of interest, hence sulphate and calcium concentrations high above 1’500 mg SO_4^{2-}/L are required, due to the sever high solubility of gypsum compared to other bivalent salts. Other sulphate salts have an even higher solubility.

Evaluation of recovery technologies on the background of present and future wastewater streams in the iWWTP

Permeates and wastewater from various industry streams are currently mixed and treated together, first anaerobically and then aerobically. The sludge from the aerobic treatment is stabilized with quicklime, dewatered and then treated anaerobically again in a nearby biogas plant, the reject water from the dewatering is treated in the aerobic plant.

Carbon utilization in forms of biogas is realised in the anaerobic treatment. Other carbon recovery methods are not implemented, due to the dilution of different wastewater and various carbon forms present in this wastewater. The total COD concentrations are currently ranging from 1’500-9’000 mg COD/L within the water streams (excluding secondary effluent) and up to 15’000 mg COD/L within sludge treatment (excluding dewatered sludge). The soluble COD concentrations ranging between 1’000 and 35’000 mg COD/L.

Although nitrogen is more concentrated in the iWWTP compared to municipal WWTP, the NH_4-N concentrations are too low for stripping or similar processes. After anaerobic treatment the NH_4-N concentration is up to 250 mg NH_4-N/L (about 60% of TN) and thereby too low for ammonia stripping. The concentration within the reject water is about 100 mg NH_4-N/L (about 15% of TN). The TN concentration in the wastewater path is around 400 mg TN/L before N removal via denitrification and up to 1’400 mg TN/L within sludge treatment.

Similar to nitrogen, the phosphate concentrations within the iWWTP are also too low for recovery processes within the wastewater treatment path of the iWWTP. Within the sludge treatment line of the iWWTP phosphorus is still bound to the dry matter and

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furthermore an extensive amount of quicklime is dosed prior dewatering, reducing the concentration of free ortho-phosphate to a minimum.

In terms of sulphur approximately 20 % of the incoming sulphur load of the anaerobic treatment is recovered via the THIOPAQ in form of S-rich sludge and then remixed into aerobic treatment. The total S-concentrations ranging up to 400 mg S/L.

Overall, it seems that the concentrations for further material recovery are too low within the iWWTP. The absence of a sludge digester and high quicklime dosage before centrifugation negate a potential NH_4-N or PO_4-P recovery in the reject water. Furthermore, sulphur in form of H_2S has been identified as a major challenge running the IC reactors in anaerobic treatment. Dosage of iron(II)chloride to capture S^{2-} is refused hence it will have adverse effects on the granules present in the EGSB process.

Meanwhile for some of the treatment processes of the industry a water reuse scheme had been implemented. This treatment scheme contains of a hybrid membrane scheme using nanofiltration (NF) and reverse osmosis (RO). Thereby the freshwater use for these processes had been reduced. The residual concentrate has higher contents of carbon, nutrients and salts. A special feature of this system is that the RO brine is re-introduced to the NF feed to dilute protein concentration and consequential fouling on the NF and reuse the pressure which is remaining with the brine. The salt concentration in the RO feed and brine is thereby concentrated. The retentate of NF is the only concentrate from the entire process containing salts and proteins. Hence the industrial treatment process is for food and feed purposes also the concentrate has food/feed grade and is low in any contaminants. Currently, this concentrate is directly mixed with other wastewater of the industry and then treated in the iWWTP. A separate treatment including material recovery of this clean and highly concentrated water stream seems promising and is therefore given special space within this concept study.

Characterization of novel concentrates from hybrid membrane treatment

The concentrate is depending on the process about 50 % from food-grade and 50 % from technical grade processing. The water consumption of this process line is reduced by about 80 %. The feed water of the combined NF-RO scheme is about 1’250 m^3/d and about 15 % of the overall wastewater influent of the iWWTP. The concentrate is about 250 m^3/d, respectively about 10 m^3/h. Table 31 shows various parameters measured in the concentrate including no. of samples, mean, median, min, max and variance.

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Table 31: No. of samples, mean, median, min, max and variance of various parameters in the concentrate of the NF-RO scheme in CS9 measured by the iWWTP

Substance	No. of samples	Mean [mg/L]	Median [mg/L]	Min [mg/L]	Max [mg/L]	Variance [%]
COD	24	20’964	20’573	5’415	48’200	51
TN	24	1’840	1’689	576	3’560	43
NH_4-N	24	368	326	123	834	43
TP	12	135	90	28	328	79
PO_4-P	22	206	93	4	692	115
SO_4^{2-}	12	3’794	3’855	760	8’350	61
Ca^{2+}	12	5’920	5’417	2’247	13’838	56
K^+	12	1’006	772	345	1’967	64
Mg^{2+}	12	181	163	87	432	52
Na^+	12	802	689	197	1’574	49
Al^{3+}	12	7.7	4.6	0.3	22.3	109
$Fe^{2+/3+}$	12	4.9	5.0	0.2	12.1	84
Zn^{2+}	12	1.1	1.0	0.3	2.2	68
Ceramide	12	14.2	1.2	0.7	92.0	190
oxFFA	12	11.5	2.4	0.4	57.8	156
Antifoam	12	113.4	68.2	3.0	545.3	133
oxAntifoam	12	2.6	1.6	0.1	9.4	96
tot. Proteins (calculated)	12	11’190	10’631	4’436	20’492	47
pH [-]	9	5.29	4,52	4,39	7,88	28
EC [mS/cm]	9	31.5	29.2	25.4	47.3	21

As shown in Table 31 the variance of most compounds is at least about 50 % or even higher. This is a direct result of the variation in the process line. The proteins are calculated based on TN content. Table 32 shows the coefficient of determination for the different parameters and thereby indicates correlations. Due to the variation in the process line several parameters are not correlating with each other. The total protein content correlates with the COD concentration. Also, a correlation of total phosphorus and phosphate is given, whereby a correlation between total nitrogen and ammonium is non-existent. This probably is a result of the high organic nitrogen content in proteins and comparably severely lower ammonium concentrations. Sulphate shows good correlations with ammonium and potassium, which might be an effect of the given process of the batch. All lipids either show very low concentrations, or high concentrations and correlate quite well with each other.

For most parameters, the data quality is very limited (12 measurements), also focussing on brines of several batches. Unfortunately, pH and EC had been measured within a different campaign, compared to the ions. pH has influence on the formation potential of carbonate and phosphate salts and it is rather unimportant in terms of sulphate salts. To improve data quality, it is recommended to measure more often and targeted on the process upstream to the UF-RO system. Also there should be dedicated measurement campaigns undertaken on concentrates for the different batch processes in the factory.

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Table 32: Coefficient of determination for the different parameters.

	COD	TN	NH_4-N	TP	PO_4-P	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}	Na^+	Al^{3+}	$Fe^{2+/3+}$	Zn^{2+}	Ceramide	oxFFA	Antifoam	oxAntifoam	pH
COD																		
TN	0,58																	
NH_4-N	0,08	0,00																
TP	0,01	0,01	0,00															
PO_4-P	0,27	0,11	0,03	0,78														
SO_4^{2-}	0,26	0,41	0,70	0,02	0,03													
Ca^{2+}	0,47	0,38	0,04	0,01	0,02	0,01												
K^+	0,12	0,20	0,61	0,00	0,01	0,70	0,03											
Mg^{2+}	0,89	0,67	0,12	0,01	0,04	0,10	0,54	0,01										
Na^+	0,40	0,44	0,01	0,04	0,05	0,00	0,47	0,00	0,39									
Al^{3+}	0,03	0,02	0,19	0,13	0,11	0,27	0,13	0,25	0,00	0,10								
$Fe^{2+/3+}$	0,47	0,35	0,31	0,24	0,34	0,34	0,05	0,17	0,45	0,01	0,52							
Zn^{2+}	0,03	0,04	0,32	0,13	0,23	0,38	0,20	0,26	0,00	0,14	0,89	0,59						
Ceramide	0,08	0,16	0,04	0,06	0,03	0,00	0,08	0,01	0,08	0,40	0,27	0,02	0,12					
oxFFA	0,13	0,21	0,03	0,05	0,03	0,01	0,12	0,02	0,12	0,48	0,21	0,01	0,11	0,96				
Antifoam	0,10	0,21	0,02	0,06	0,03	0,00	0,13	0,00	0,10	0,49	0,27	0,02	0,12	0,96	0,93			
oxAntifoam	0,02	0,11	0,00	0,11	0,07	0,02	0,09	0,04	0,04	0,36	0,26	0,04	0,11	0,76	0,69	0,85		
tot. Proteins	0,84	1,00	0,21	0,02	0,01	0,37	0,41	0,17	0,68	0,46	0,01	0,33	0,03	0,16	0,21	0,21	0,11	
pH	0,16	0,00	0,02		0,48													
EC	0,59	0,83	0,06		0,10													0,02

2.9.2. Results of new approaches

Evaluating potential salt scaling in the concentrate and derivation of recovery strategies and potentials

Based on the twelve samples with ion measurements, potential salt scaling in the concentrate were investigated. Therefore, the software Visual MINTEQ 3.1 (Gustafsson 2019) was used to investigate whether solubility equilibria for different salts were reached. For the investigated concentrates (see concentrations in Table 33), this had been the case for the salts: hydroxyapatite, gypsum and syngenite (see Table 33)

Table 33: Possible solids in Visual MINTEQ 3.1 and their properties

Trivial name	Formula	log K	ΔH
Hydroxyapatite	$Ca_5(PO_4)_3OH$	-44.333	0
Gypsum	$CaSO_4x2H_2O$	-4.61	1
Syngenite	$K_2Ca(SO_4)_2xH_2O$	-10.97	0

- **Precipitation of phosphates**

The precipitation of phosphates (with calcium) in various forms is pH-dependent: phosphate solubility decreases with increasing pH. As shown in Figure 98, the total phosphate concentration in the concentrates varies significantly depending on the fermentation process in the industry. Depending on the corresponding calcium content

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and the pH-value the theoretical phosphate solubility is in general below 50 mg PO_4-P/L and in the case of low total phosphate even below 1 mg PO_4-P/L due to excess of available calcium.

Targeted precipitation of phosphates is especially of interest for industry processes resulting in concentrates with a phosphate content of > 200 mg PO_4-P/L (samples 1, 8 and 11 in Figure 98). Thereby a theoretical recovery rate of > 80 % related to phosphate is expected.

The calculated phosphate content of these theoretical precipitates is ranging in dependency from gypsum precipitation between 18 and 31 % P_2O_5 and could be thereby interesting as substitute for phosphate rock or as slow release blend in fertiliser industry.

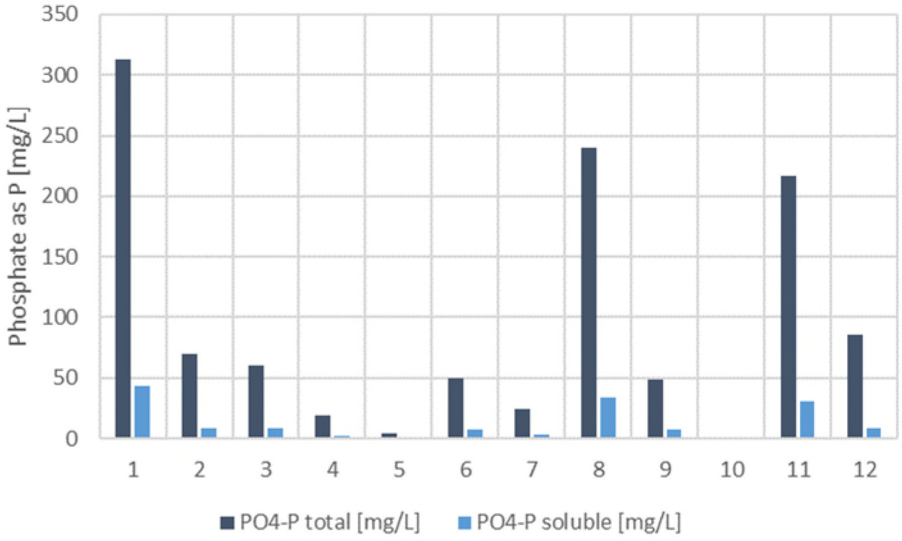

Figure 98: total and soluble phosphate in concentrate according to equilibrium model

- **Precipitation of sulphates**

The precipitation of sulphates (with calcium and eventually potassium) as gypsum and syngenite is rather pH-independent. Also, the sulphate concentration varies significantly depending on the fermentation process within the industry. Depending on the sulphate content, theoretical precipitation and recovery rates can be up to 80 % or slightly higher (sample 3, 4, 5 and 11 in Figure 99). This also corresponds with the total calcium content.

In case of lower sulphate concentrations (samples 8, 10 and 12), the potential recovery rate of sulphate in significantly lower (10-40 %), hence the concentration is near the solubility equilibrium of gypsum.

The sulphate content of the calculated precipitated salts is for most concentrate samples > 50 % SO_3 except for the concentrates with significantly lower sulphate content.

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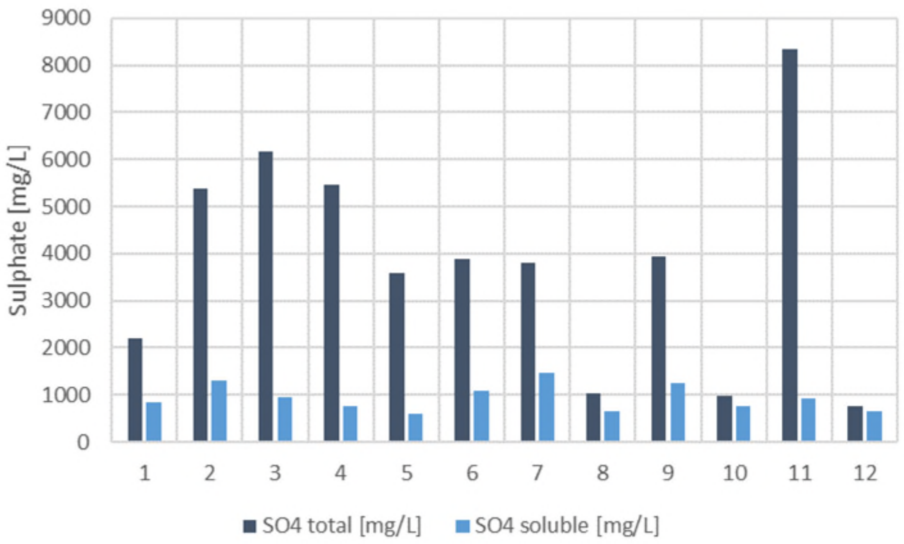

Figure 99: total and soluble sulphate in concentrate according to equilibrium model

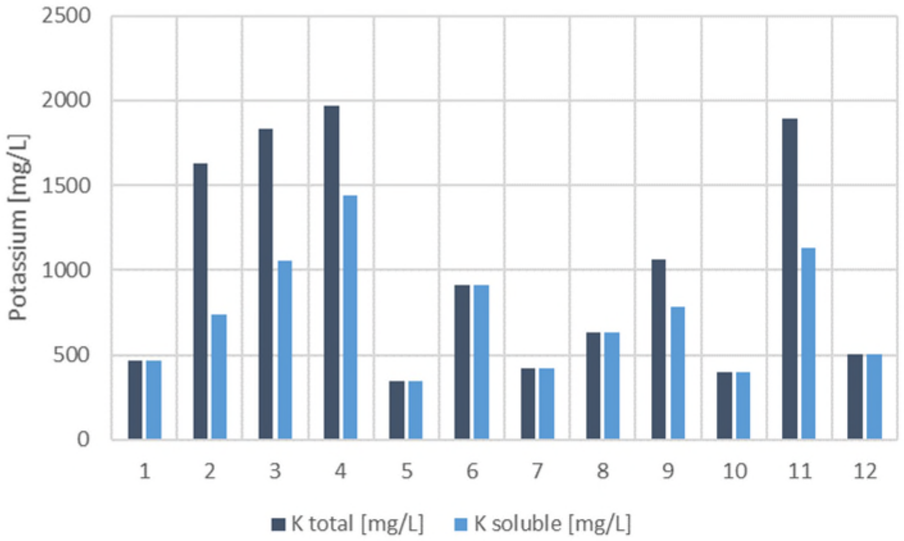

Figure 100: total and soluble potassium in concentrate according to equilibrium model

The precipitation of the double salt syngenite (potassium calcium sulphate monohydrate) directly correlates with potassium content of the concentrate, corresponding average calcium contents and high sulphate contents. In that case the calculated precipitation efficiency is between 26 and 55 % for potassium.

The potassium content of resulting salts is between 16 and 33 % K_2O (Figure 100) and therefore eventually interesting as blend in fertiliser production.

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- **Effects on and role of calcium content**

Calcium serves for all the salts as main cationic coagulant. Hence, calcium is for each sample compared to the anions in excess (m(Ca):m(P) > 14, median(m(Ca):m(P)) = 57 and m(Ca):m(S) > 1,3, median(m(Ca):m(S)) = 3), so that it is not the limiting parameter and correspondingly the calculated precipitation ratios for calcium are lower than for the anions (below 50 % or even negligible around 1 %).

Meanwhile the calcium content of the calculated precipitates is between 30 and 55 % CaO (rather low for syngenite precipitation, hence potassium competes with calcium on sulphate and rather high for high phosphate contents, due to the high Calcium content in apatite).

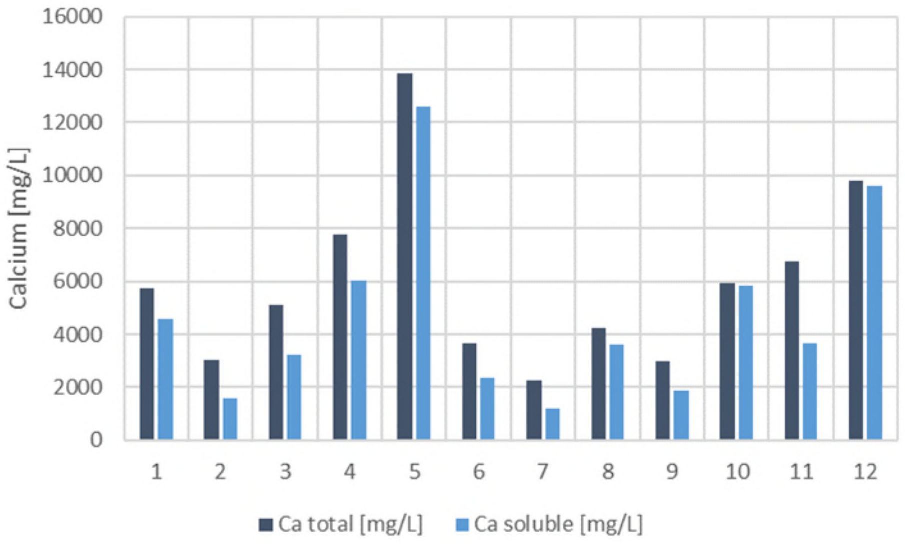

Figure 101: total and soluble calcium in concentrate according to equilibrium model

Based on this modelling results, the precipitation of corresponding salts within the concentrate is a first step to potentially recover resources with minimal effort. Therefore, the concentrate should be stirred and afterwards a solid material might be removed from the concentrate via filtration.

The scheme is shown in Figure 102.

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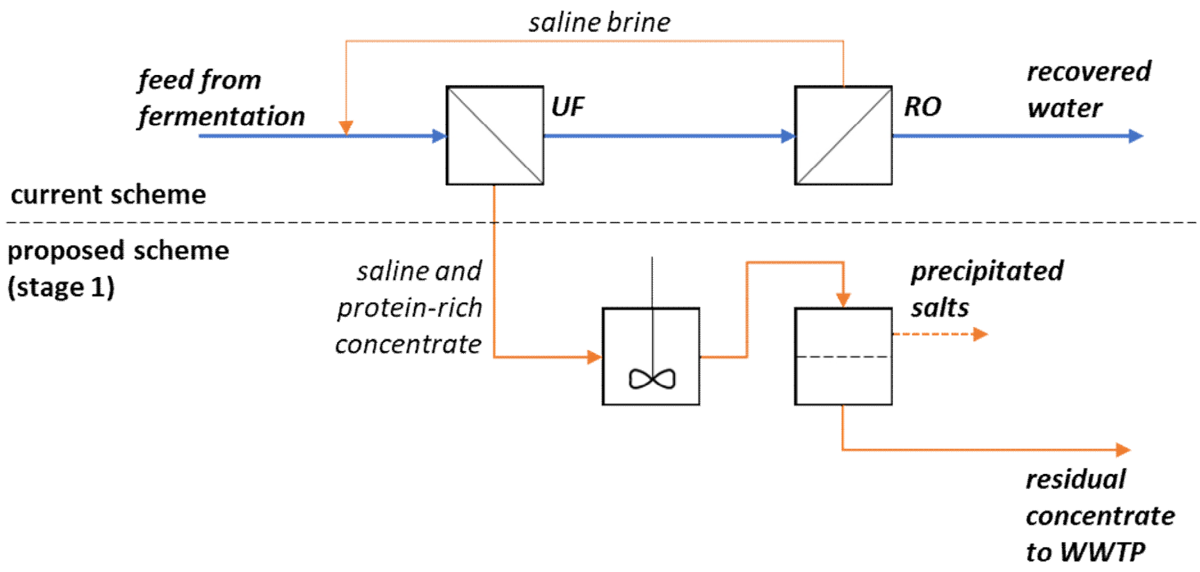

Figure 102: Current membrane scheme and proposed scheme to precipitate salts

Potential strategies for protein recovery

The major goal is to separate proteins from water in a solid form without denaturation of proteins. Proteins denaturise with drastic pH shift or under heat, so that such treatment steps are not recommended. Therefore, to other methods ‘salting precipitation’ and ‘alcohol precipitation’ are discussed. As several molecules, proteins have positively and negatively charged dipoles. That is why water dipoles are forming around proteins resulting in a hydration shell. This shell is crucial for protein solubility in aqueous solutions. However, if the hydration shell is displaced from the proteins they act as hydrophobic substances and are exposed to each other and bind. This can be either achieved with salts or organic solvents.

- **Salting precipitation**

If salt ions are added to a solution containing proteins, ions compete with the protein dipoles on water dipoles. Hence the binding ion-dipole is stronger than the binding dipole-dipole the ions of the salts are hydrated, leading to a restriction of available water molecules for protein hydration.

So, the interaction between proteins is stronger, causing protein aggregation and precipitation – so called “salting out” (Bioquochem 2024). However, the effect of different salts on protein solubility is different (Hofmeister series). The anions are usually ordered (Hyde, Zultanski et al. 2017):

$$SO_4^{2-} > HPO_4^{2-} > CH_3COO^- > Cl^- > NO_3^- > ClO_4^-$$

The cations are usually ordered (Hyde, Zultanski et al. 2017):

$$NH_4^+ > K^+ > Na^+ > Mg^{2+} > Ca^{2+}$$

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Consequently, one of the preferred salts for salting out is diammonium sulphate – resulting in terms as “diammonium sulphate precipitation”.

- **Alcohol precipitation**

Organic solvents as ethanol, methanol or acetone can also be used for protein aggregation and precipitation. Thereby the added alcohol reduces the hydration of the protein and remove the water hydration shell, favouring protein binding and precipitation.(Bioquochem 2024)

- **Consideration of present boundary conditions**

Industrial-grade organic solvents are expected to be expensive. An option could be to use a potential waste stream from another industry rich in organic solvents to precipitate proteins via alcohol precipitation.

The availability of such a waste stream in the industrial area is unknown as its particular grade. Therefore, a detailed assessment needs to be undertaken regarding the principle availability and suitability of such a stream as well as its impact on quality and grade of the residual product “precipitated proteins”.

A potential integration is shown in Figure 103.

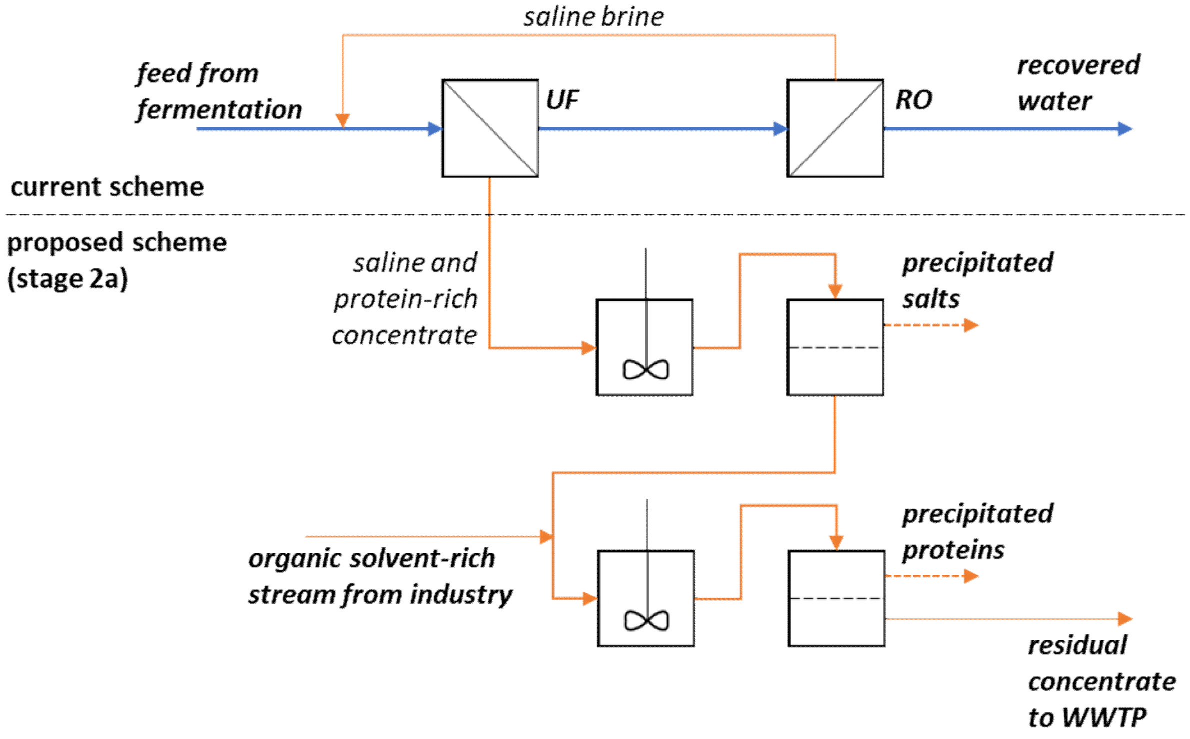

Figure 103: Current membrane scheme and proposed scheme to precipitate salts and proteins via alcohol precipitation

The other option regarding salting precipitation can be realised via addition of soluble monovalent salts, which might also be an expensive option. A problem regarding the Hofmeister-series is that the most suitable anions as Sulphate or Phosphate is

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unsuitable due to the excessive calcium concentration in the brine resulting in direct precipitation of these anions.

A possibility could be to concentrate the remaining salts (e.g. sodium, chlorine) in the concentrate via an additional reverse osmosis step and recycle this brine to the feed to increase the salt concentration. Proteins and the insoluble salts could be either precipitated in one step (see Figure 104) or separately depending on which point this brine is mixed with the concentrate.

However, this requires a concentration of salts in the RO by approximately factor 20, resulting in a very high specific energy consumption and increasing the risk of scaling on this membrane.

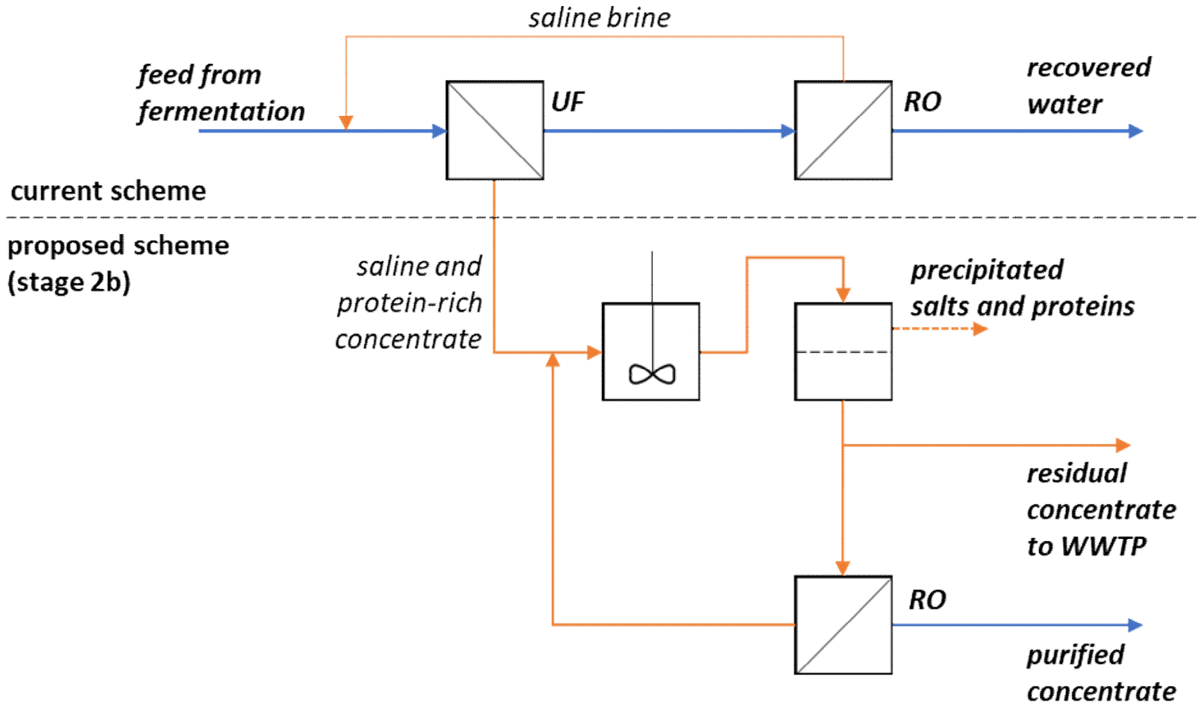

Figure 104: Current membrane scheme and proposed scheme to precipitate salts and proteins via salting precipitation

Technical requirements for its implementation and operating conditions

Before any implementation, the considerations and theoretical calculations undertaken in the previous chapters should be tested at lab scale. This includes simple stirring tests (20 minutes) with and without pH adjustment for salt recovery. Furthermore, stirring tests with the addition of saline streams or organic solvents for protein precipitation are recommended.

In principle the following tests are recommended:

- **Testing gypsum precipitation:** Testing gypsum precipitation for concentrates with high sulphate content via stirring for 20-30 minutes without pH adjustment and filtration of potentially formed solids.

  Calcium and sulphate should be measured within the feed (concentrate from NF) and after filtration. The received solid should also be analysed.

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- **Testing phosphate precipitation:** Testing Apatite or Struvite precipitation for concentrate with high phosphate content via stirring for 20-30 minutes with pH adjustment.

  Titration of samples with NaOH, to identify buffers and derivation of appropriate strategy to increase the pH (e.g. via stripping of carbonate species in solution or dosage of NaOH or other alkaline streams from production or the iWWTP (e.g. sludge reject)).

  Phosphate and corresponding cations (ammonium, magnesium, calcium) should be measured within the feed (concentrate from NF) and after filtration. The received solid should also be analysed.

- **Testing strategies to recover proteins:** To precipitate and harvest proteins, the protein rich solution should be spiked with organic solvents as ethanol or methanol or with chloride salts (e.g. sodium chloride). Sulphate salts should be avoided; hence it is assumed that they will form gypsum due to the superior calcium content.

  In terms of salting precipitation an amount near saturation concentration is needed (e.g. about 300 g/L water). In terms of alcohol precipitation dosing should be tested gradually to test the effectiveness of different dosages. Based on the results and an analysis of available streams of salts and organic solvents, potential concepts can be developed (comparable to the flow schemes within this study) and should be further tested within lab trails, before piloting.

Testing parameters should be similar to the analyses of brines (e.g. DM, COD, TN, TP, ions as NH_4-N, PO_4-P, SO_4^{2-}, Ca^{2+}, K^+, Mg^{2+}, Na^+, Al^{3+}, $Fe^{2+/3+}$, tot. Protein content, pH and electric conductivity).

Titration with HCl/NaOH should be conducted towards pH 4/pH 10 to identify present buffer substances.

The number of measurements should be at least 10-20 for respective concentrates from similar process of the industry, to have a certain reproducibility. Based on such a data-set it can be analysed, whether the proposed strategies towards salt and protein recovery may be feasible or not.

Estimation of recovery rates and loads and comparison with KPI

It has been shown that the concentrations of various nutrients and corresponding salts within the streams of the iWWTP are too low for recovery these compounds. However, a hybrid membrane treatment for one of the production processes of the industry results in a concentrate with potential for nutrient, salt and protein recovery. The influent loads of the iWWTP and the concentrate and the respective expected calculated average recovery rates over all samples are shown in Table 34.

Table 34: Influent loads within the iWWTP (industrial waste water treatment plant), the conc. (concentrate under study), ratio of concentrate in total load, potential recovery rate in concentrate and related to iWWTP influent

Substance	Unit	Potential iWWTP	Potential conc.	Ratio conc./ iWWTP	Recovery rate conc.	Recovery rate iWWTP
Volume	m^3/year	2.975.115	91.250	3,1 %	0 %	0 %
COD	t/year	17.203	2.412	14,0 %	0 %	0 %
TN	t/year	1.196	190	15,9 %	0 %	0 %
TP	t/year	216	17	7,9 %	87,0 %	6,9 %
S	t/year	714	115	16,1 %	63,0 %	10,1 %
Ca	t/year	998	540	54,1 %	26,5 %	14,3 %
K	t/year	970	92	9,5 %	15,9 %	1,5 %
Mg	t/year	73	17	23,2 %	0 %	0 %
Na	t/year	2.721	73	2,7 %	0 %	0 %
tot. Proteins (calculated)	t/year	n/a	1.021	n/a	n/a	n/a

Although the recovery rates for phosphate (and sulphate) related to the respective stream are comparably high, the overall recovery rate is comparably low. For Phosphorus it is about 6.9 % (≈ 15 t P/year) and for Sulphur it is 10.1 % (≈ 70 t S/year). According to the industry it is the aim to replicate similar a hybrid membrane scheme at several production lines to replicate the current flow rates by factor 3. Thereby it is expected that the concentration is fundamentally different per industry process, so it cannot be extrapolated from the recovery rates shown in Table 34.

Particular effects on the iWWTP operation cannot be estimated. A potential reduction of the influent of the Sulphur load of roughly 10 % may will result in an advantage for the IC operation. This may result in lower H_2S loads within the biogas and less pressure on the THIOPAQ system.

If such a membrane hybrid scheme is implemented for several production lines, different material recovery concepts should be developed for the concentrates. The receiving iWWTP will treat less and an in particular substances more concentrated wastewater in the future. This will result in changing demands towards industrial wastewater treatment. Based on the different expected brines, it must be evaluated, whether a material recovery plant is feasible on the entire stream, on selected concentrates or on singular concentrates.

2.9.3. Conclusion

This chapter summarizes the main findings of the analysis of the iWWTP and concentrates from hybrid-membrane scheme in terms of derivation of a concept for material recovery:

- The concentration in the industrial wastewater is currently too low for nutrients, salts, proteins or material recovery in general besides a valuable sludge stream for agricultural valorisation

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- Reduction of the overall water consumption via hybrid-membrane schemes in the industrial production lines generate water for reuse within industry. Thereby this scheme also results in concentrates with high nutrient, ion and protein content, which serve as ideal streams for material recovery.
- The interpretation of several measurements revealed high varying concentrates depending on the batch process in the industry. Therefore, also the recovery strategy and recoverable substances must be adapted to the batch process in feed.
- Overall a high recovery potential in the particular for phosphate and sulphate was simulated as apatite, gypsum or syngenite
- Protein recovery seems to be more complex. Different strategies as salting or alcohol precipitation have been identified. Also, further concentration of the protein-rich concentrate might be useful, however membrane fouling might be a crucial factor.
- To test the identified strategies, it is recommended to perform various lab tests with the concentrates. Tests should include a pH adjustment for precipitation of apatite and without pH adjustment for precipitation of gypsum. For protein precipitation, the addition of chloride salts and short-chain alcohols might be interested to test in the lab.
- Based on the results of these lab-test, further investigation in form of alternative approaches or piloting is necessary.
- The estimated overall recovery rate for P related to the iWWTP is about 7 %, however up to 90 % related to the concentrate stream. For S the related recovery rate to the iWWTP is about 10 % and roughly 70 % related to the concentrate stream. The reduction of S could be beneficial for the IC reactors and their methane production in the iWWTP.
- Further implementation of such hybrid membrane systems reduces the overall water consumption and wastewater production of the industry. Thereby these schemes generate additional concentrates which are particular interesting for material recovery as the latter under study.
- In overall, this will result also in less wastewater for the iWWTP, which is higher concentrated (e.g. higher salinity, higher overall COD or TN). This will result in new challenges in the overall industrial wastewater treatment plant.

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3. Summary and conclusion of material recovery concepts

In five of nine ULTIMATE case studies, material recovery technologies were conceptualised, developed and demonstrated. Innovative technologies were tested to recover fertilizers at CS2, CS5, CS7 treating different industrial wastewater. On the other hand, technologies for the recovery of added values compounds from industrial wastewater were tested at CS4, CS6 and CS8. In addition, conceptual studies for recovery of both nutrients and high-value products from industrial wastewater were tested at CS5, CS8, CS9. Furthermore, at CS3, it was tested the possibility to use industrial by-products for wastewater treatment to allow industrial reuse and reinforce an already existing public-private partnership. In this case study, innovative fluorescence sensors were also tested to monitor the removal of organic micropollutants during quaternary treatments of wastewater to comply with recent EU regulations on urban wastewater treatment and reuse.

Recovery of nutrients

Recovery of nutrients from greenhouse wastewater was tested at CS2. In particularly, monovalent selective membranes were utilized to remove detrimental ions (Na+ and Cl-) from wastewater and reuse it for crop irrigation. The technology can provide the benefits to increase the recirculation of wastewater in the greenhouse cultivation system with the advantage to use the same nutrients already dissolved in water for fertigation. ULTIMATE tests showed promising results for the removal of Na^+ and Cl^- ions. However, energy costs may represent a bottleneck for the large-scale implementation of the technology. In addition, it was concluded that still research is needed to increase the selectivity of membranes, increase the performance of the process and evaluate nutrients uptake by plants from recirculated wastewater.

CS5 and CS7 investigated the recovery of struvite from supernatant of sludge dewatering and distillery wastewater, respectively. At CS7 was also tested the recovery of ammonium sulphate solution by stripping and precipitation processes. Even though those technologies have a good maturity for market uptake, constrains for large-scale implementation are related to the economical convenience to implement the process. In this case, industrial symbiosis systems may be helpful to reduce treatment and commercialization costs and satisfy end of waste criteria. Finally, through a concept study at CS5, it was concluded that the recovery of fertilizers from hydrochar of brewer’s spent grain and sewage sludge is possible, but still research is needed to evaluate the convenience of the process and to develop a technology implementable at full-scale level.

Recovery of added value compounds

CS4 and CS6 tested at demonstrative level, the mobile VesperX technology, which was developed by the Greener than Green (GtG) Technologies to recover polyphenol compounds from fruit processing wastewater and from olive mill wastewater, respectively. The process required adsorption and extraction steps and was able to show promising recovery rate of polyphenols from both the wastewaters. However, future technological advancements in the production of adsorbent materials and

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extraction methods will be strategical to reduce treatment costs for the large-scale implementation of the technology and to make the recovery of polyphenols competitive for the market.

At the Chemical Platform Roussillon in France (CS8), it was tested a demonstrative plant for the recovery of sulfur from flue gas by different treatment steps involving condensation, dust cleaning and scrubbing. Performed tests enabled the production of sodium bisulphite solution and showed room for improving the process and the recovery of sulphur by optimization of operational parameters (e.g., temperature and pH of the process). In addition, treatment of salts before recovery can be improved to obtain a product of higher quality. Future fundings and commercial agreements will provide benefits for possible scale-up of the system and satisfaction of end of waste criteria.

Concept studies at CS8 and CS9 showed the possibility to recover molybdenum from flue gas washing waters and phosphate and sulphate salts during industrial wastewater treatments. However, experimental tests are required to confirm those theoretical possibilities.

Recovery of industrial by-products and test of innovative fluorescence sensors

CS3 tested the possibility to use industrial by-products for wastewater treatment to reinforce an already existing PPP between water utilities and industrial partners, which allow the production of 3,8 Mm^3/y of reclaimed water to be reused for the industry, mainly for the cooling towers, but also for agricultural irrigation. The tested by-products included bentonite, partially cooked limestone, soda out of specification, hydrochar from sewage sludge, aluminium sludge. However, successful pilot tests were obtained only when using soda out of specification for clariflocculation treatment that allow the concurrent removal of COD and hardness from wastewater. The effectiveness of treatment resulted highly dependent on the pH of the process. Other by-products did not show suitable properties to be used for wastewater treatment. Furthermore, adsorbent material can be produced from hydrochar of sewage sludge, but activation procedures have not yet the technological maturity to produce material for large-scale implementations.

In CS3, fluorescence sensors were tested at pilot scale to monitor removal of organic micropollutants during quaternary wastewater treatments to comply with requirements of the new EU directive concerning urban wastewater treatments. Very good correlations were observed between removal of fluorescence signal and removal of six organic micropollutants during adsorption and UV/H_2O_2 treatments. Cleaning and correct operation of the sensors are the only requirement for the use of this innovative technology, which resulted to be promising for large-scale implementation.

Benefits and observed challenges for full-scale implementation of the material recovery technologies studied during ULTIMATE project are reassumed in Table 35. On the other side, in Table 36 are reported the TRL increase during ULTIMATE project, the tested treatment capacity (i.e., flowrate), the obtained performance in terms of % of recovered material (performance KPI) and feasibility of the proposed technology.

A bottleneck common to all the technologies for material recovery tested in ULTIMATE is the need of an economical convenience to implement the process, which is also a limitation for the satisfaction of legislative end of waste criteria. In this context,

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symbiosis network between different private and public partners is strategical to provide synergetic advantages between partners, which include reduction of costs for waste management, reduction of cost for implementation of the material recovery technology and satisfy legislative constrains for the end of waste procedure.

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Table 35 Benefits and challenges for the implementation of the investigated technologies for material recovery in ULTIMATE

CS	Technology	Benefits	Challenges for the scale-up and implementation of the technology
2	Monovalent selective electrodialysis	• Increase the reusability of greenhouse wastewater • allow the recovery of nutrients in water • reduce the amount of discharged wastewater	• Still research is needed to have the technology ready for the market • The final uptake of reclaimed nutrients needs testing • Cost of membranes and energy consumption can be bottleneck for economic feasibility
3	Clariflocculation using industrial by-products	• Replacement of commercial coagulant with consequent costs saving • Allow concurrent removal of organic matter and hardness	• Continuous control of pH is needed to optimize the dosage • Slight increase of produced sludge from the process
3	Adsorption by using hydrochar from sewage sludge	• Replacement of commercial product with consequent costs saving	• The available technology is not able to produce activated hydrochar from sewage sludge for full scale application
3	Fluorescence sensors to monitor Adsorption and AOP (i.e., UV/H_2O_2) quaternary treatments	• Monitoring of organic micropollutants as required by recent EU regulations • Monitoring of water quality and organic matter content • Optimization of quaternary wastewater treatment	• The technology needs standardization to be ready for the market
4	Hybrid adsorption/subcritical water extraction (VesperX)	• Recovery of antioxidant from food industry wastewater • Recovery of water for reuse	• Increase of treatment costs • End of waste criteria and legislative requirements need to be respected

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		• Improvement of water treatment processes • Possible revenue from phenols recovery	
5	Aquavite(R) – Struvite precipitation	• Recovery of fertilizers • Possible revenue from struvite recovery	• End of waste criteria and legislative requirements need to be respected • Cost of the technology may be not convenient
5	Hydrotermal carbonization of the brewer’s spent grain	• Fertilizers recovery	• Research is still needed to evaluate the feasibility of the process
6	Adsorption on resins and extraction	• Recovery of polyphenols • Possible revenue from polyphenols recovery • Improvement of wastewater treatment	• Increase of treatment costs • Research is needed to improve extraction method
7	Struvite precipitation and ammonia stripping	• Fertilizers recovery • Possible revenue from polyphenols recovery	• End of waste criteria and legislative requirements need to be respected
8	Condensation, dust cleaning and scrubbing	• sodium bisulphite recovery • Possible revenue from sodium bisulphite recovery	• End of waste criteria and legislative requirements need to be respected • Define a commercial agreement for recovery and selling/using the recovered product
8	Ion exchange resins (concept study)	• Molybdenum recovery	• Research is still needed to evaluate the feasibility of the process
9	Concentration by hybrid-membrane schemes and precipitation (concept study)	• Recovery of phosphate and sulphates salts	• Research is still needed to evaluate the feasibility of the process

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Table 36 Summary of material recovery technologies with TRL increase in ULTIMATE, treatment capacity, KPIs and their feasibility

CS	Technology	TRL	Material(s) recovered	Capacity	Performance (KPIs)	Feasibility and/or successful operation
2	Monovalent selective electrodialysis	4→6	Nutrients	Treated flowrate 1-2 cm/s	Nutrient recovery up to 30% (NO_3-), 33% (K^+), 70% (Ca^{2+}), 76% (Mg^{2+}), 84% (SO_4^{2-}), 93% (PO_4^{3-})	Successful system operation
3	Clariflocculation	5→7	Soda out of specification (industrial by-product)	Treated flowrate 0.25 m3/h	100% replacement of commercial coagulant	Successful pilot operation
3	Adsorption	4→6	Hydrochar from sewage sludge	Treated flowrate 3.5 m^3/h	The material activated at lab scale has very good adsorption capacity	Hydrochar activation procedures are not available for pilot scale application
3	Fluorescence sensors to monitor Adsorption and AOP (UV/H_2O_2) quaternary treatments	4→7	Treated wastewater, H_2O_2 from Solvay plant	Treated flowrate 3.5 m^3/h	Observed correlations with six organic micropollutants Promising performance in water quality monitoring	Successful pilot operation
4	Hybrid adsorption/subcritical water extraction (VesperX)	5→7	Value added Compounds (i.e., antioxidants)	Treated flowrate 10 m^3/d	75% recovery of total phenolic content in the food industry wastewater	Successful pilot operation
5	Aquavite(R).	-	Struvite	-	-	Concept study
5	Hydrothermal carbonization (HTC)	-	Hydrochar from brewer's spent grain and sewage sludge	-	-	Concept study

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6	Adsorption on resins and extraction	4→6	Value added Compounds (i.e., polyphenols)	Treated flowrate 1 L/min	Reduction of 38% of the polyphenols content in wastewater	Successful pilot operation Resin extraction operated in the lab
7	Struvite precipitation and ammonia strippring	5→7	Fertilizers	Treated flowrate 0.5 m^3/h	80% nitrogen recovery 80% phosphorus recovery	Successful pilot operation
8	Condensation, dust cleaning and scrubbing	4→6	Sodium bisulfite ($NaHSO_3$)	flue gas 500 Nm^3/h	80% organic sulfur waste recovery	Successful pilot operation
8	Ion exchange resins	-	Molybdenum	-	-	Concept study
9	Concentration by hybrid-membrane schemes and precipitation	-	Value added Compounds (i.e., phosphate and sulphate)	-	-	Concept study

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Annex 1: Recovery of sulphur at the Chemical Platform Roussillon (FR)

Anne Reguer, Stéphane Deveughèle

A.1 Results of the feasibility study (complements)

Section 2.7.2 presented the business results of the **Sulphur recovery** study, obtained by SUEZ RR IWS Chemicals (SUEZ RR), as part of the French case study CS8. This section completes section 2.7.2 by presenting the technical results, obtained by SUEZ Smart Solutions (3S), concerning the configuration and integration of the ULTIMATE IT application, deployed as part of CS8. The design and functional specifications for the ULTIMATE application are presented in subsection “Design, IT development, configuration and test of a monitoring and control application (ULTIMATE IT ***application)***” of section 2.7.1.

It is recalled that the ULTIMATE application was configured for both studies:

- **Sulphur recovery** (see section 2.7 of this deliverable D1.5)
- **Heat recovery** (see section 2.7 of this deliverable D1.4)

Connection to the ULTIMATE application

As already shown in the section 2.7.2, the ULTIMATE IT application is operational and can be accessed online for users for whom accounts have been created in advance (Figure 85). User accounts have been created for:

- **3S** to configure the ULTIMATE application and monitor its operation
- **SUEZ RR** to use the ULTIMATE application within the framework of the project and to identify anomalies, which were then communicated to 3S for correction

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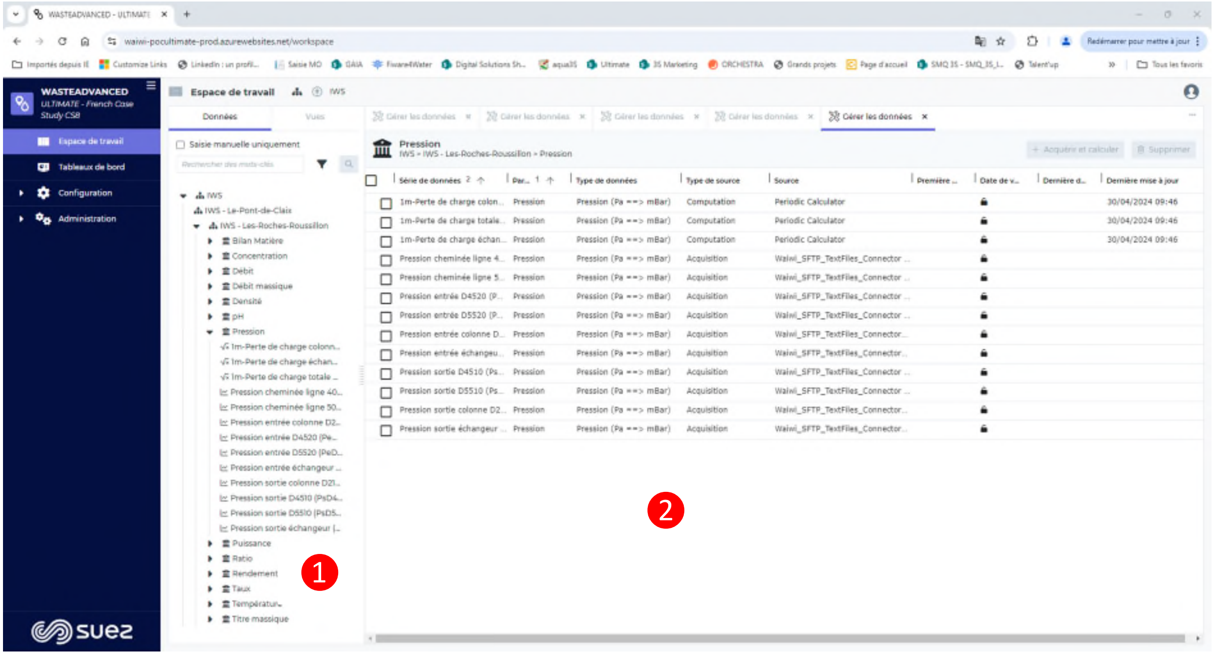
Figure 105 illustrates the data tree (measurements and calculated business indicators) of the ULTIMATE application. This data tree is common for the two CS8 studies: **Sulphur recovery** (see section 2.7 of this deliverable D1.5) and **Heat recovery** (see section 2.7 of deliverable D1.4).



☐	Série de données	Par...	Type de données	Type de source	Source	Première ...	Date de v...	Dernière d...	Dernière mise à jour
☐	1m-Perte de charge colon...	Pression	Pression (Pa ==> mBar)	Computation	Periodic Calculator		🔒		30/04/2024 09:46
☐	1m-Perte de charge totale...	Pression	Pression (Pa ==> mBar)	Computation	Periodic Calculator		🔒		30/04/2024 09:46
☐	1m-Perte de charge échan...	Pression	Pression (Pa ==> mBar)	Computation	Periodic Calculator		🔒		30/04/2024 09:46
☐	Pression cheminée ligne 4...	Pression	Pression (Pa ==> mBar)	Acquisition	Waiwi_SFTP_TextFiles_Connector ...		🔒		
☐	Pression cheminée ligne 5...	Pression	Pression (Pa ==> mBar)	Acquisition	Waiwi_SFTP_TextFiles_Connector ...		🔒		
☐	Pression entrée D4520 (P...	Pression	Pression (Pa ==> mBar)	Acquisition	Waiwi_SFTP_TextFiles_Connector ...		🔒		
☐	Pression entrée D5520 (P...	Pression	Pression (Pa ==> mBar)	Acquisition	Waiwi_SFTP_TextFiles_Connector ...		🔒		
☐	Pression entrée colonne D...	Pression	Pression (Pa ==> mBar)	Acquisition	Waiwi_SFTP_TextFiles_Connector...		🔒		
☐	Pression entrée échangeu...	Pression	Pression (Pa ==> mBar)	Acquisition	Waiwi_SFTP_TextFiles_Connector...		🔒		
☐	Pression sortie D4510 (Ps...	Pression	Pression (Pa ==> mBar)	Acquisition	Waiwi_SFTP_TextFiles_Connector ...		🔒		
☐	Pression sortie D5510 (Ps...	Pression	Pression (Pa ==> mBar)	Acquisition	Waiwi_SFTP_TextFiles_Connector ...		🔒		
☐	Pression sortie colonne D2...	Pression	Pression (Pa ==> mBar)	Acquisition	Waiwi_SFTP_TextFiles_Connector...		🔒		
☐	Pression sortie échangeur ...	Pression	Pression (Pa ==> mBar)	Acquisition	Waiwi_SFTP_TextFiles_Connector...		🔒		

Figure 105: Data tree (measurements and calculated business indicators) of the ULTIMATE application

Frame ① is the list of all the parameters configured in the ULTIMATE application for the two studies **Sulphur recovery** (see section 2.7 of this deliverable D1.5) and **Heat recovery** (see section 2.7 of deliverable D1.4) in the French case study CS8: the collected measurements (see icons 📈) and the business indicators (see icons √x). These parameters are organised by type ("Bilan Matière", "Concentration","Débit", etc., in English: Material Balance, Concentration, Flow, etc.).

Frame ② is the list of all "Pressure" type parameters. The 4th column ("Type de source" = Source type) indicates whether each parameter is a collected measurement ("Acquisition") or a business indicator ("Computation").

All the business indicators have been created and configured in the ULTIMATE IT application, in accordance with SUEZ RR requirements (see details in subsection "d. Create and configure business indicators").

The following two subsections show 2 of the 18 widgets configured, in the ULTIMATE IT application, for the **Sulphur recovery** study:

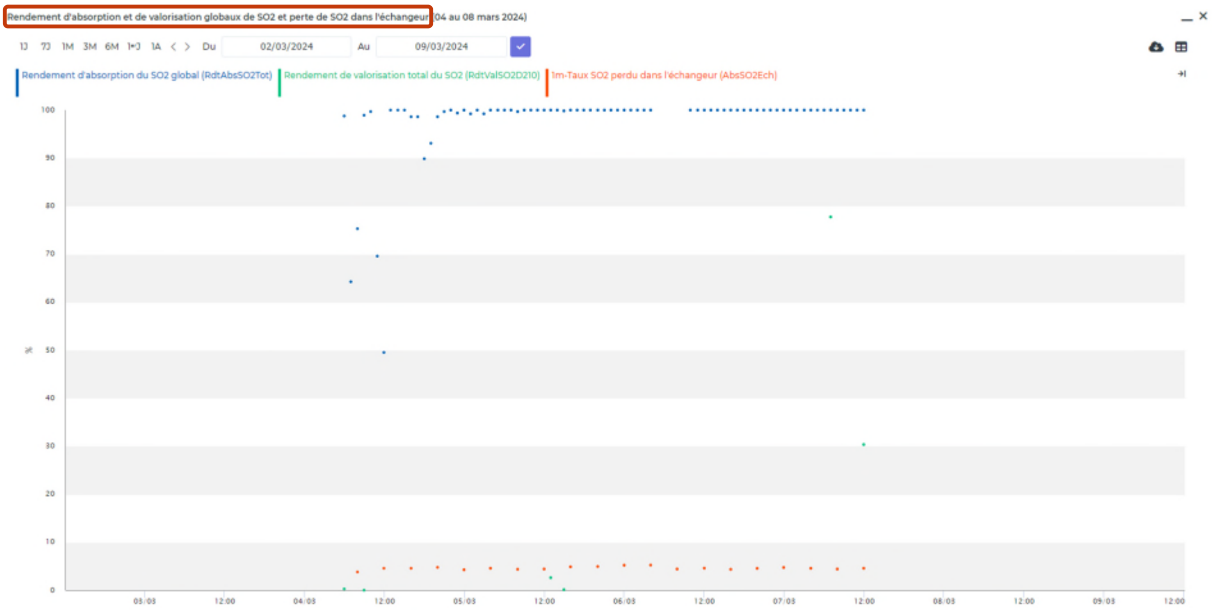
- Global SO2 absorption and recovery efficiencies and SO2 loss in the exchanger (in French, "*Rendements d'absorption et de valorisation globaux de SO2 et de perte de SO2 dans l'échangeur*")
- SO2 absorption efficiency in D5 (in French, "*Taux d'absorption du SO2 en D5*")

All the widgets have been created and configured in the ULTIMATE IT application, in accordance with SUEZ RR requirements (see details in subsection “e. Create and configure widgets”).

Widget “Global SO2 absorption and recovery efficiencies and SO2 loss in the exchanger”

Widget

Figure 106 shows the widget “Global SO2 absorption and recovery efficiencies and SO2 loss in the exchanger” (in French, “*Rendements d'absorption et de valorisation globaux de SO2 et de perte de SO2 dans l'échangeur*”).



Rendement d'absorption et de valorisation globaux de SO2 et perte de SO2 dans l'échangeur (04 au 08 mars 2024)

Du 02/03/2024 Au 09/03/2024

Figure 106: Widget “Global SO2 absorption and recovery efficiencies and SO2 loss in the exchanger” (in French, “Rendements d'absorption et de valorisation globaux de SO2 et de perte de SO2 dans l'échangeur”)

This widget contains 3 calculated business indicators:

1. Global SO2 absorption efficiency (in French, “*Rendement d'absorption du SO2 global*”)
2. Total SO2 recovery efficiency (in French, “*Rendement de valorisation total du SO2*”)
3. Rate of SO2 lost in the exchanger (in French, “*Taux de SO2 perdu dans l'échangeur*”)

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Business indicators

Figure 107 shows the display of the 1st of the 3 above-mentioned business indicators “Global SO2 absorption efficiency” (in French, *“Rendement d'absorption du SO2 global*”), also displayed in the widget in Figure 106.

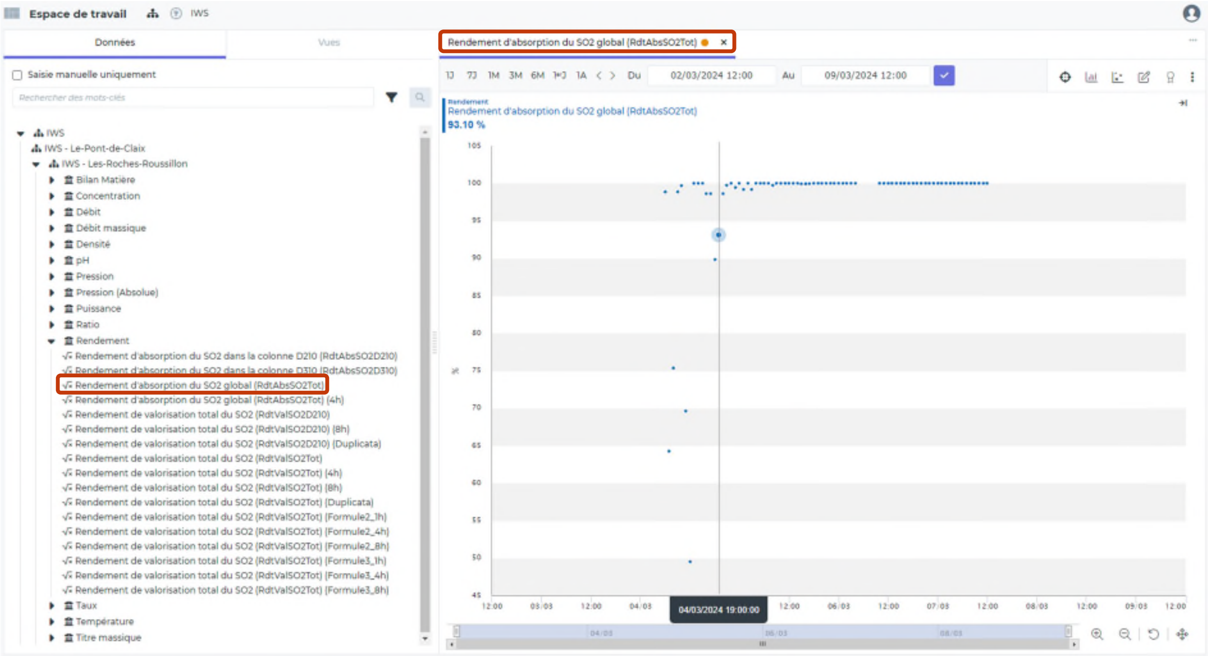

Figure 107: Display of the business indicator “Global SO2 absorption efficiency” (in French, “Rendement d'absorption du SO2 global”), also displayed in the widget in Figure 106

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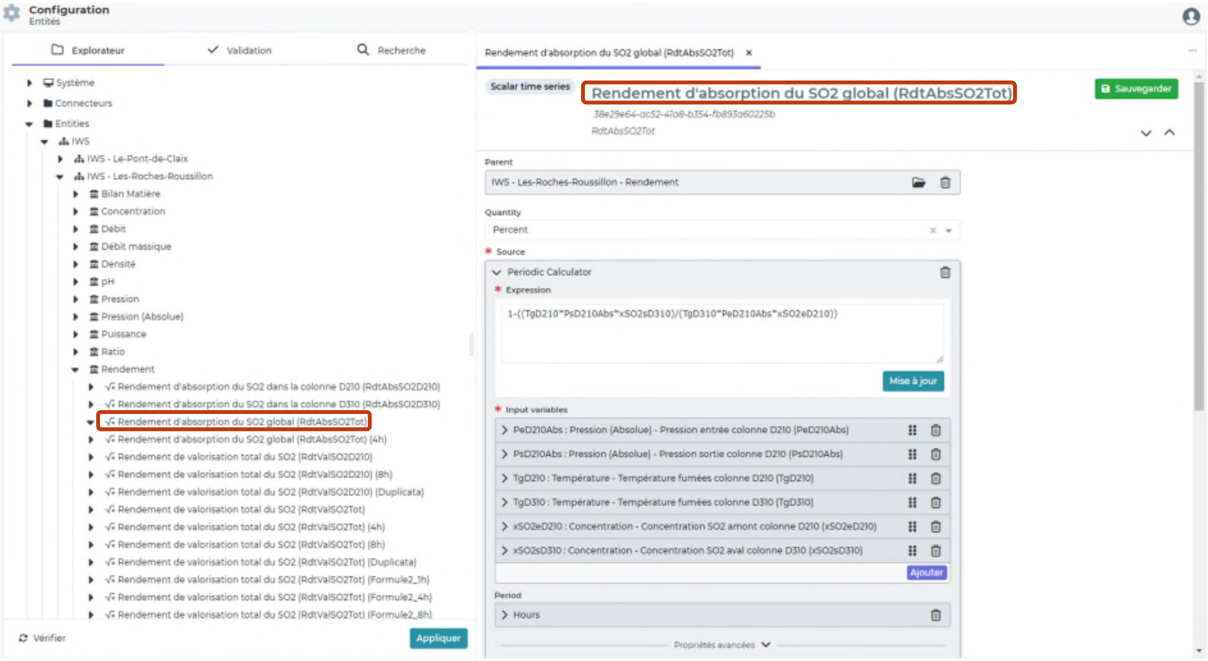
Figure 108 shows the configuration of the 1st of the 3 above-mentioned business indicators “Global SO2 absorption efficiency” (in French, *“Rendement d'absorption du SO2 global*”), displayed in Figure 107 and in the widget in Figure 106.



Scalar time series: Rendement d'absorption du SO2 global (RdtAbsSO2Tot)
38e29e64-ac52-41a8-b354-fb893a60225b
RdtAbsSO2Tot

Parent: IWS - Les-Roches-Roussillon - Rendement

Quantity: Percent

* Source: Periodic Calculator

* Expression:

```
1-((TgD210*PsD210Abs*xSO2sD310)/(TgD310*PeD210Abs*xSO2eD210))
```

* Input variables:
- PeD210Abs : Pression (Absolue) - Pression entrée colonne D210 (PeD210Abs)
- PsD210Abs : Pression (Absolue) - Pression sortie colonne D210 (PsD210Abs)
- TgD210 : Température - Température fumées colonne D210 (TgD210)
- TgD310 : Température - Température fumées colonne D310 (TgD310)
- xSO2eD210 : Concentration - Concentration SO2 amont colonne D210 (xSO2eD210)
- xSO2sD310 : Concentration - Concentration SO2 aval colonne D310 (xSO2sD310)

Period: Hours

Figure 108: Configuration of the business indicator “Global SO2 absorption efficiency” (in French, “Rendement d'absorption du SO2 global”), displayed in Figure 107 and in the widget in Figure 106

This business indicators is calculated from 6 inputs:

1. D210 column input pressure (in French, “*Pression entrée colonne D210*”)
2. D210 column output pressure (in French, “*Pression sortie colonne D210*”)
3. D210 flue gas temperature (in French, “*Température fumées colonne D210*”)
4. D310 flue gas temperature (in French, “*Température fumées colonne D310*”)
5. D210 column upstream SO2 concentration (in French, “*Concentration SO2 amont colonne D210*”)
6. D310 column downstream SO2 concentration (in French, “*Concentration SO2 aval colonne D310*”)

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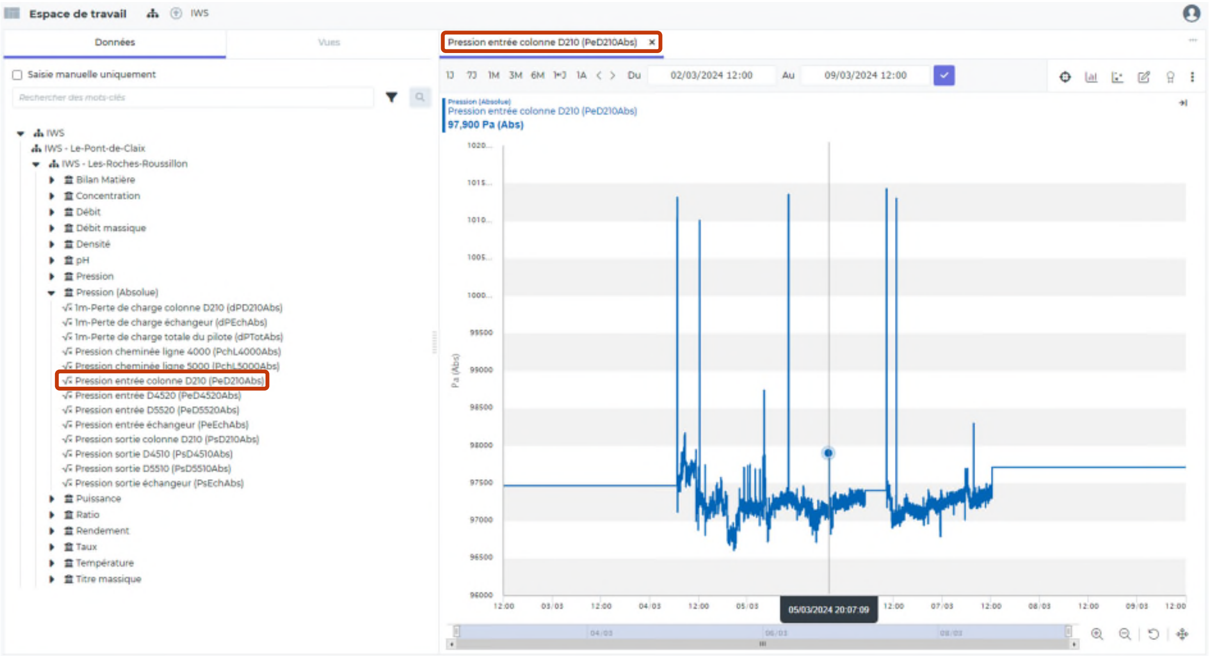
Inputs

Figure 109 shows the display of the 1st of the 6 above-mentioned inputs “D210 column input pressure” (in French, “*Pression entrée colonne D210*”), required to calculate the business indicator “Global SO2 absorption efficiency” (in French, “*Rendement d'absorption du SO2 global*”).



Du 02/03/2024 12:00 Au 09/03/2024 12:00

Pression (Absolue)
Pression entrée colonne D210 (PeD210Abs)
97,900 Pa (Abs)

Figure 109: Display of the input “D210 column input pressure“ (in French, “Pression entrée colonne D210”)

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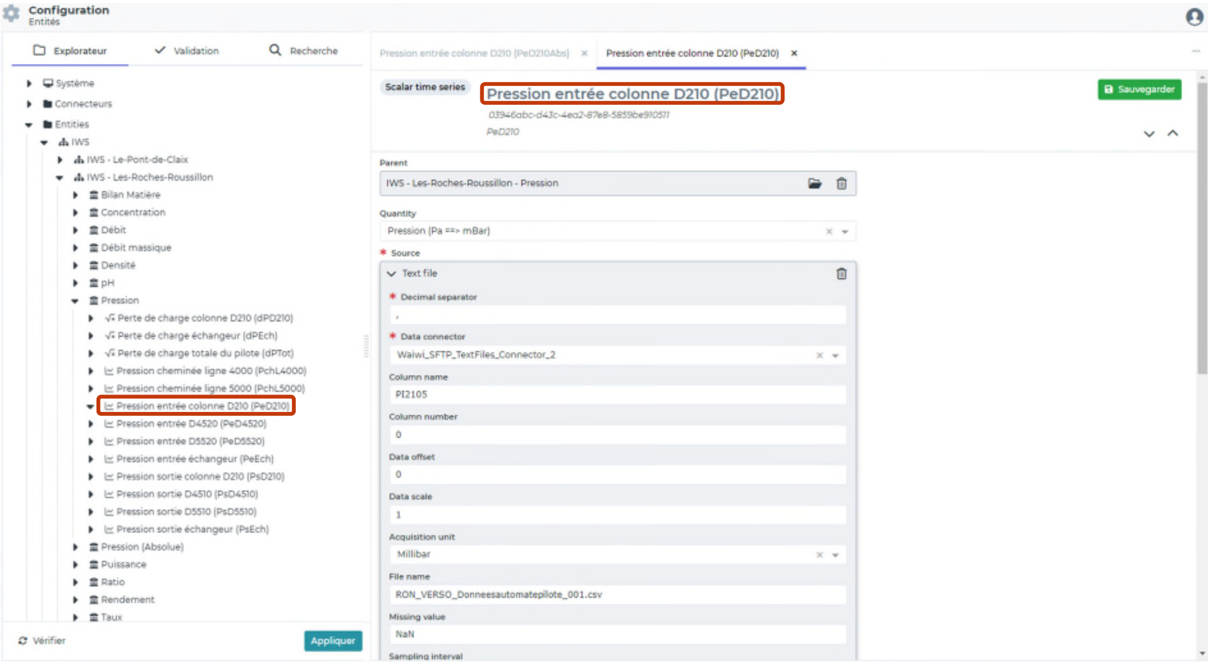
Figure 110 shows the configuration of the 1st of the 6 above-mentioned inputs “D210 column input pressure” (in French, “*Pression entrée colonne D210*”), displayed in Figure 109, required to calculate the business indicator “Global SO2 absorption efficiency” (in French, “*Rendement d'absorption du SO2 global*”).



Pression entrée colonne D210 (PeD210)
03946abc-d43c-4ea2-87e8-5859be910511
PeD210

Parent: IWS - Les-Roches-Roussillon - Pression
Quantity: Pression (Pa ==> mBar)
* Source: Text file
* Decimal separator: ,
* Data connector: Waiwi_SFTP_TextFiles_Connector_2
Column name: PI2105
Column number: 0
Data offset: 0
Data scale: 1
Acquisition unit: Millibar
File name: RON_VERSO_Donneesautomatepilote_001.csv
Missing value: NaN
Sampling interval

Figure 110: Configuration of the input “D210 column input pressure“ (in French, “Pression entrée colonne D210”)

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Widget “SO2 absorption efficiency in D5”

<u>*Widget*</u>
Figure 111 shows the widget “SO2 absorption efficiency in D5” (in French, “*Taux d'absorption du SO2 en D5*”).

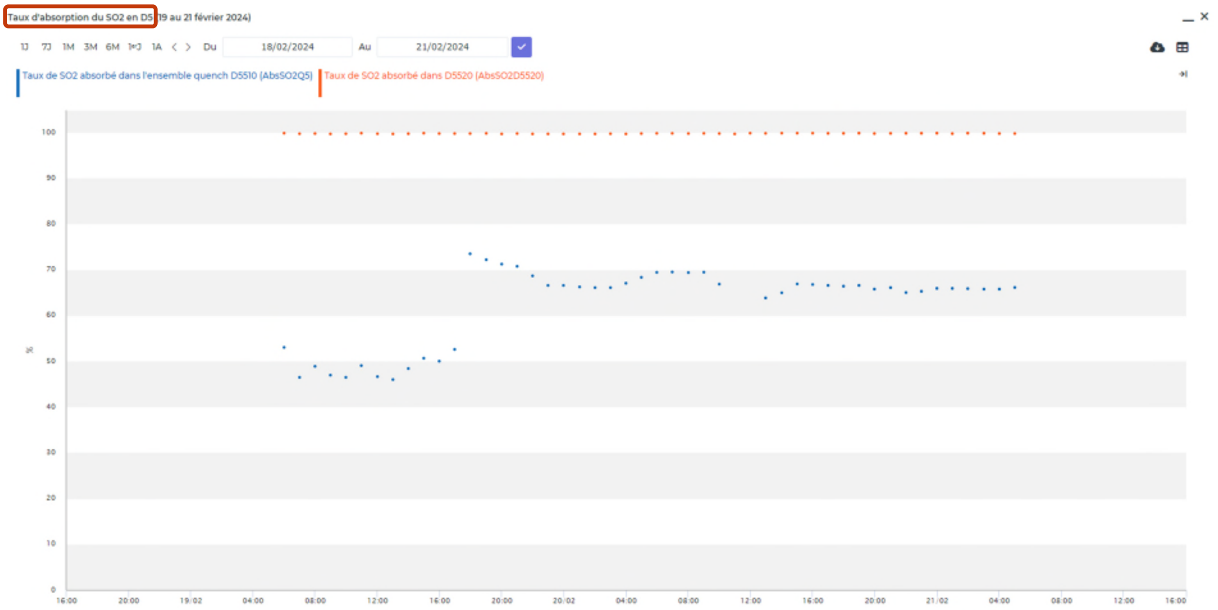


Figure 111: Widget “SO2 absorption efficiency in D5” (in French, “Taux d'absorption du SO2 en D5”)

This widget contains 2 calculated business indicators:

1. Rate of SO2 absorbed in the quench D5510 unit (in French, “*Taux de SO2 absorbé dans l'ensemble quench D5510*”)
2. Rate of SO2 absorbed in D5520 (in French, “*Taux de SO2 absorbé dans D5520*”)

The project leading to this application has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 869318

Business indicators

Figure 112 shows the display of the 1st of the 2 above-mentioned business indicators “Rate of SO2 absorbed in the quench D5510 unit” (in French, *“Taux de SO2 absorbé dans l'ensemble quench D5510*”), also displayed in the widget in Figure 111.

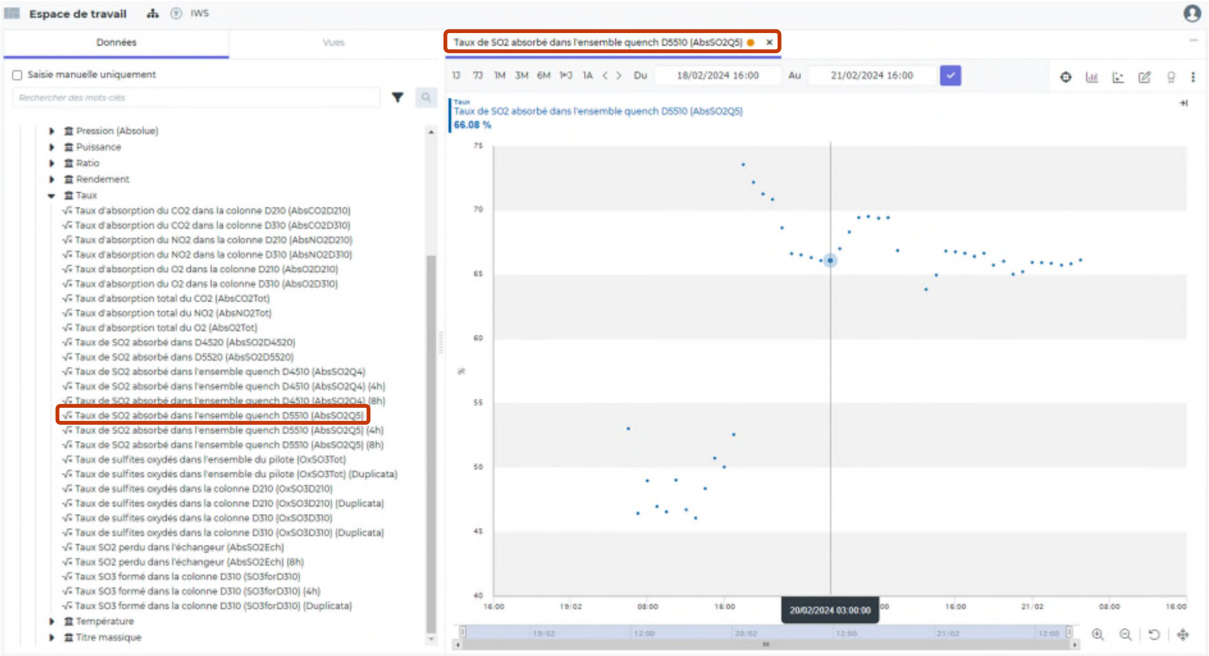
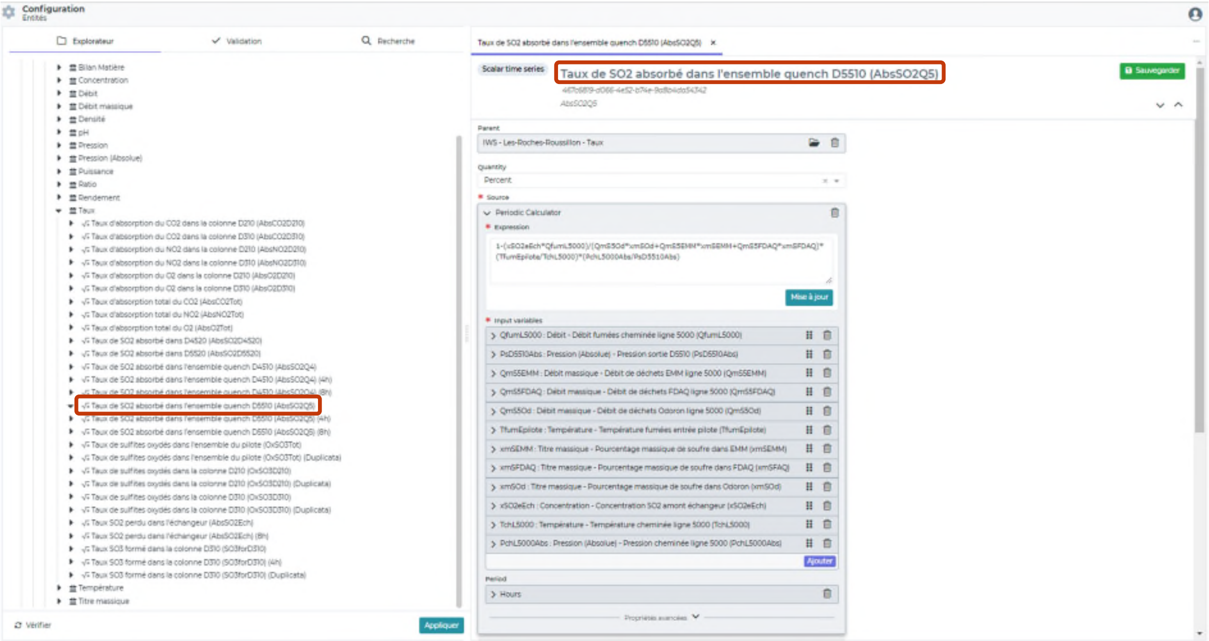


*Figure 112: Display of the business indicator “Rate of SO2 absorbed in the quench D5510 unit” (in French, “*Taux *de SO2 absorbé dans l'ensemble quench D5510”), also displayed in the widget in Figure 111*

The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869318

Figure 113 shows the configuration the 1st of the 2 above-mentioned business indicators “Rate of SO2 absorbed in the quench D5510 unit” (in French, *“Taux de SO2 absorbé dans l'ensemble quench D5510*”), displayed in Figure 112 and in the widget in Figure 111.



Taux de SO2 absorbé dans l'ensemble quench D5510 (AbsSO2Q5)
467c6819-d066-4e52-b74e-9a8b4da54342
AbsSO2Q5

Parent: IWS - Les-Roches-Roussillon - Taux

Quantity: Percent

Source: Periodic Calculator

Expression:

```
1-(xSO2eEch*QfumL5000)/(Qm55Od*xmSOd+Qm55EMM*xmSEMM+Qm55FDAQ*xmSFDAQ)*
(TfumEpilote/TchL5000)*(PchL5000Abs/PsD5510Abs)
```

Input variables:
- QfumL5000 : Débit - Débit fumées cheminée ligne 5000 (QfumL5000)
- PsD5510Abs : Pression (Absolue) - Pression sortie D5510 (PsD5510Abs)
- Qm55EMM : Débit massique - Débit de déchets EMM ligne 5000 (Qm55EMM)
- Qm55FDAQ : Débit massique - Débit de déchets FDAQ ligne 5000 (Qm55FDAQ)
- Qm55Od : Débit massique - Débit de déchets Odoron ligne 5000 (Qm55Od)
- TfumEpilote : Température - Température fumées entrée pilote (TfumEpilote)
- xmSEMM : Titre massique - Pourcentage massique de soufre dans EMM (xmSEMM)
- xmSFDAQ : Titre massique - Pourcentage massique de soufre dans FDAQ (xmSFAQ)
- xmSOd : Titre massique - Pourcentage massique de soufre dans Odoron (xmSOd)
- xSO2eEch : Concentration - Concentration SO2 amont échangeur (xSO2eEch)
- TchL5000 : Température - Température cheminée ligne 5000 (TchL5000)
- PchL5000Abs : Pression (Absolue) - Pression cheminée ligne 5000 (PchL5000Abs)

Period: Hours

*Figure 113: Configuration of the business indicator “Rate of SO2 absorbed in the quench D5510 unit” (in French, “*Taux *de SO2 absorbé dans l'ensemble quench D5510”), displayed in Figure 112 and in the widget in Figure 111*

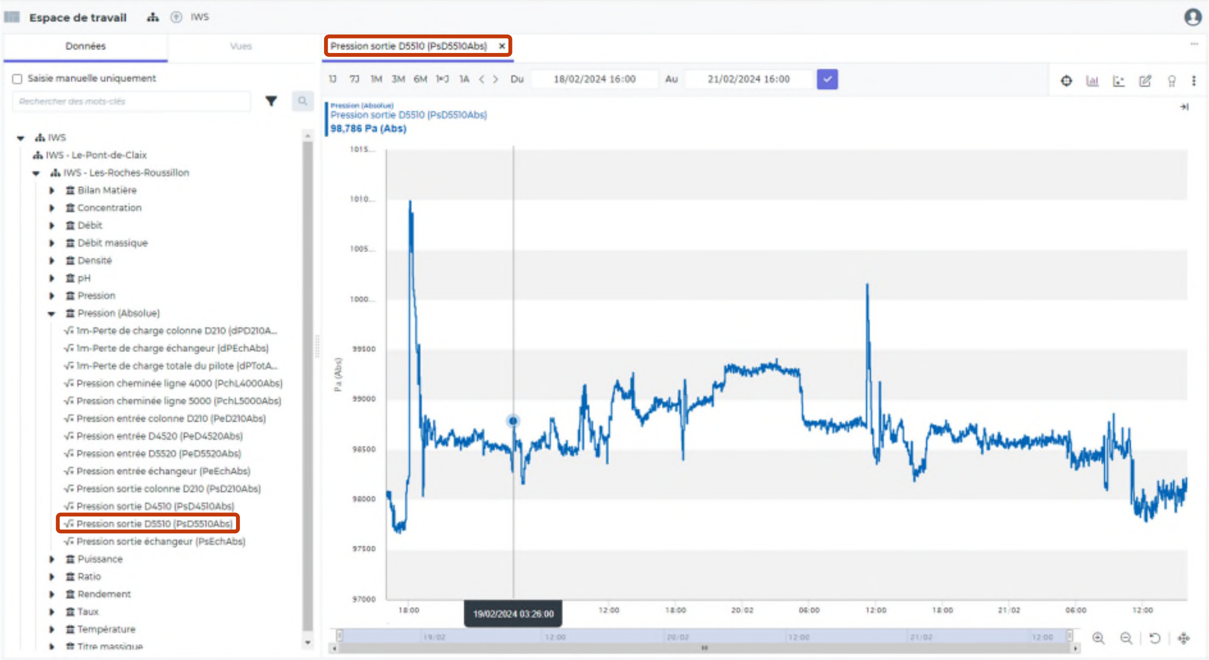
This business indicators is calculated from 12 inputs:

1. Line 5000 flue gas flow (in French, “*Débit fumées cheminée ligne 5000*”)
2. D5510 output pressure (in French, “*Pression sortie D5510*”)
3. Line 5000 EMM waste mass flow (in French, “*Débit de déchets EMM ligne 5000*”)
4. Line 5000 FDAQ waste mass flow (in French, “*Débit de déchets* FDAQ *ligne 5000*”)
5. Line 5000 Odoron waste mass flow (in French, “*Débit de déchets* Odoron *ligne 5000*”)
6. Pilot input flue gas temperature (in French, “*Température fumées entrée pilote*”)
7. Mass percentage of sulphur in EMM (in French, “*Pourcentage massique de soufre dans EMM*”)
8. Mass percentage of sulphur in FDAQ (in French, “*Pourcentage massique de soufre dans FDAQ*”)
9. Mass percentage of sulphur in Odoron (in French, “*Pourcentage massique de soufre dans Odoron*”)
10. SO2 concentration upstream of exchanger (in French, “*Concentration SO2 amont échangeur*”)
11. Line 5000 flue gas temperature (in French, “*Température cheminée ligne 5000*”)
12. Line 5000 flue gas pressure (in French, “*Pression cheminée ligne 5000*”)

The project leading to this application has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 869318

Inputs

Figure 114 shows the display of the 2nd of the 12 above-mentioned inputs “D5510 output pressure” (in French, “*Pression sortie D5510*”), required to calculate the business indicator “Rate of SO2 absorbed in the quench D5510 unit” (in French, “*Taux de SO2 absorbé dans l'ensemble quench D5510*”).


☐ Saisie manuelle uniquement

Du 18/02/2024 16:00 Au 21/02/2024 16:00

Pression (Absolue)
Pression sortie D5510 (PsD5510Abs)
98,786 Pa (Abs)

Figure 114: Display of the input “D5510 output pressure“ (in French, “Pression sortie D5510”)

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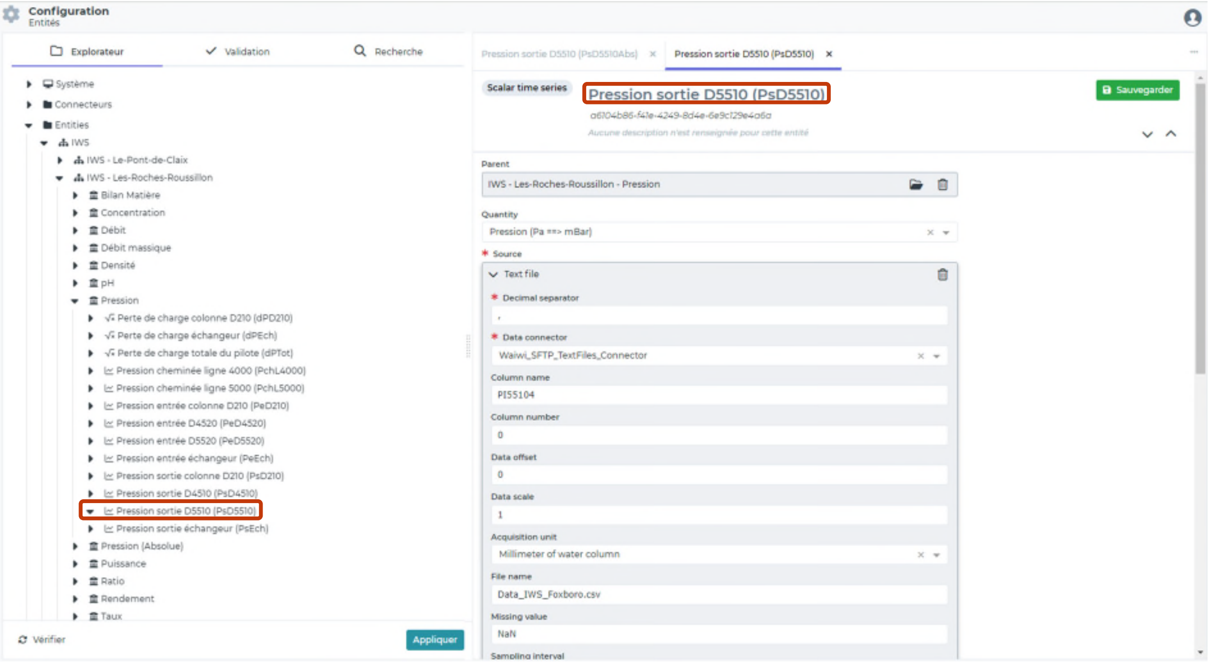
Figure 115 shows the configuration of the 2nd of the 12 above-mentioned inputs "D5510 output pressure" (in French, "*Pression sortie D5510*"), displayed in Figure 114, required to calculate the business indicator "Rate of SO2 absorbed in the quench D5510 unit" (in French, "*Taux de SO2 absorbé dans l'ensemble quench D5510*").



Scalar time series **Pression sortie D5510 (PsD5510)**

a6104b86-f41e-4249-8d4e-6e9c129e4a6a

Aucune description n'est renseignée pour cette entité

Parent: IWS - Les-Roches-Roussillon - Pression

Quantity: Pression (Pa ==> mBar)

* Source: Text file

* Decimal separator: ,

* Data connector: Waiwi_SFTP_TextFiles_Connector

Column name: PI55104

Column number: 0

Data offset: 0

Data scale: 1

Acquisition unit: Millimeter of water column

File name: Data_IWS_Foxboro.csv

Missing value: NaN

Sampling interval

Figure 115: Configuration of the input "D5510 output pressure" (in French, "Pression sortie D5510")

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WATER SMART INDUSTRIAL SYMBIOSIS

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