ULTIMATE

WATER SMART INDUSTRIAL SYMBIOSIS

Adsorption technology webinar

S.Casas, A. Naves

March, 31st 2021

ULTIMATE-Adsorption technology webinar

Please mute your microphone

Use the chat for questions!

Presenters have your presentation open and ready!

Write your name and email in the chat if you want to keep posted or receive presentations of today's meeting!

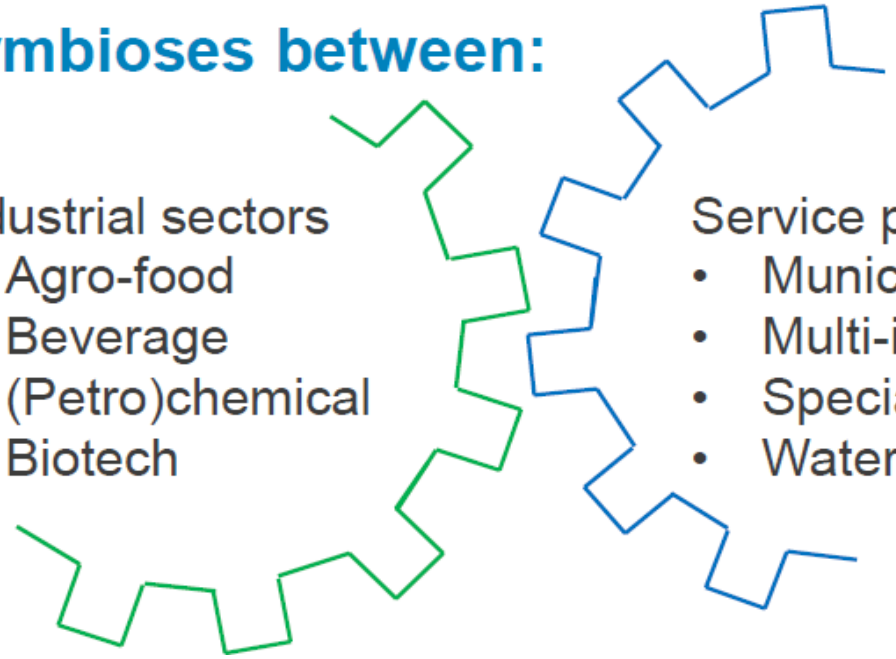
The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869318

Ultimate (June 2020 – May 2024):

Industry water-utility symbiosis for a smarter water society

- Promotion, establishment and extension of **Water Smart Industrial Symbioses**
- Development and demonstration of **innovative technologies** for symbioses
- **Assessment** of the technologies and development of **digital „support tools“**
- Development of **new business models** towards marketability

9 Symbioses between:



Industrial sectors
- Agro-food
- Beverage
- (Petro)chemical
- Biotech

Service providers
- Municipal utility
- Multi-industry utility
- Specialized SME
- Water services provider

Coordinator: KWR

9 Case Studies

27 Partners

37 Technologies

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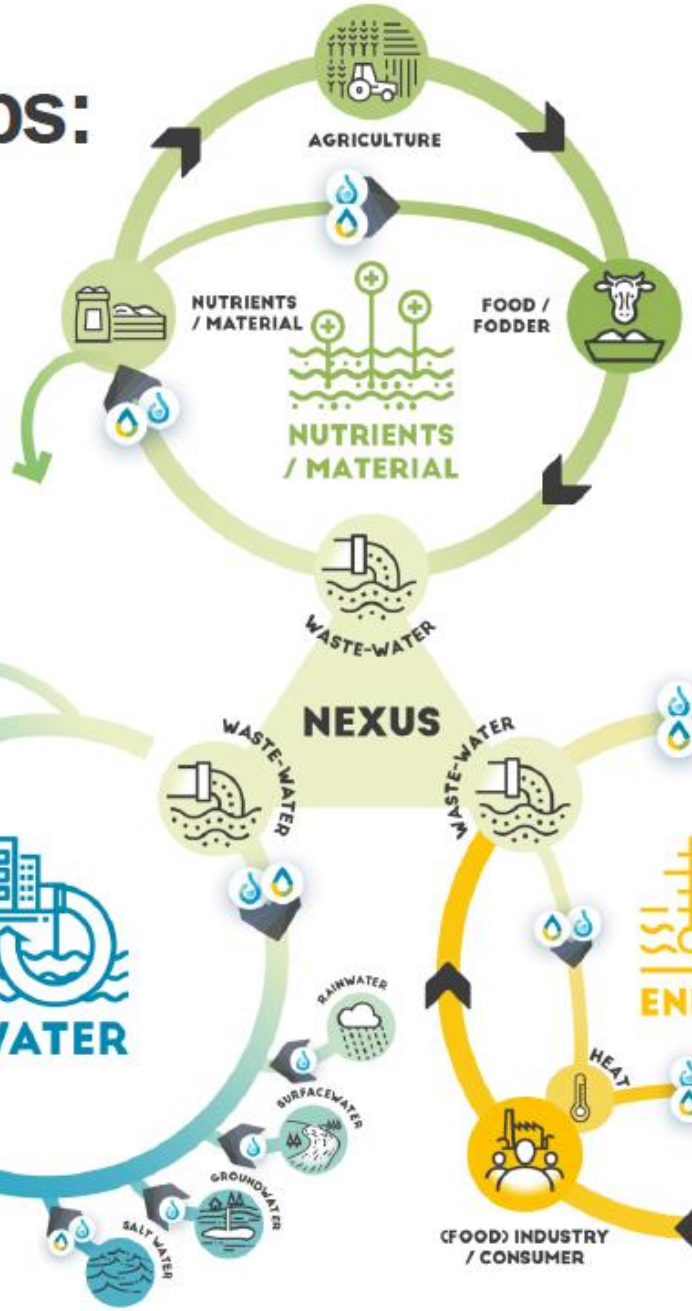
3 Cross-cutting Technology Groups: 9 Topics



F. Fatone C. Bruni

UNIVERSITÀ POLITECNICA DELLE MARCHE

- Nutrient recovery
- High added value products
- Metal recovery

eurecat
Centre Tecnològic de Catalunya

A.Naves S. Casas

- Membrane technologies
- Adsorption technologies
- Advanced oxidation processes

A. Kleyböcker

KOMPETENZZENTRUM Wasser Berlin

- Biogas technologies
- Heat recovery
- Digitalization

Coordinator: KWR

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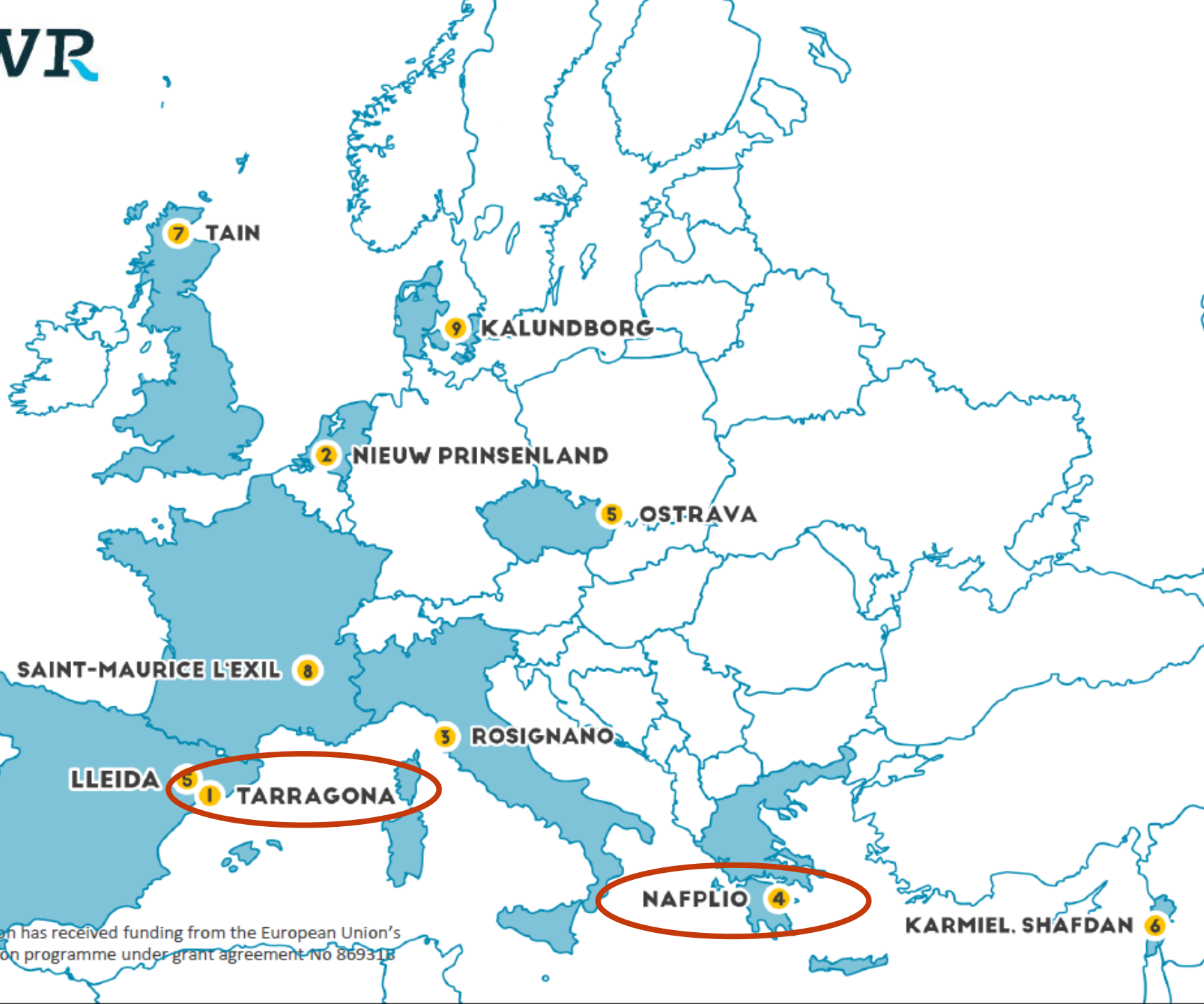

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Agenda

11:00 h	**Opening and Welcome.** Sandra Casas (EURECAT)
11:10 h	**ULTIMATE: Removal of ammonia from wastewater by adsorption with zeolites (CS1).** Andrea Naves (EURECAT)
11:25 h	**ULTIMATE: Adsorption - extraction methodologies for the extraction of value-added compounds from food- processing wastewater (CS4 y CS6).** Dimitri Iossifidis (GREENER THAN GREENER)
11:40 h	**SMARTPLANT: Removal of key pollutants from wastewater by adsorption: N, P and COD.** Ana Soares (CRANFIELD UNIVERSITY)
11:55 h	**SEA4VALUE: 3D-printed adsorbents for metal recovery.** Eveliina Repo (LAHTI UNIVERSITY OF TECHNOLOGY)
12:10 h	**WATERMINING: BioPhree: Reversible phosphate adsorption for P-removal to ultra-low levels and P-recovery. Demonstrations and perspectives.** Wokke Wijdeveld (WETSUS)
12:20 h	**NEXTGEN: Renewable granular active carbon for removal of organic micropollutants in urban wastewater**. Luca Loreggian (Fachhochschule Nordwestschweiz)
12:30 h	**Open questions and closure.** Sandra Casas (EURECAT)

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ULTIMATE

WATER SMART INDUSTRIAL SYMBIOSIS

Removal of ammonium from wastewater by adsorption with zeolites (CS1)

D. Montserrat, J.E. Manero (AITASA)

S. Casas, A. Naves (EURECAT)

CS1: Petrochemical Complex of Tarragona (Spain)

AITASA was founded in 1965 to supply water to the Tarragona petrochemical complex.

This industrial area groups several companies **of the chemical and petroleum field.** it has been considered the most important of this type in Catalonia, Spain and the south of Europe.

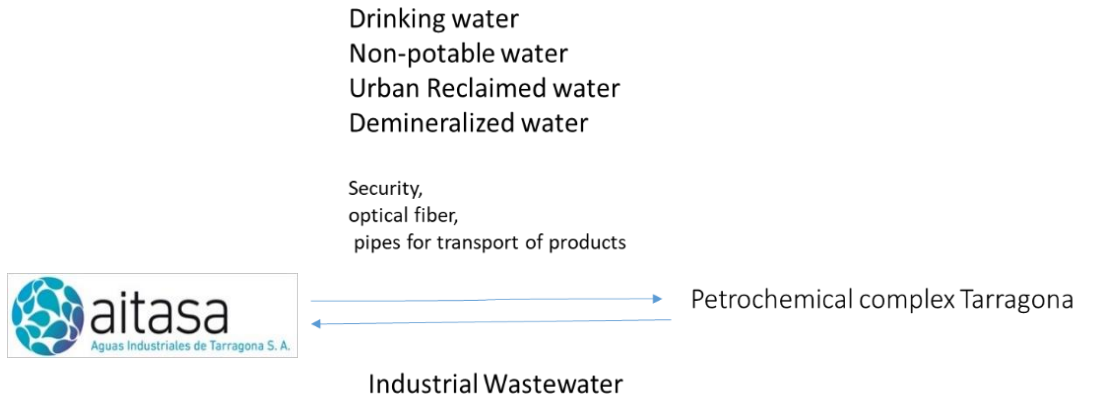
More than 30 companies operate in the petrochemical complex focusing on production of chlorine, alkaline salts, oxygen gas, fertilizers, insecticides, fuels, plastics and synthetic essences.

In 2012, a water reclamation plant was put in operation to supply industrial water and, currently, it is runned by AITASA.

Partners:

eurecat
Centre Tecnològic de Catalunya

aitasa
Aguas Industriales de Tarragona S. A.



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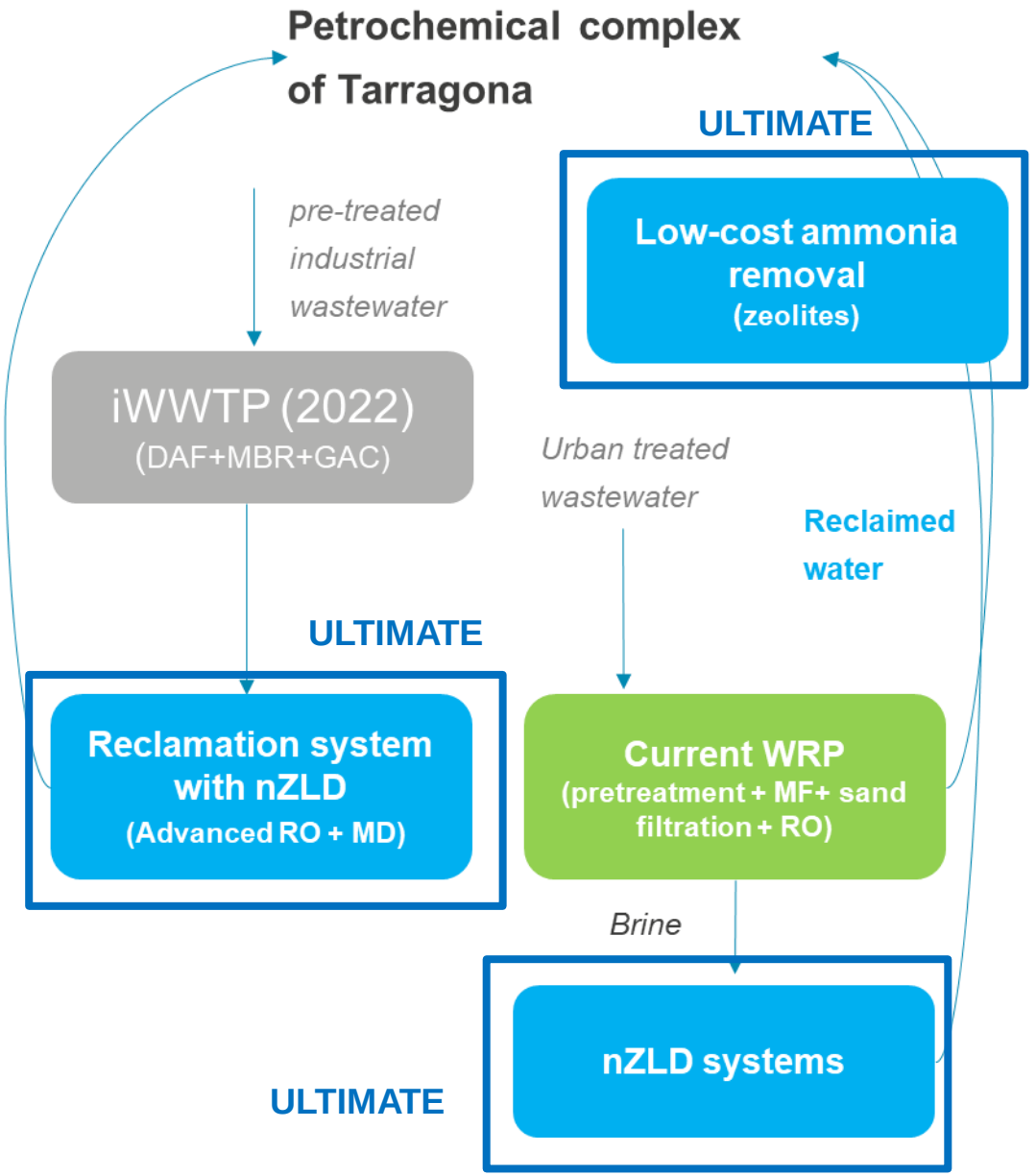
WATER - Task 1.2.1

Increasing reclaimed water availability in the petrochemical complex of Tarragona

OBJECTIVE:
Increase reclaimed water availability for the complex by 20%:

→ **Current WWRP**:
- → Increase water recovery of the current WWRP with nZLD technologies
- → Remove the ammonium with low-cost technologies

→ **Future iWWTP**:
- → Defining a tertiary treatment with nZLD technologies from the future



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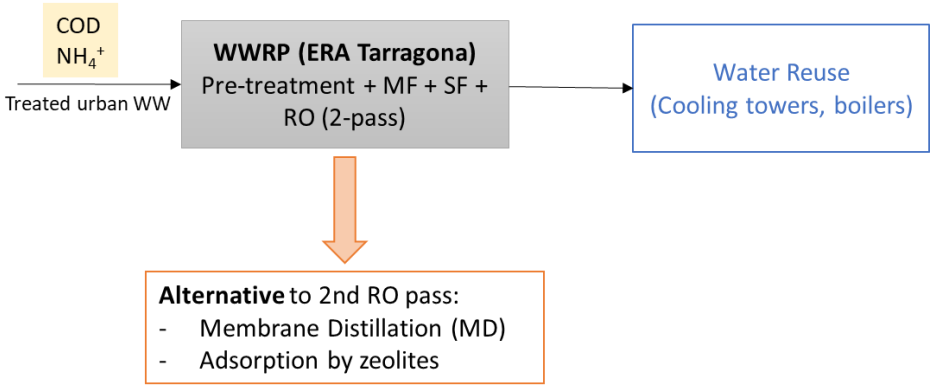
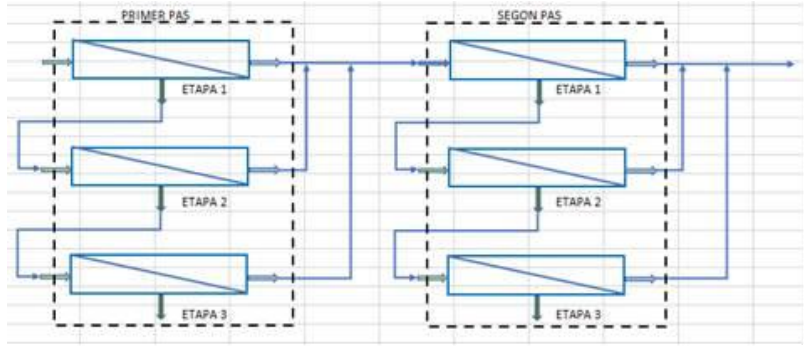
Ammonium removal from wastewater

- Current implemented technology to remove ammonium from water in WRP:
  - AITASA removes ammonium from water by 2-pass RO



AITASA CURRENT AMMONIUM REMOVAL PROCESS (RO)



NH^{+4} inlet (average)	22 mg/L
NH^{+4} outlet (required value)	0.8 mg/L

- Other technologies to remove ammonium from wastewater:
  - Electrodeionization/electrodyalisis
  - Anaerobic oxidation process (biological treatment)
  - Membrane distillation (direct contact membrane distillation DCMD, vacuum membrane distillation VMD, sweeping gas membrane distillation SGMD)
  - Adsorption → Technical-economical feasibility assessment

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Ammonium removal from wastewater by adsorption with zeolites

AMMONIUM ADSORPTION MATERIALS

There are different materials to adsorb ammonium from wastewaters: zeolites, zeolite-like sepiolite, bentonite, bioadsorbents *(Boston ivy leaf powder),* biochar

Adsorbent material	Adsorption capacity
Bioadsorbent *(Boston ivy leaf powder)*	3.3-6.6 mg N/g (15-35ºC)
Sepiolite	0.8-1.5 mg N/g
Biochar (from rice straw)	2.9-4.6 mg N/g (20-50ºC, pH=7.5)
Clinoptilolite (natural zeolite)	8.1-15.2 mg N/g

ZEOLITES CHARACTERISTICS

- **Structure:** zeolites are **crystalline microporous solids** formed by TO_4 tetrahedra (with T being Si, Al, Ge, B… and staying in the tetrahedral position) whose structures contain channels of diameters between 0.3-1.5 nm.
- **Properties:** exceptional physicochemical properties, high functionality, **great adsorption capacity**.
- **Types:** silicate-based materials can be commonly found in volcanic areas, and there are about 45 **natural types.** However, the presence of impurities and the lack of uniformity lead to requiring their processing to avoid limiting their adsorption capacity, which in turn end up leading to the use of **synthetic zeolites**. This tendency to opt for synthetic zeolites widen the number of commercially available structures, and also stimulate the development of tailored adsorption properties by controlling the framework (Si/Al ratio) as well as the extra-framework (use of cations) and other post-synthesis modifications.

APPLICATIONS

Applications for **ammonium removal by adsorption with zeolites**:

- landfill leachates
- livestock wastewaters
- effluents from anaerobic digestion tanks
- livestock manure effluents

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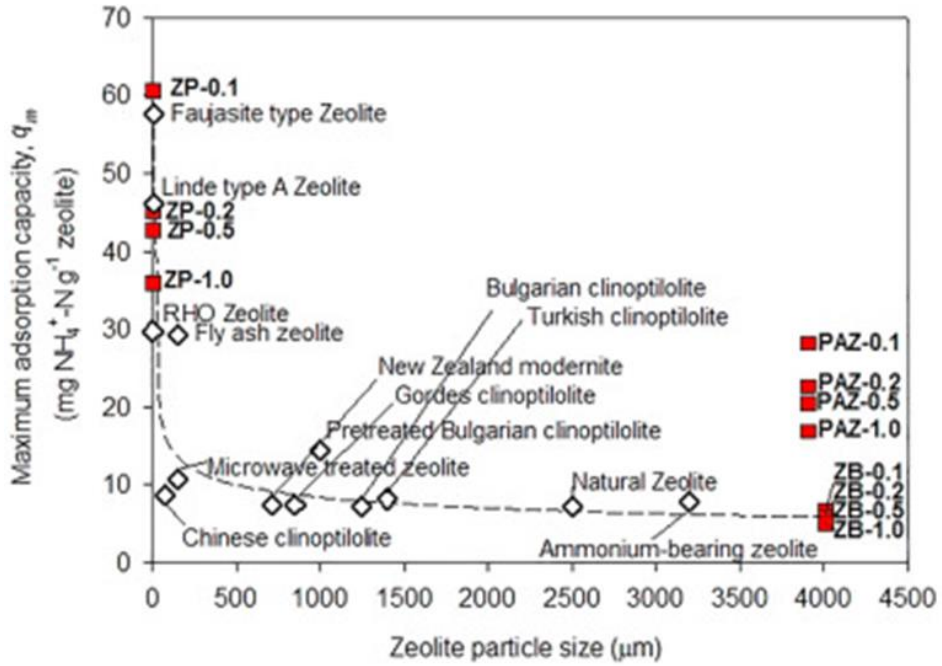
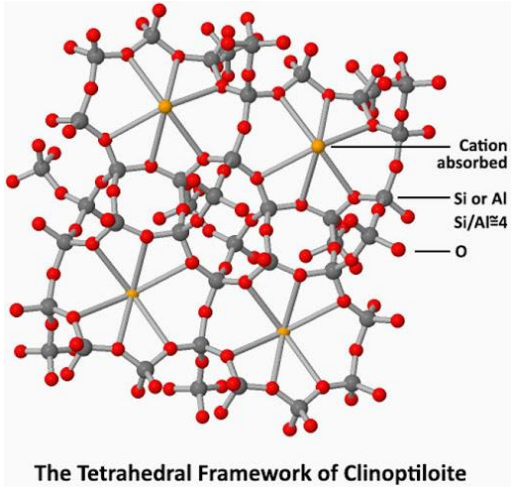
Ammonium removal from water by adsorption with zeolites

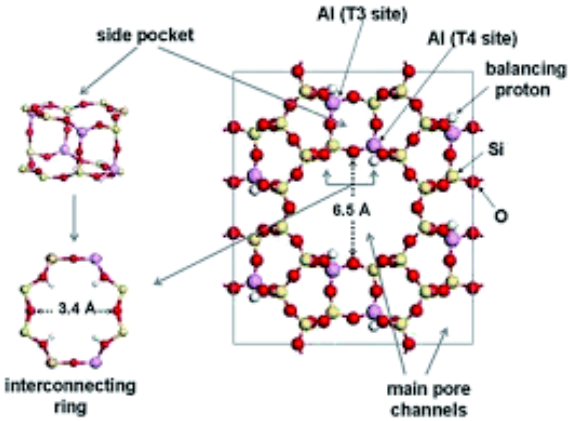
ZEOLITES SELECTION

- Clinoptilolite: $Ca_3(Si_{30}Al_6)O_{72}\cdot 20H_2O$
- Mordenite: $(Na_2,Ca,K_2)_4(Al_8Si_{40})O_{96}\cdot 28H_2O$





The Tetrahedral Framework of Clinoptiloite



Mordenite structure

Zeolite	Crystal framework Si/Al ratio	Crystal structure symmetry	Crystal density[b] (g/cm^3)	Common ion-exchanged forms	Pellet density (g/cm^3)	Bulk density (g/cm^3)	Nominal pore opening (A)
A	0.7–1.2	Cubic	1.52	Na,K,Ag, Mg,Ca	1.20	0.72	3,4,5
X	1.0–1.5	Cubic	1.47	Na,Li, Ca,Ba	1.05	0.65	7.5(NaX) 10.0(CaX)
Mordenite (small port)	4.5–5.0	Orthorhombic	1.83	Na,H,Ca	1.39	0.88	4
Chabazite	1.6–3.0	Trigonal	1.67	Na,Ca	1.16	0.73	4.9
Clinoptilolite	4.2–5.2	Monoclinic	1.85	K,Ca	—	—	3.5
Silicalite	very high	Orthorhombic	1.79	none	—	—	5.5

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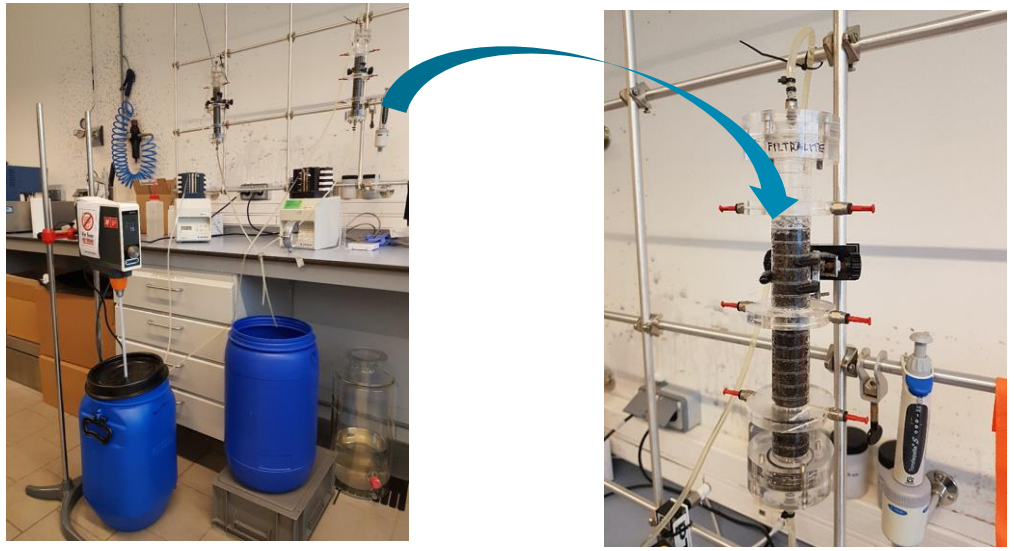
Ammonia removal by adsorption with zeolites

BENCH SCALE TESTS

- **Experimental plan at bench scale:**
  - Zeolite type
  - Zeolite granulometry
  - Water flow rate (hydraulic time)
  - Bed length
  - pH
  - Zeolite regeneration cycle (NaCl)

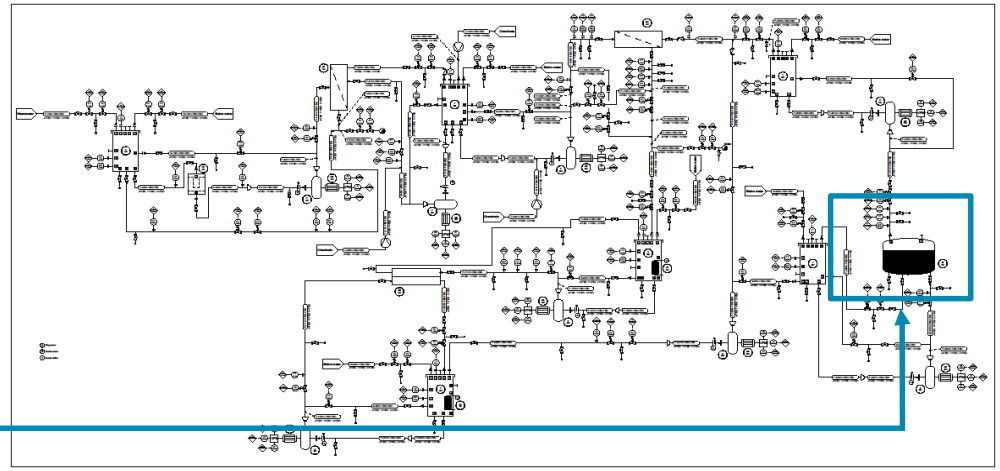
Experimental set-up



- **Optimization of the operational parameters and adsorption performance (breakthrough curve)**

- **Design zeolite adsorption column to be implemented at pilot plant scale**

P&ID FOR CS1 PILOT PLANT



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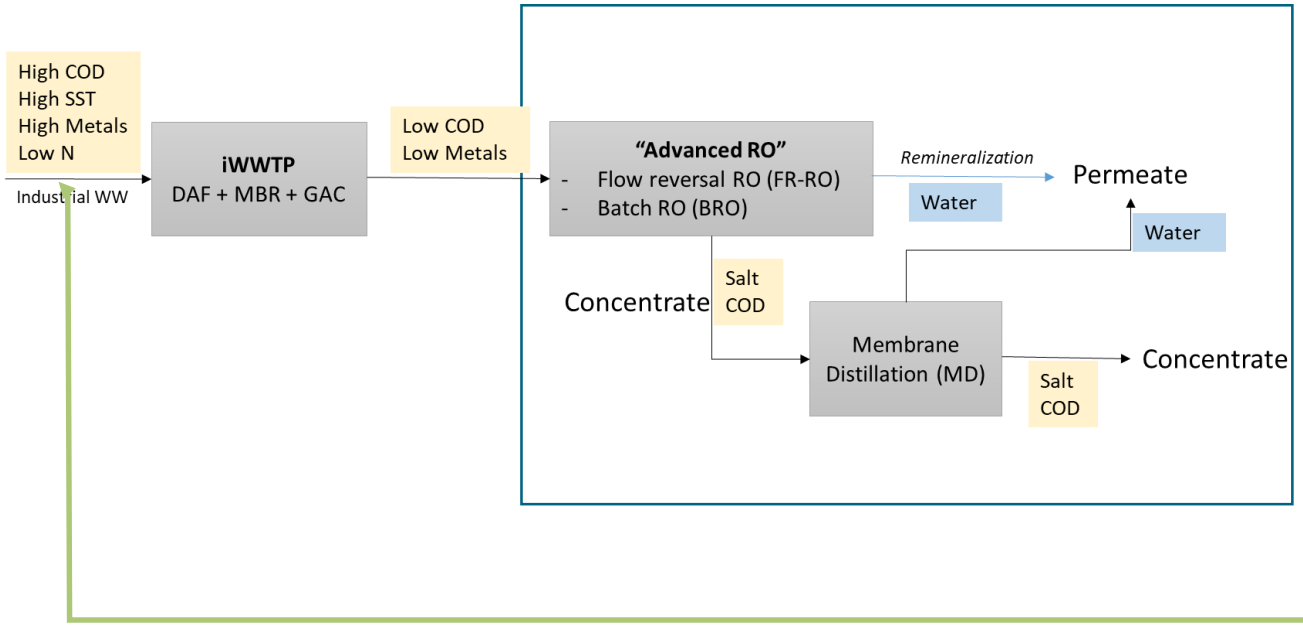
Ammonia removal by adsorption with zeolites

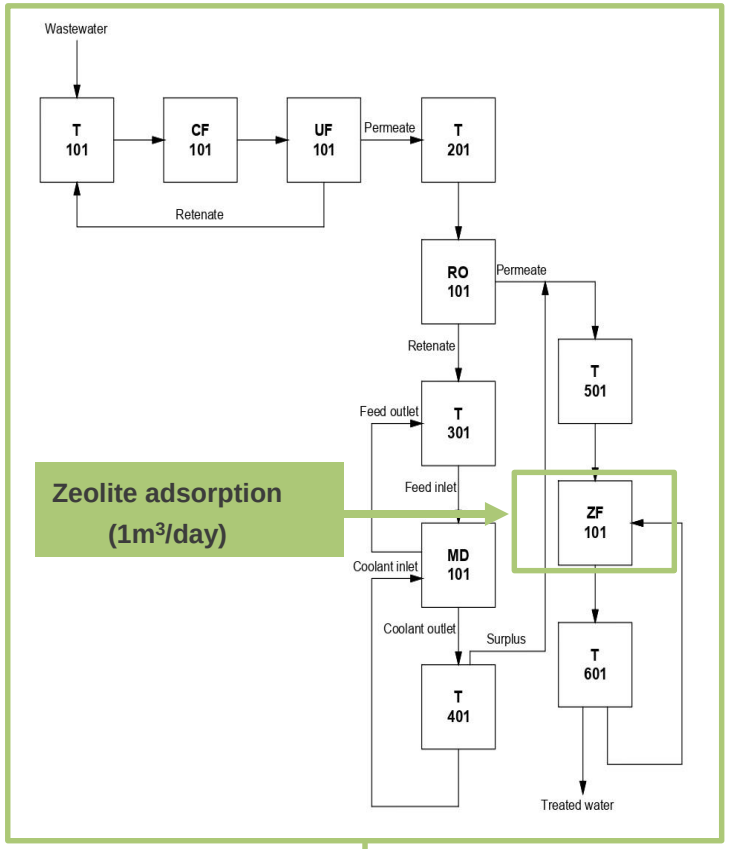
PILOT PLANT SCALE TESTS

Only one pilot plant will be built and it will include all the technologies to be tested in CS1.

ULTIMATE: Proposed WWRP scheme to maximize water recovery (near ZLD)



PILOT PLANT PROCESSES SCHEME



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Next steps in CS1

TIMING

ULTIMATE CS1 Internal milestones:		2020							2021												2022												2023												2024				
		6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
Review of historical operation and quality data of the site. Definition of extra campaigns required. Analysis of samples.	EUT																																															
Sampling and analysis for extra analitical campaigns and collection of data for baseline	AIT																																															
Set-up experimental plan and laboratory equipment	EUT																																															
Definition of requirements for reuse	AIT																																															
Trials of proposed technologies at bench scale. Optimitzation of the system	EUT																																															
Site adaptation	AIT																																															
Definition of prototype for construction	EUT																																															
Prototype construction and installation	AIT																																															
Operation of prototype and optimizatin	AIT																																															
Prototype follow-up and monitoring	EUT																																															
Evaluation of results and integration of water sources	EUT																																															

Trials at bench scale with real water from the AITASA WRP

Trials at pilot plant scale when the pilot is installed at the industrial site

Technical-economical feasibility assessment

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Conclusions

Ammonium adsorption by zeolites will be evaluated in CS1 of ULTIMATE with the aim of:

- Assess its technical and economic feasibility as an alternative technology to current 2 pass-RO in the current Water Reclamation Plant.

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ULTIMATE

WATER SMART INDUSTRIAL SYMBIOSIS

Thank you!

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