ULTIMATE

WATER SMART INDUSTRIAL SYMBIOSIS

Adsorption and advanced oxidation processes (AOP) technologies webinar

A. Naves, S. Casas

July, 10th 2023

ULTIMATE- Adsorption and advnaced oxidation processes (AOP) technologies workshop

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

Agenda

14:30h **Opening and welcome.** Andrea Naves (EURECAT).

14:40h **ULTIMATE: Ammonium adsorption on zeolites for reclaimed water production for the chemical and petrochemical industrial sector (CS1).** Andrea Naves (EURECAT, Spain).

15:00h **ULTIMATE: Innovative sensors and alternative materials for the removal of organic matter and micropollutants by adsorption and AOP technologies in ARETUSA (CS3).** Cecilia Bruni (Università Politecnica delle Marche, Italy).

15:20h **ULTIMATE: Coupling technologies in recovery methodologies in industrial water by-product treatment (CS4).** Dimitri Iossifidis (Greener than Greener, Greece).

15:40h **Break**

15:55h **ULTIMATE: MET 3D printing of catalytic membranes and supports for cleaning AOPs in water (CS5).** Pablo Ortega (Colfeed4Print).

16:15h **Discussion and closure.**

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Key Ultimate information

Call	2017 - H2020 – Greening the economy in line with the Sustainable Development Goals (SDGS) - H2020-SC5-2018-2019-2020
Topic	CE-SC5-04-2019 - Building a water-smart economy and society
Budget	**TOTAL:** Budget 16.614.814€
Duration	53 months (01/06/2020 – 31/10/2024)
Partners	27 (12 private companies; 8 non-profit/private centers; 7 public centers) from 11 countries
Coordinator	KWR WATER (NL)

Web del proyecto: https://ultimatewater.eu/

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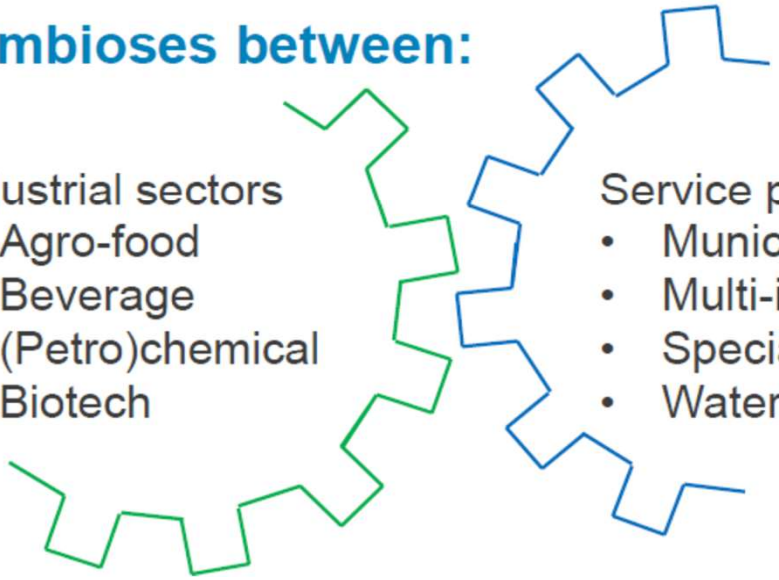
Ultimate (June 2020 – May 2024):

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

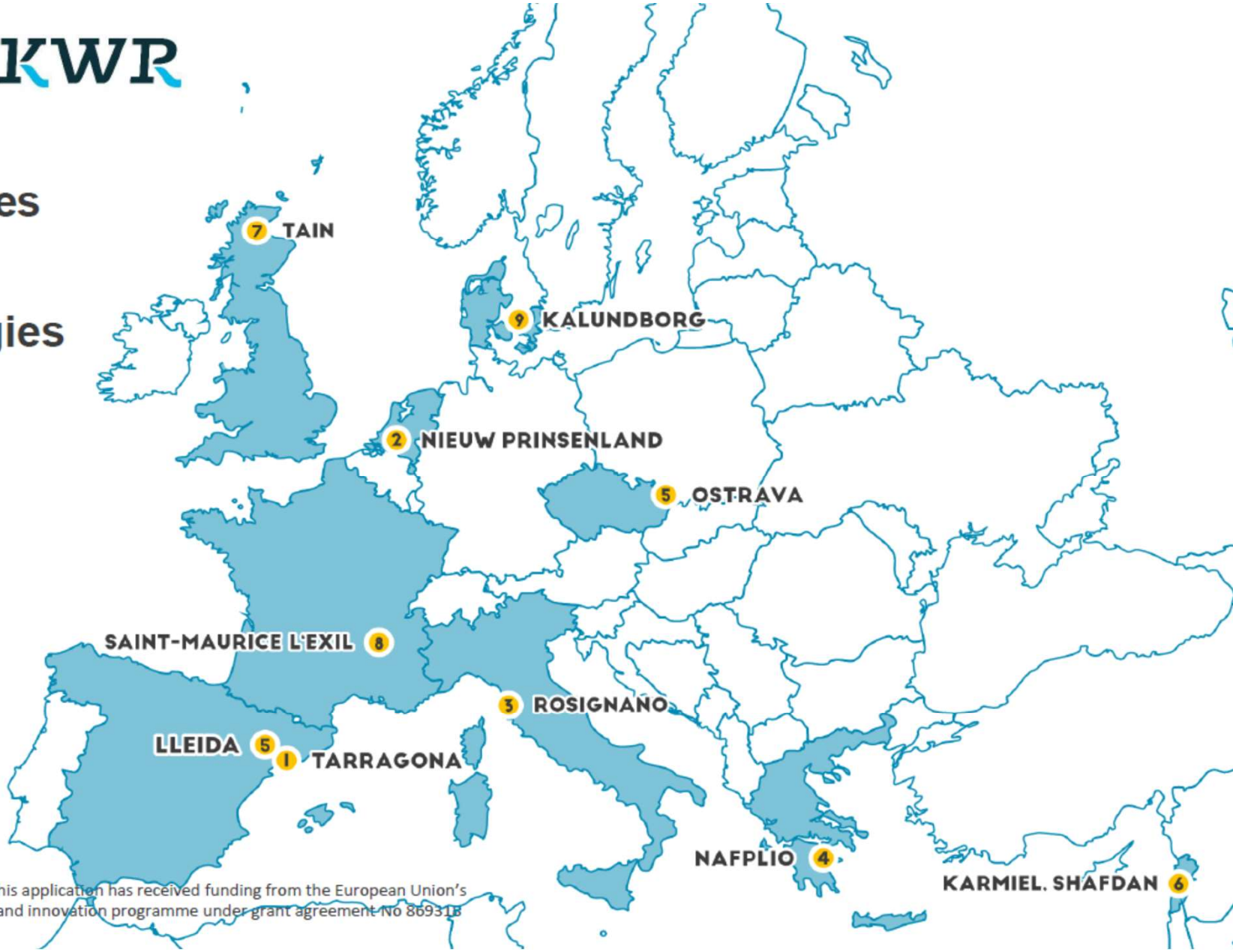
Service providers
- Municipal utility
- Multi-industry utility
- Specialized SME
- Water services provider

Coordinator: KWR

9 Case Studies

27 Partners

37 Technologies



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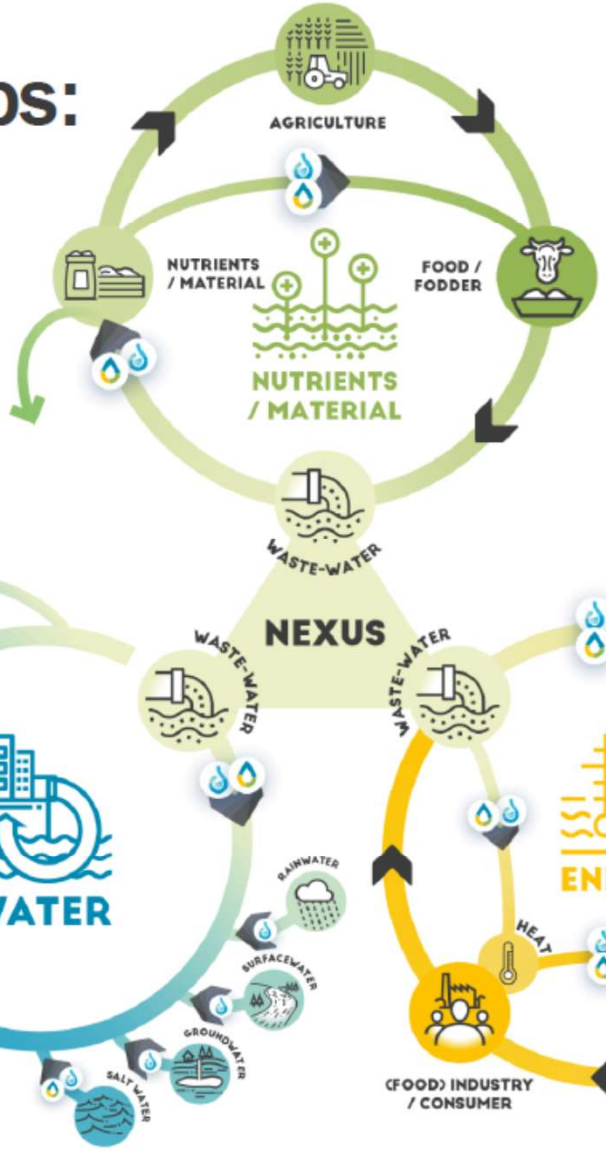
3 Cross-cutting Technology Groups: 9 Topics



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

9 Case Studies

27 Partners

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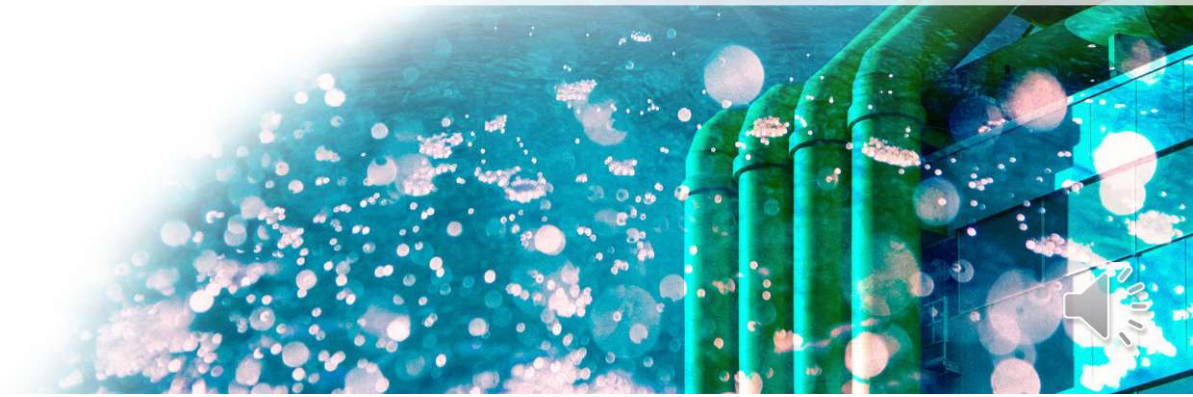
WATER SMART INDUSTRIAL SYMBIOSIS

Ammonium adsorption on zeolites for reclaimed water production for the chemical and petrochemical industrial sector (CS1)

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

S. Casas, A. Naves (EURECAT)



Petrochemical Complex of Tarragona (Spain): CS1

AITASA (Aguas Industriales de Tarragona) 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.

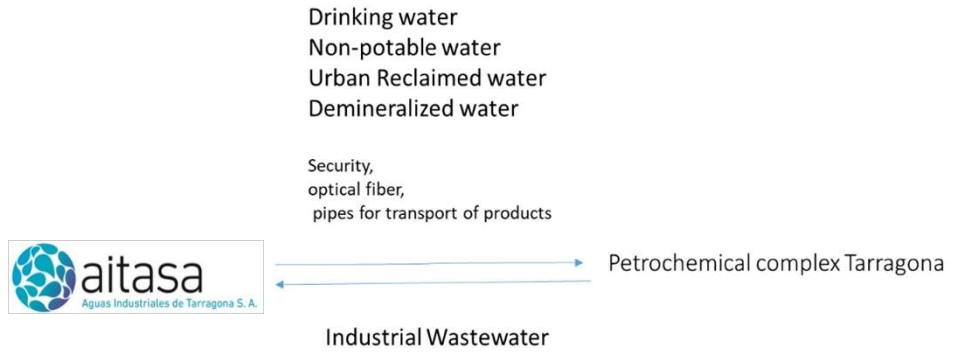
More than 30 companies operate in the petrochemical complex focusing on production of chlorine, alkaline salts, oxygen gas, fertilizers, insecticides, fuels, plastics and synthetic essences.

In 2012, a water reclamation plant was put in operation to supply industrial and reclaimed 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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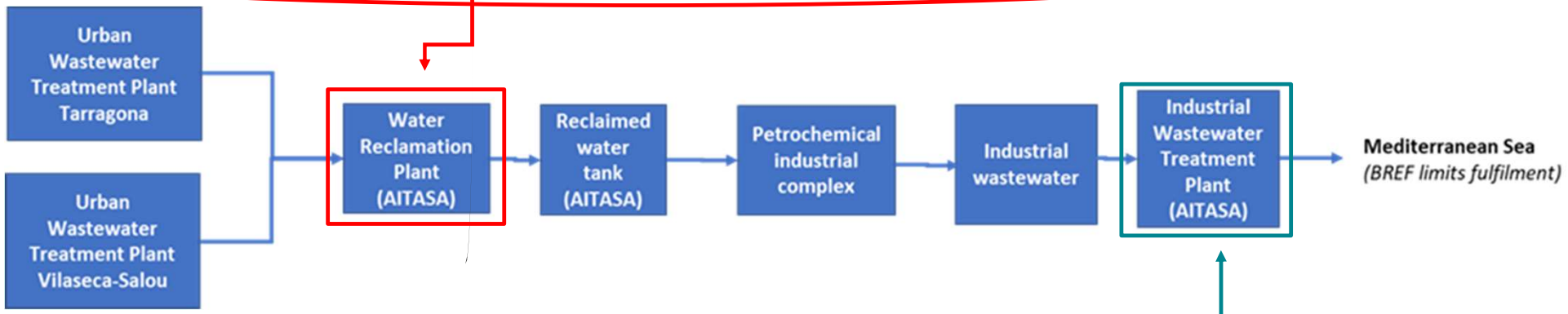
Objectives of the Ultimate solutions

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

→ **Water Reclamation Plant**:
- → Increase water recovery of the current WWRP with nZLD technologies
- → Remove the ammonium with low-cost technology (zeolite adsorption)



→ **Industrial Wastewater Treatment Plant**:
- → Defining a novel tertiary treatment with nZLD technologies (reverse osmosis and membrane distillation) to obtain reclaimed water

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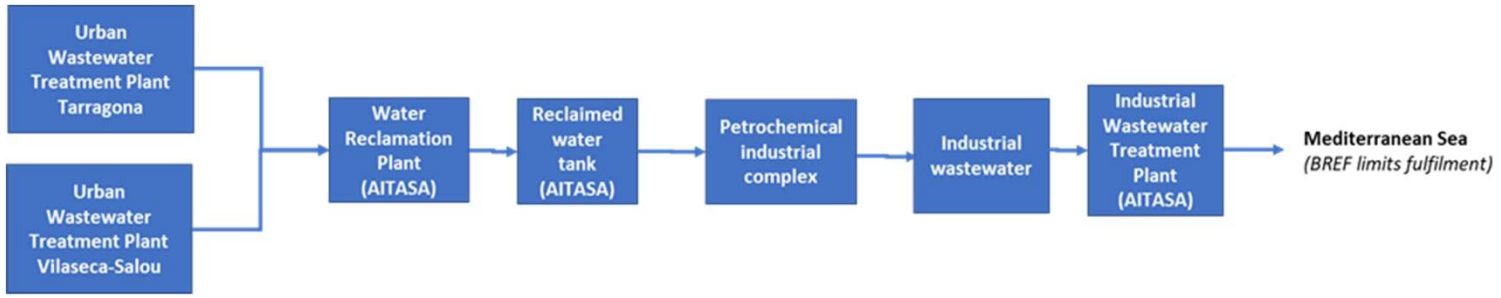
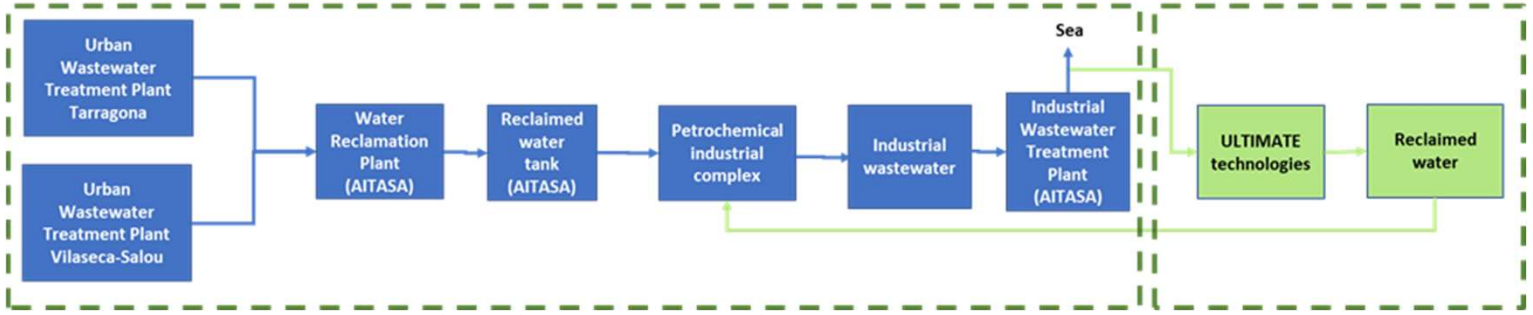
Increase reclaimed water production capacity

Phase 1:19,000 m^3/day (current)→ **Phase 2:** 29,000 m^3/day

Option 1: to increase reclaimed water production capacity in the current Water Reclamation Plant



Option 2: to produce reclaimed water treating the outlet of the Industrial Wastewater Treatment Plant→ ULTIMATE Project (Case Study 1)



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Camp de Tarragona Advanced Water Reclamation Plant

RECLAIMED WATER QUALITY

Since 2012, AITASA operates the Water Reclamation Plant (WRP) of Camp de Tarragona producing reclaimed water for boilers and cooling towers of the industry. Reclaimed water has to fulfil with Spanish Royal Decree 1620/2007 that includes the water requirements to be reused in the industry.

Parameter	Requirement	Units
Legionella	Absence	CFU/1 L
Nematode eggs	<1	Eggs/10 L
Escherichia coli	Absence	CFU/100 mL
Suspended solids	<5	mg/L
Turbidity	<1	TNU

Additionally, some restrictions are established for the reclaimed water at the outlet of the WRP to be reused in cooling towers.

Parameter	Requirement	Units
Ammonium	< 0.8	mg/L
Ortho-PO_4	<3	mg/L
BOD_5	<4	mg/L
TOC	< 15	mg/L
Conductivity	20-40	µS/cm

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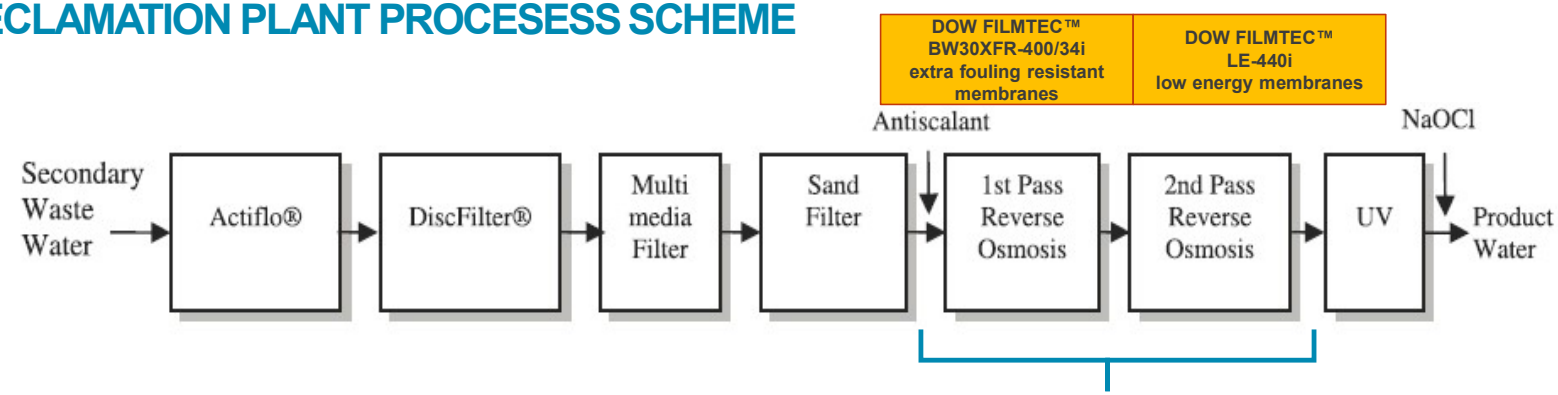
Camp de Tarragona Advanced Water Reclamation Plant

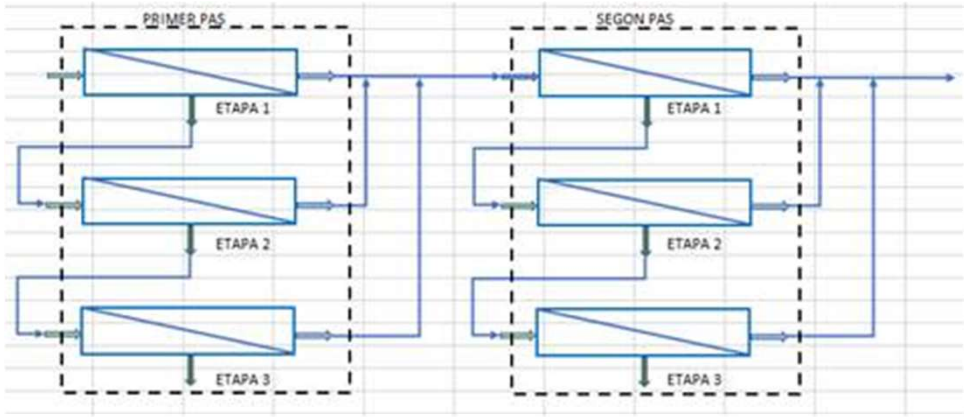
WATER RECLAMATION PLANT PROCESESS SCHEME



AMMONIUM REMOVAL ALTERNATIVE TECHNOLOGIES

- 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

AITASA CURRENT AMMONIUM REMOVAL PROCESS (RO)



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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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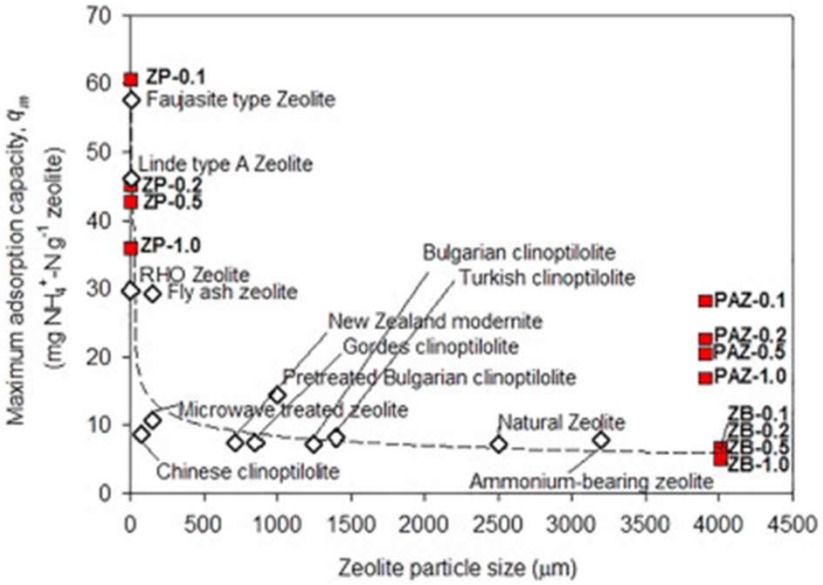
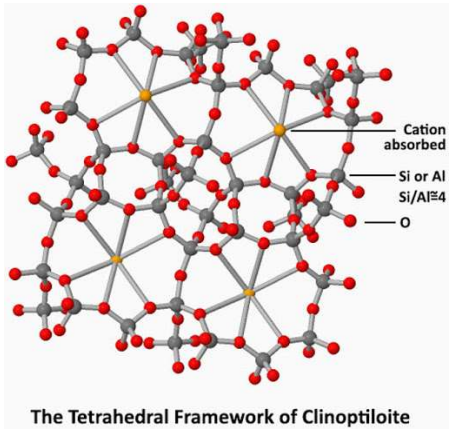
Ammonium removal from water by adsorption with zeolites

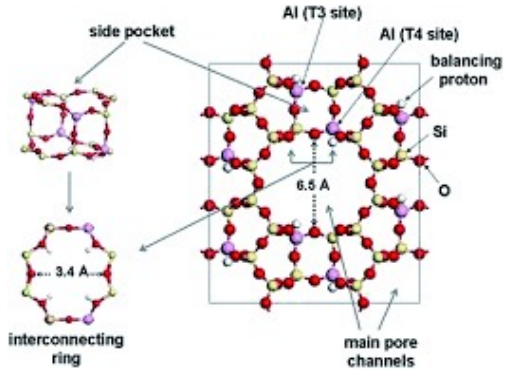
ZEOLITES SELECTION

- 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

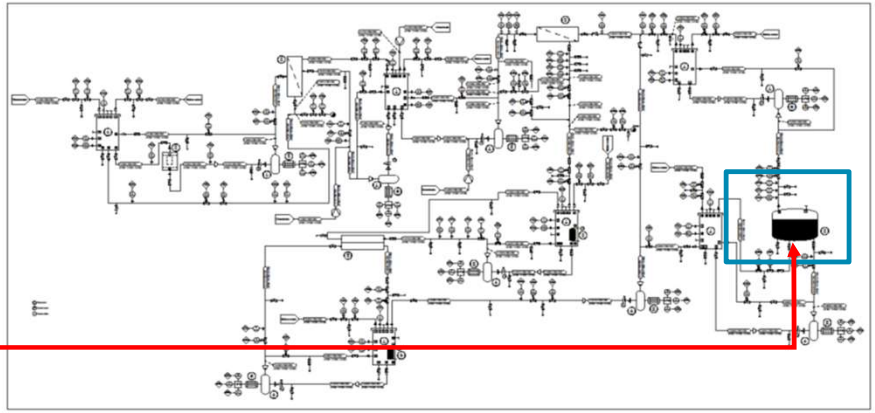
- **Experimental plan at laboratory scale:**
  - Zeolite type
  - Zeolite granulometry
  - Water flow rate (hydraulic time)
  - Bed length
  - Zeolite regeneration cycle (NaCl)

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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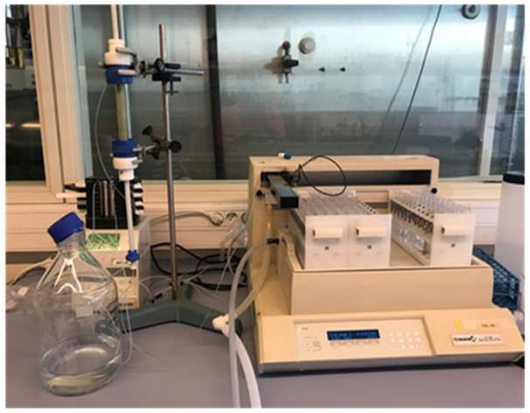
Pictures of the technologies at lab scale

Optimal operation conditions obtained experimentally at bench scale→ Pilot plant design

UF bench scale experimental set-up

RO bench scale experimental set-up

MD bench scale experimental set-up



Zeolite adsorption bench scale experimental set-up

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Ammonium adsorption on zeolite: experimental plan

General remarks:

- Tests were carried out with permeate from RO previous tests at laboratory scale
- This permeate was doped with ammonium to obtain ~35 mg NH_4/L at the inlet (ammonium concentration at the inlet of the RO process in WWRP)

Experimental plan:

1.- Zeolite selection: batch tests to determine adsorption capacity
2.- Break-through curves: ammonium adsorption capacity in continuous operation
3.- Regeneration

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Ammonium adsorption on zeolites: zeolite selection in batch tests

- Three different comercial zeolites were tested:
  - Zeolite 4 A(IQE) and Zeolite 13X (IQE)→ synthetic zeolite
  - Zeolita ZN Aqua (Zeocat)→ natural zeolite
- (*) Batch tests carried out with real water doped to 35 mg NH_4/L
- 2,5 g zeolite in 50 mL water
- Test duration=3h

Feed water		Zeolite		Outlet NH_4, mg/L	Adsorption capacity, mg NH_4^+/g zeolite
Type	NH_4, mg/L (*)	Type	Granulometry, mm		
Real water	35	Zeolite 4 A	0,003-0,005	19,7	0,31
Real water	35	SiOLITE 13X	0,002-0,006	7,1	0,56
RO permeate (70% recovery)	35	Zeocat ZN Aqua	0,5-1	3,5	0,63

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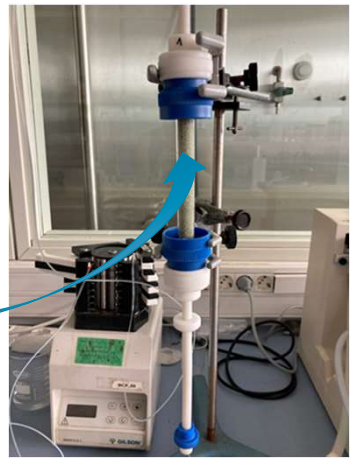
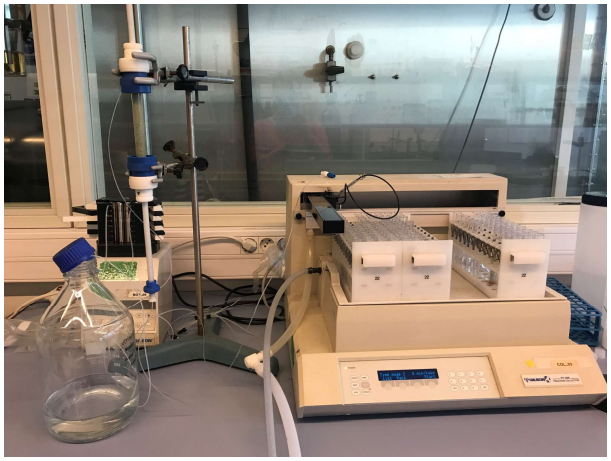
Ammonium adsorption on zeolites: experimental set-up





Column diameter=1 cm

Column height=10 cm

Zeolite Zeocat ZN Aqua (technical data sheet)	
Granulometry, mm	0.5-1
Composition	Clinoptilolite, 82-86%
Ammonium adsorption capacity	1,2-1,5 meq NH4/g media (21.6-27 mg NH4/g media)

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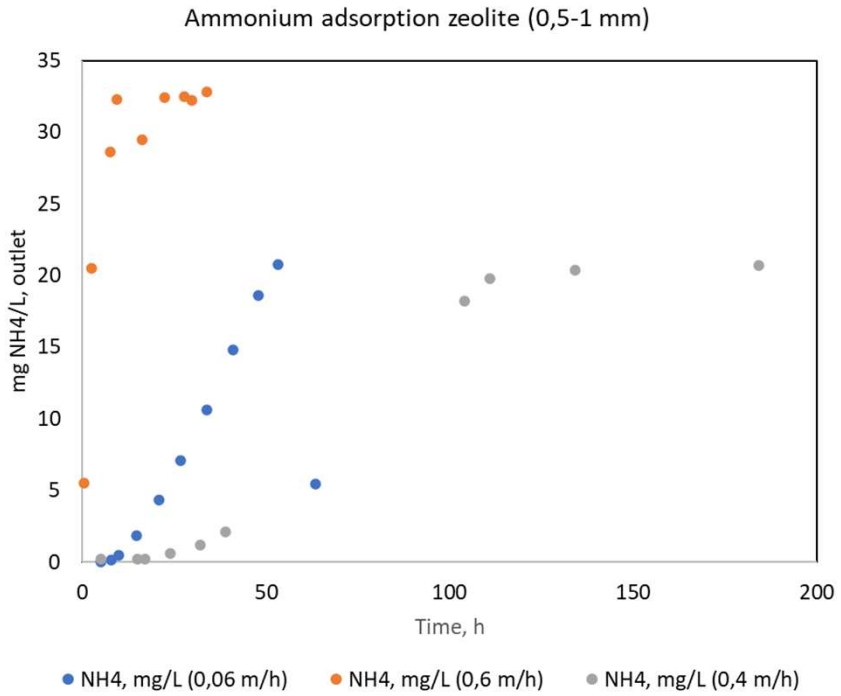
Ammonium adsorption on zeolites: breakthrough curves (continuous operation)

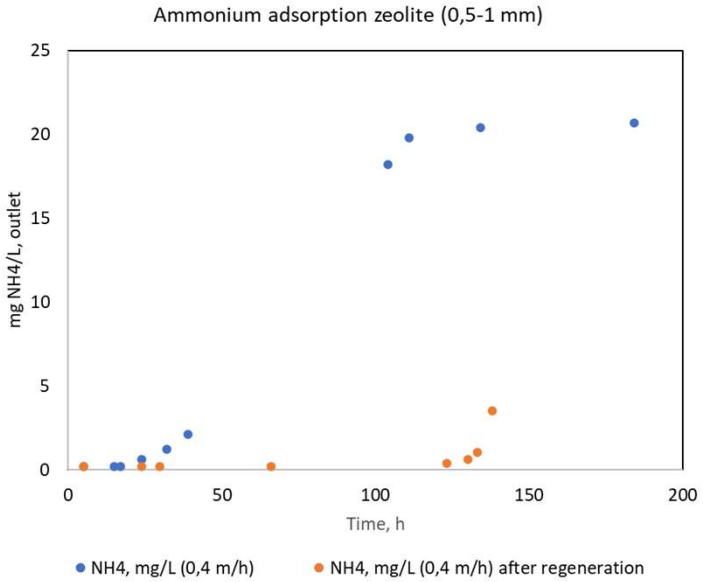


- Tests carried out with RO permeate obtained in previous tests and doped with ammonium
- Downflow operation
- Breakthrough time was calculated when NH_4 at the outlet was 0,8 mg NH_4/L.
- Three different bed contact times were tested (1,10 and 15 min)
- New zeolite was used in each experiment

Experimento	Column diameter, m	Column height, m	Zeolite weight, g	Water flow rate, mL/min	Water linear velocity, m/h	Hydraulic time, min	Break-through time, h	Initial concentration, mg NH4/L	Adsoprtion capacity, mg NH4/ g zeolita
1	0,01	0,1	7,74	0,78	0,60	10,1	11,1	41	2,8
2	0,01	0,1	7,68	7,86	6,00	1,0	0,07	36,7	0,2
3	0,01	0,1	7,68	0,5	0,38	15,7	26,7	28	2,9

Ammonium adsorption on zeolites: regeneration

- Regeneration with NaCl 10%
- Higher ammonium adsorption capacity after zeolite regeneration

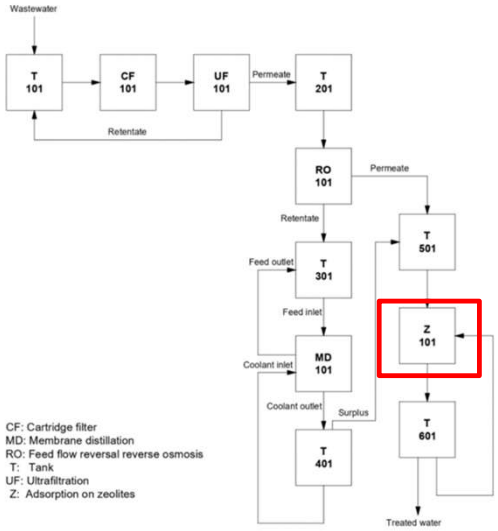


Experimento	Column diameter, m	Column height, m	Zeolite weight, g	Water flow rate, mL/min	Water linear velocity, m/h	Hydraulic time, min	Break-through time, h	Initial concentration, mg NH4/L	Adsoprtion capacity, mg NH4/ g zeolita
1-adsorption	0,01	0,1	7,74	0,78	0,60	10,1	11,1	41	2,8
2-adsorption-	0,01	0,1	7,68	7,86	6,00	1,0	0,07	36,7	0,2
3-adsorption	0,01	0,1	7,68	0,5	0,38	15,7	26,7	28	2,9
4-regeneration	0,01	0,1	7,68	1	0,76	7,9			0,0
5-adsorption	0,01	0,1	7,68	0,5	0,38	15,7	131,3	28,76	14,8

Technologies at pilot plant scale

Process	Treatment capacity
Cartridge filter (pre-treatment)	12 m^3/day
Ultrafiltration	12 m^3/day
Reverse Osmosis	12 m^3/day
Membrane Distillation	1 m^3/day
Zeolite adsorption	1 m^3/day

Maritim container and tanks



UF unit (left) and RO unit (right)

Membrane distillation

Adsorption with zeolites column

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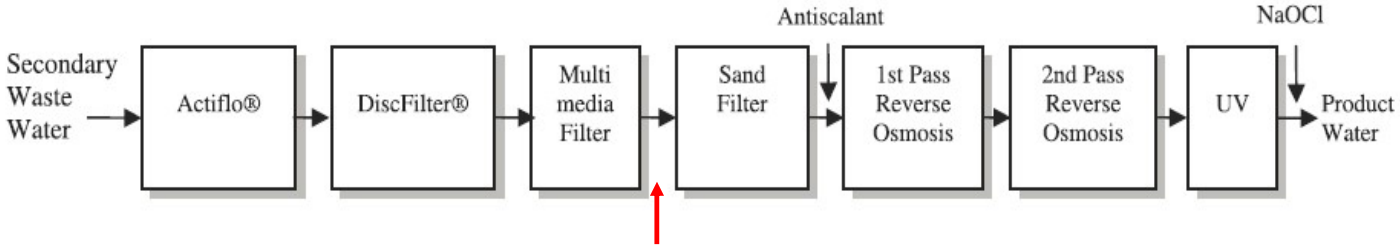
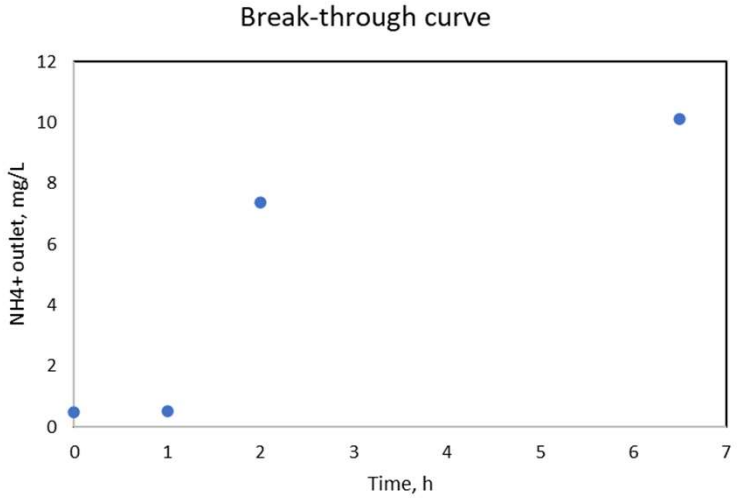
Pilot plant scale results

WATER RECLAMATION PLANT PROCESESS SCHEME



Pilot plant test was carried out with water at the inlet of the sand filters (before sodium hypochlorite)

Zeolita mass, kg	14.7
NH4 inlet water, mg/L	64.7
Linear velocity, m/h	5.5
EBCT, min	6.8
Adsorption capacity, mg NH4/g zeolite	0.7



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Pilot plant scale next steps

- To determine ammonium adsorption capacity at different linear velocities and EBCT
- To determine ammonium adsorption capacity at different ammonium inlet concentration
- To assess regeneration process and reuse of the regeneration solution and ammonium recovery
- To estimate operational costs: energy, regeneration solution, etc

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WATER SMART INDUSTRIAL SYMBIOSIS

Thank you!

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