ULTIMATE

WATER SMART INDUSTRIAL SYMBIOSIS

Use of by-products of local industries for wastewater treatment in Rosignano

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June, 23rd 2021

ULTIMATE Project

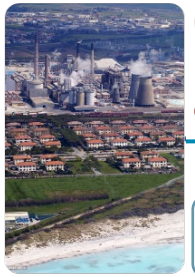
9 DEMOSITES

ULTIMATE will implement Water Smart Industrial Symbiosis in nine large-scale business cases from the international agro-food, petrochemical and biotech sector.

- 1- Tarragona (ES)
- 2- Nieuw Prinsenland (NL)
- 3- Rosignano (IT)
- 4- Nafplio (EL)
- 5- Lleida (ES), Ostrava (CZ)
- 6- Karmiel, Shafdan (IL)
- 7- Tain (UK)
- 8- Saint-Maurice l'Exil (FR)
- 9- Kalundborg (DK)

Cecina municipality

Unpredicted Saltwater intrusion



Unpredicted Saltwater intrusion

Rosignano municipality

Cecina WWTP

Rosignano WWTP

Aretusa WWTP

High values of salinity, hardness and COD

Groundwater

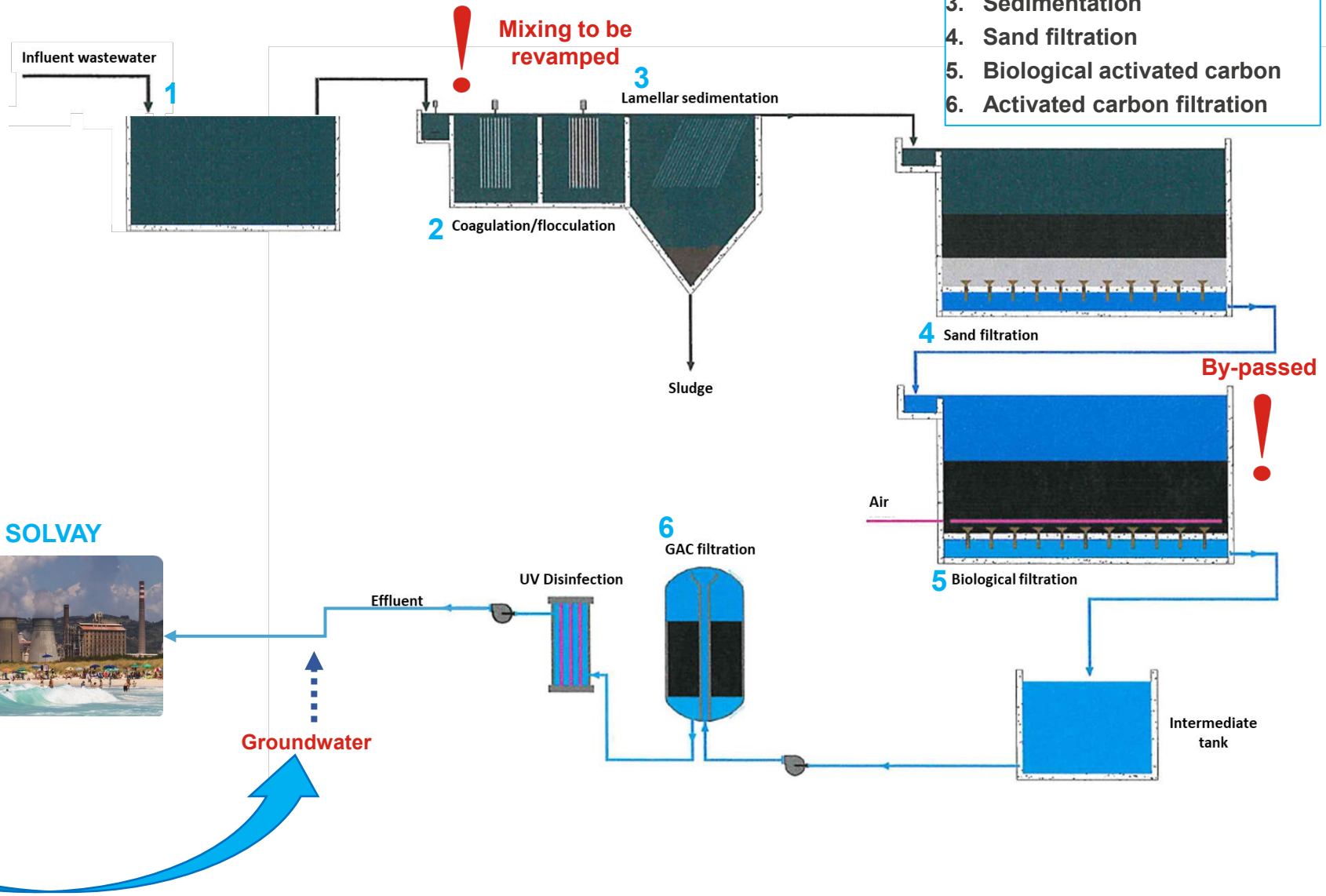
Solvay industry

ARETUSA WWRP

1. Equalization
2. Coagulation/flocculation
3. Sedimentation
4. Sand filtration
5. Biological activated carbon
6. Activated carbon filtration

Contractual parameters to be respected for SOLVAY reuse

PARAMETRI SPECIFICI - SPECIFICA TECNICA DI QUALITA' DEI REFLUI POST-TRATTATI			
N°	Descrizione file:specar1	Unità di misura	Specifica Tecnica
			.Riferimento contrattuale
1	Cl-	ppm	≤ 500
2	NH4	ppm	≤ 8
3	Solidi Sospesi	ppm	≤ 2
4	Conduncibilità	micros.	≤1.030
5	Alcalinità	ppm CaCO3	≤ 340
6	Ca	ppm Ca	≤ 160
7	Mg	ppm	≤ 45
8	SO_4	ppm	≤ 140
9	Fe	ppm	≤ 0,1
10	Si	ppm SiO2	≤ 30
11	Mn	ppm	≤0,4
12	PO_4	ppm	≤ 3
13	Al	ppm	≤ 0,1
14	As	ppm	≤ 0,2
15	Ba	ppm	≤ 2,5
16	Fluoruri	ppm F	≤ 0,1
17	Grassi ed Olii Totali	ppm	≤ 1
18	COD	ppm O2	≤ 10
19	Tensioattivi Totali	ppm	≤ 0,5
20	BOD		≤10
21	Esch. Coli	CFU/100ml	≤ 250
22	Coli Tot.	CFU/100ml	≤ 250
23	Strep. Coli	CFU/100ml	≤ 20
24	Batteri Filamentosi		assenti

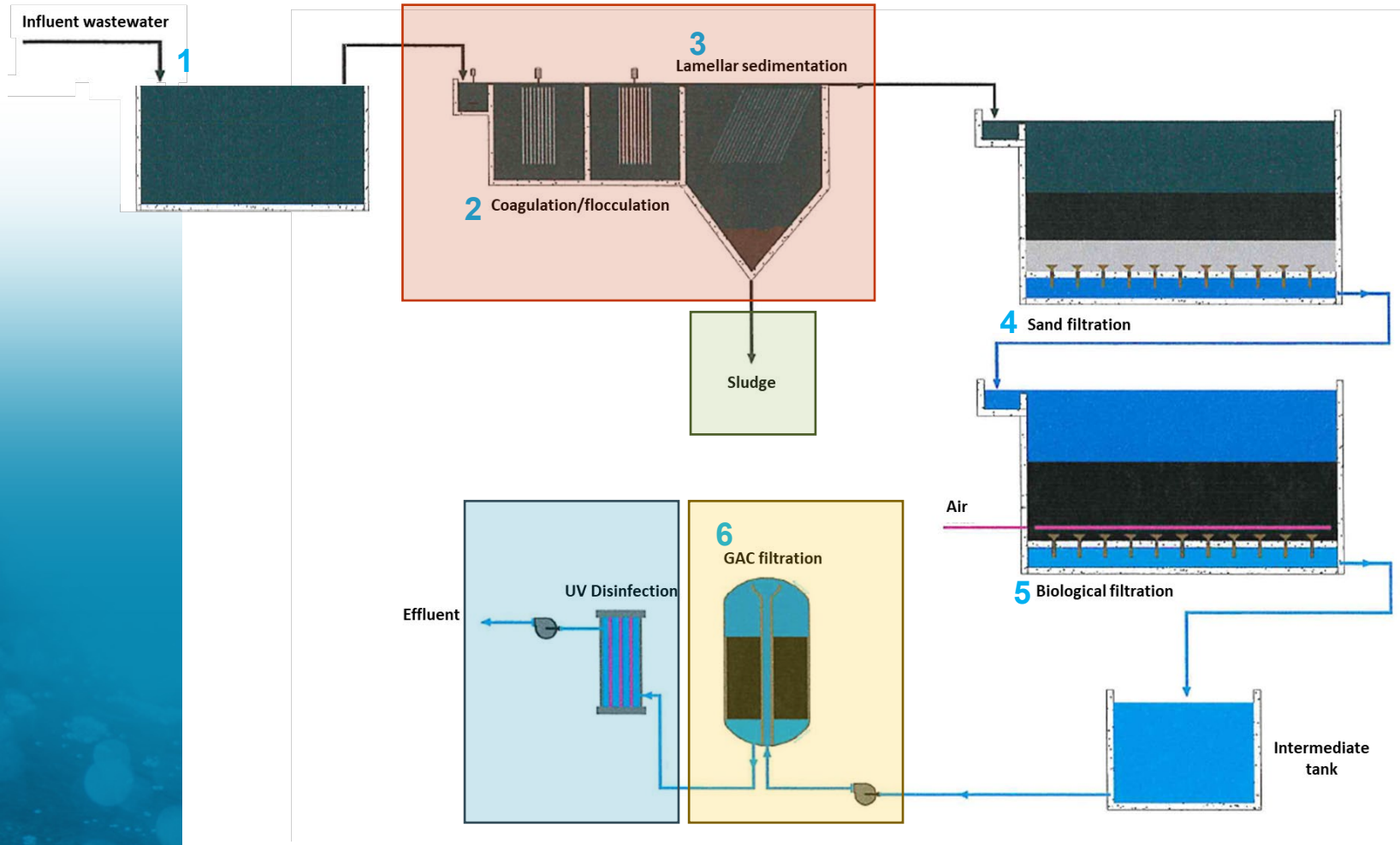


When needed (internally agreed) water quality standard are not reached

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 Solutions

1. Equalization
2. Coagulation/flocculation
3. Sedimentation
4. Sand filtration
5. Biological activated carbon
6. Activated carbon filtration



ULTIMATE SOLUTIONS

✓ The possibility to re-use the chemical (alum/ferric) sludge from coagulation/flocculation in the WWRP will be analysed and potential users will (potentially) be identified via the Alu Circles initiative.

✓ A pilot scale adsorption system will be tested with alternative sludge-biowaste-originated GAC.

✓ Mineral by-products will be used as alternative coagulants and/or adsorbent.

✓ Possible residual disinfectant agents will be tested in order to improve disinfection.

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Possibility to re-use the chemical (alum/ferric) sludge and potential users identified via the Alu Circles initiative

The ALU Circles initiative (https://www.alliedwaters.com/project/alucircles/) is addressing the challenge to convert the alum sludge from one-off use of material into a sustainable solution, such as upcycling or recycling, at a lower cost.

PLANNED ACTIVITIES

1. Mass flow analysis : Production of Al/Fe sludge in Italy and contacts with major water utilities (problem owners)

2. Fate of the Al/Fe sludge: Current disposal/reuse routes and related costs

3. Characterization of Al/Fe sludge: Physical-chemical parameters

4. Preliminary assessment of possible applications: absorbents/coagulants in wastewater treatmnent, geotechnical, geo-environmental and building sectors

5. Experimental tests: Mechanical properties in construction materials / removal efficiencies in tertiary wastewater treatment

6. Local and regional impact by LCA and LCC of the most promising solutions

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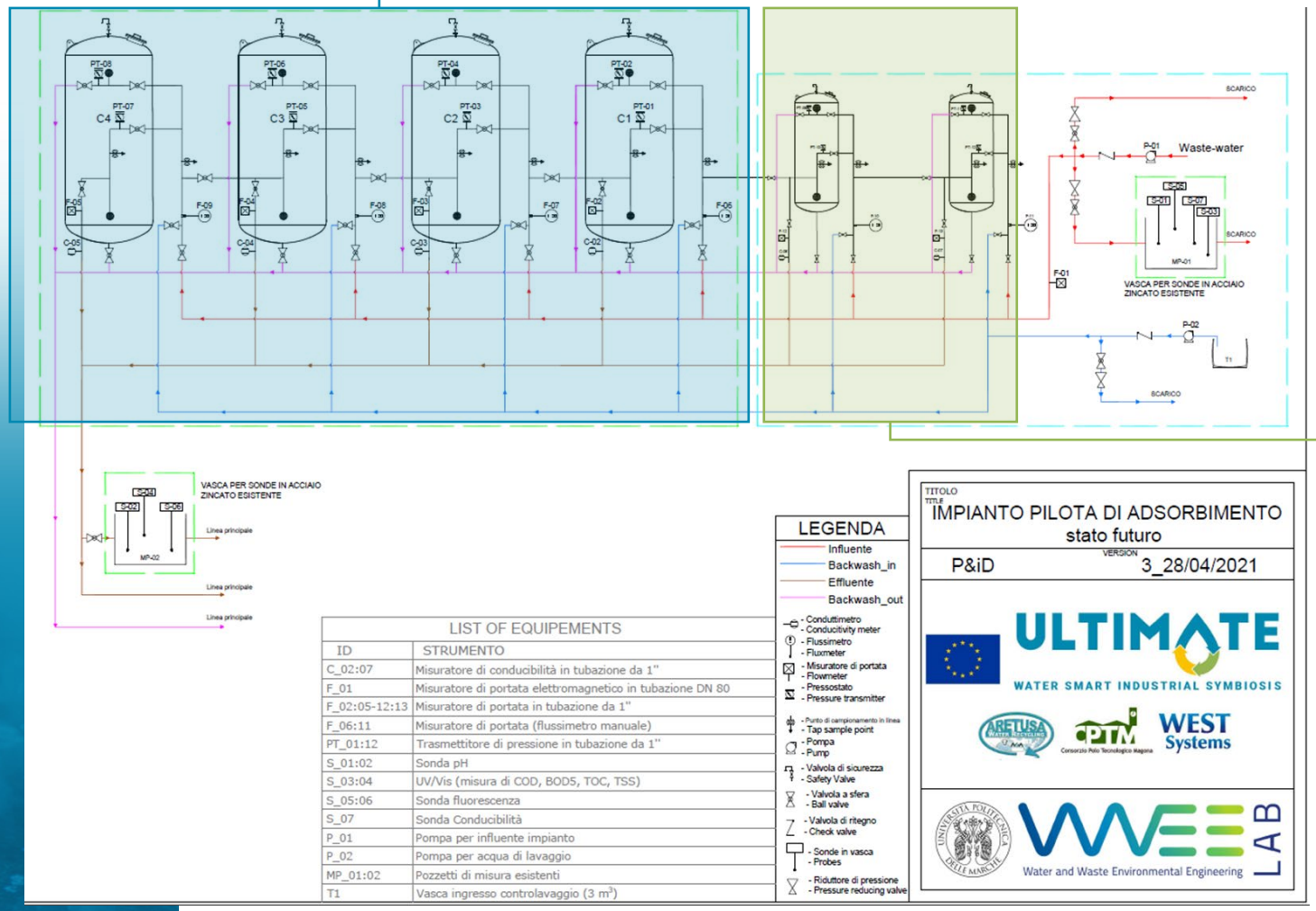
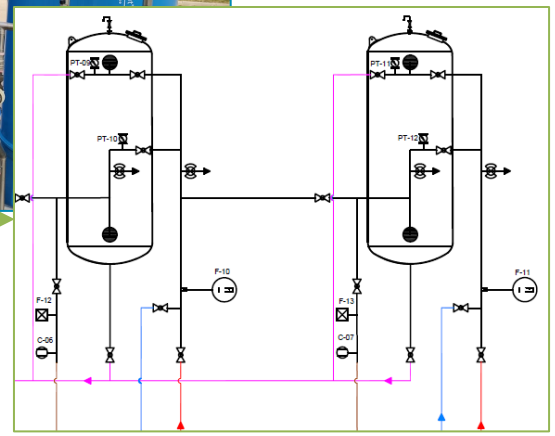
A pilot scale adsorption system will be tested with alternative GAC.



LIST OF EQUIPEMENTS

ID	STRUMENTO
C_02:07	Misuratore di conducibilità in tubazione da 1"
F_01	Misuratore di portata elettromagnetico in tubazione DN 80
F_02:05-12:13	Misuratore di portata in tubazione da 1"
F_06:11	Misuratore di portata (flussimetro manuale)
PT_01:12	Trasmettitore di pressione in tubazione da 1"
S_01:02	Sonda pH
S_03:04	UV/Vis (misura di COD, BOD5, TOC, TSS)
S_05:06	Sonda fluorescenza
S_07	Sonda Conducibilità
P_01	Pompa per influente impianto
P_02	Pompa per acqua di lavaggio
MP_01:02	Pozzetti di misura esistenti
T1	Vasca ingresso controlavaggio (3 m³)



	Bigger columns	Smaller columns
Numbers	4	2
Volume (m3)	0.6	0.11
Diameter (m)	0.8	0.32
Material (kg)	325	60

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A pilot scale adsorption system will be tested with alternative GAC.

ULTIMATE INNOVATIONS

✓ **Monitoring system → sensors and probes**

Influent and effluent from the pilot will be monitored with:

- Conductivity
- pH
- UV/Vis (COD, BOD5 and TOC)
- Fluorescence

ID	INSTRUMENTS	Q. ty	Position	Characteristics
PT-01:08	Pressure transmitter	12	Influent and effluent from each column	0 – 1 bar
F-02:05	Electromagnetic water meter	6	Effluent from each column	0 – 10 m3/h
C-02:05	Insertion inductive conductivity digital probe	6	Effluent from each column	250 µS - 2,5 S/cm
S-01:02	pH meter	2	Influent and effluent	pH:0-14; T=-5° C - 50° C
S-03:04	UV/Vis meter (254 nm)	2	Influent and effluent	Measuring cell: 5 mm Measuring range: 0.1-600.0 m-1 Calibrable on the COD and TOC parameters Compensation: 550 nm Cleaning system: automatic by wiper Measuring interval:> 1 min
S-05:06	Fluorimeter	2	Influent and effluent	filter band for wavelengths centered on ex/em 345/440 nm
S-07	Conductivity meter	1	Influent	250 µS - 2,5 S/cm
F-01	Electromagnetic water meter	1	Influent	0 – 50 m3/h

✓ **Innovative material as adsorbents →** **EXPERIMENTAL ANALYSIS ONGOING!**

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Mineral by-products will be used as alternative coagulants and/or adsorbent

In the past 140 t per year of aluminium polychloride, and 12 t per year of polyelectrolyte were used. **At the moment no reagent is used, and some mixers needs revamping**

ULTIMATE will test and assess the possibility of using industrial by-products

EXPERIMENTAL ANALYSIS ONGOING

COAGULATION/FLOCCULATION UNIT	Rapid mixing (coagulation)	Medium agitation (primary flocculation)	Slow mixing (secondary flocculation)
Number of tanks	2	2	2
Volume (m3)	5.73	73	72

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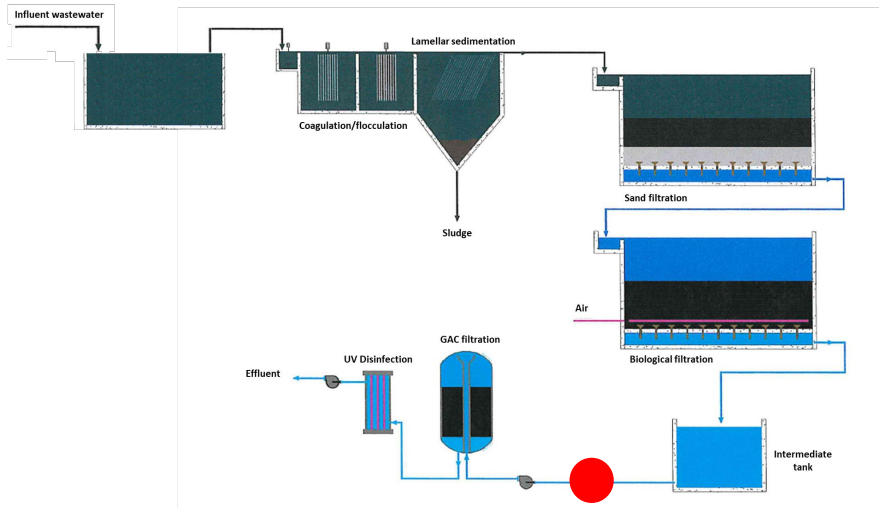
Characterization of the water sample collected in May 2021

Sample was collected at Aretusa plant before the final GAC stage in order to find a higher COD concentration.

Measured values are compared with the average, minimum and maximum from historical data, and with the Aretusa specification.

		Average	Min	Max	Measured	Aretusa-Solvay contractual constraint
pH	-	7.6	7.0	7.9	7.7	
Electrical conductivity	µS/cm	2580	1010	7340	2134	1030
Cl^-	mg/l	568	159	2079	398	400
$NO3^{--}$	mg NO3/l	57	8	128	45	
$PO4^{---}$	mg PO4/l	/	5	15	10	
$SO4^{--}$	mg/l	/	100	150	132	
Ca	mg/l	/	140	180	145	
Mg	mg/l	/	45	60	54	
K	mg/l	/	13	18	17	
Na	mg/l	/	225	305	232	
COD	mg O2/l	25	10	88	20	10



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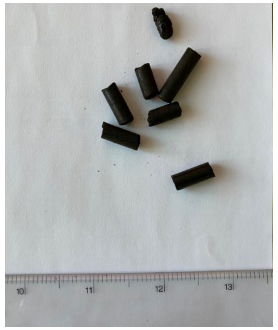
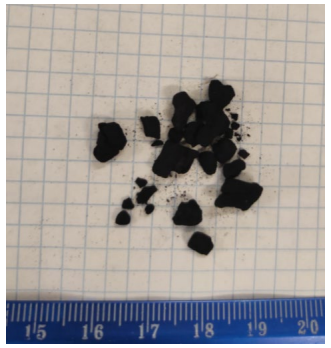
Industrial by-product

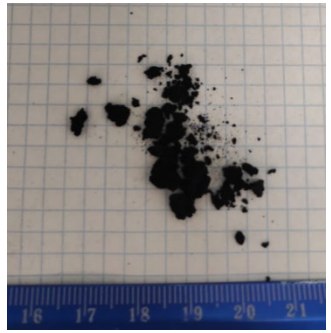
- Bentonite OC by-product “Scarto centrifuga”

- Hydro-char from municipal sewage sludge



Hydrochar activated with different processes





- Granulated Limestone rocks only partially calcinated

- Na2CO3 “Soda Solvay® Light” >> out of specification

- NaHCO3 >> out of quality standard

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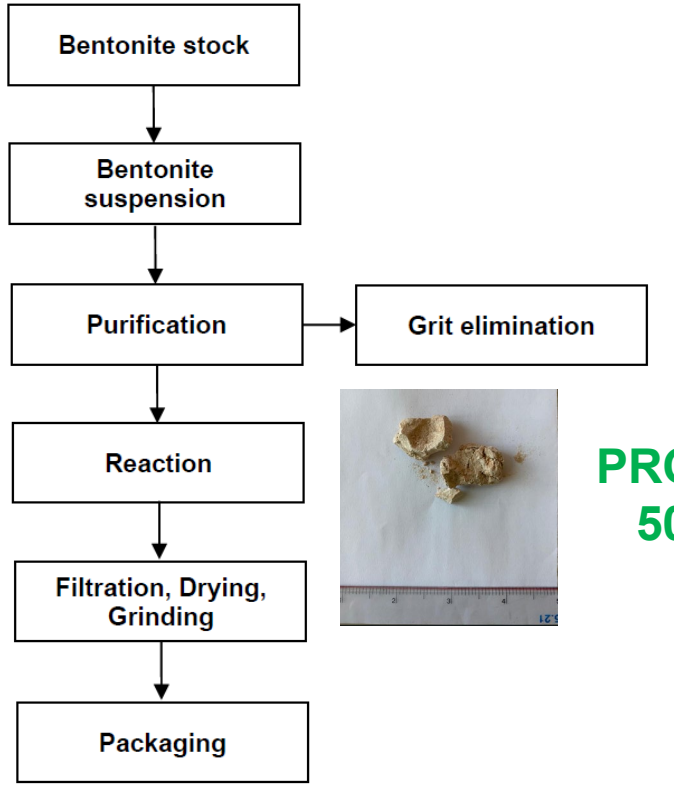
Horizon 2020 research and innovation programme under grant agreement

Adsorbent materials for COD removal

Bentonite OC by-product “Scarto centrifuga” – LAV1

This **by-product** comes from **Laviosa Chimica Mineraria SpA** plant (located about 30 km from Aretusa).
Laviosa activities consists in extracting, processing and distributing industrial mineral products, in particular bentonitic products and special ‘modified’ bentonitic products called “Organo-clay”.
From the necessary purification stages in the organo-clay production process comes this **‘grit’ that is poor in bentonite but rich in zeolite and other silicates: it comes from a decanter separation and looks like a semi solid sludge.**



PRODUCTION
50 t/month

Technical specifications

Le analisi effettuate di diffrazione ai raggi X dimostrano che la fase più abbondante risulta quella zeolitica e le altre fasi sono silicate quali calcite, plagioclasio, miche ed altri riportati nella tabella sottostante:

XRD

Fase	Quantità [%]
Zeoliti	33
Calcite	28
Plagioclasio	15
Quarzo	10
Mica	8
K-feldspato	6

L’umidità risulta mediamente del 35 % in massa e la perdita alla calcinazione del 11,67 %.

La composizione degli ossidi invece risulta come nella seguente tabella:

Oxides composition

Analita	Quantità [%]
Na_2O	1,80
MgO	0,86
Al_2O_3	11,75
SiO_2	59,05
P_2O_5	0,35
K_2O	2,76
CaO	9,85
TiO_2	0,30
MnO	0,40
Fe_2O_3	1,22

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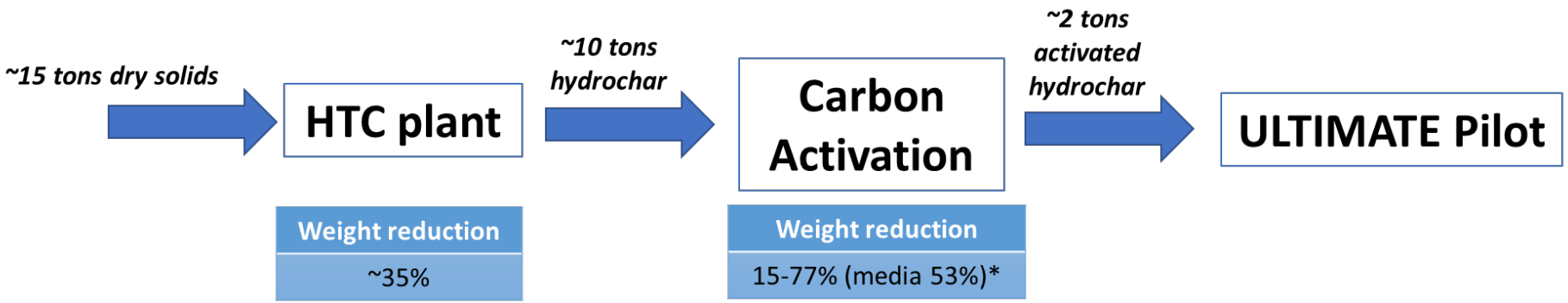
Adsorbent materials for COD removal

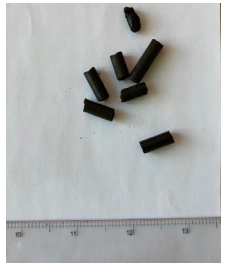
Activated Hydro-char from municipal sewage sludge

Hydrochar (HC) was supplied by the **Spanish company Ingelia SL**: this biocarbon is the product of a **Hydrothermal Carbonization (HTC)** process which, operating at relatively low temperature and pressure conditions in the presence of liquid water, **converts the biomass or municipal sewage sludge, in a carbonaceous solid (bio-lignite).**

Operating on small quantities, in CPTM laboratory, the **HC was activated** in order to be tested as an adsorbent material. **The activation procedures**, suggested by the scientific literature, **were physical (thermal) and chemical**.



Hydrochar from municipal sewage sludge



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Adsorbent materials for COD removal

Activated Hydro-char from municipal sewage sludge

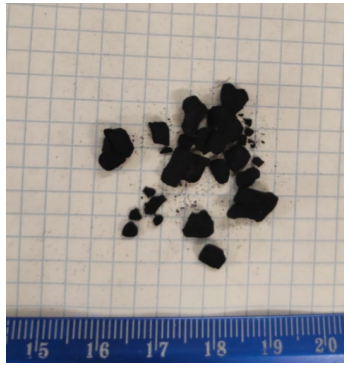
Physical activation – ATT1

- Heating of the char pellets in a tubular oven up to 700°C (5°C/min) with N_2 purging.
- CO_2 flushing and isotherm for 2 hr.
- Cooling of the tubular furnace in N_2 purging.

47% WEIGHT LOSS

Chemical activation – ATT4

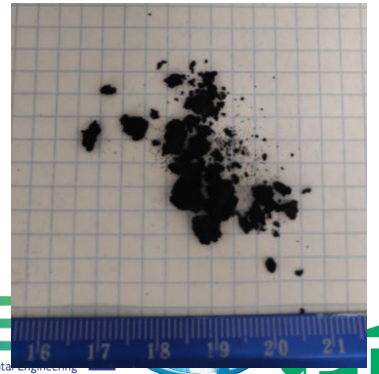
- Impregnation of char pellets in KOH aq. solution (KOH to char ratio: 1:1) at 60°C for 6 hr.
- Drying of the impregnated char at 105°C.
- Heating in a tubular oven up to 600°C (5°C/min), isotherm at 600°C for 1 hr and cooling (5°C/min) with N_2 purging.
- Washing with 1M HCl and demi water (up to pH 7).
- Drying at 105°C until constant weight.



55% WEIGHT LOSS

Chemical activation – ATT5

- Mixing of the char pellets (previously grounded) with KOH in flakes (KOH to char ratio: 1:1).
- Heating in a tubular oven up to 600°C (5°C/min), isotherm at 600°C for 1 hr and cooling (5°C/min) with N_2 purging.
- Washing with 5M HCl and demi water (up to pH 7).
- Drying at 105°C until constant weight.



60% WEIGHT LOSS

Horizon 2020 research and innovation programme under grant agreement No 869318

Adsorbent materials for COD removal

Commercial activated carbon – CA1

CARBONITALIA
activated carbon & bleaching earths

Review : 6
Date of issue : February, the 1st 2018

Technical Data Sheet

FILTERCARB GCC 8X30

Granular Activated Carbon obtained from specially selected grades of coconut shell, specially designed to remove pollutants from water, odours and bed tests from beverages like edible oils, wine, beer, ex...

STANDARD SPECIFICATIONS

Specification	Units	Values	Methods
BET Surface	m^2/g	1100-1150	BET N2
Ash content	%	2-4	CEFIC 1986
Bulk content	g/cm^3	0,45-0,50	CEFIC 1986
Moisture	%	5	CEFIC 1986
Iodine index	mg/g	1000-1100	CEFIC 1986
CTC	%	55-65	Method on request
Hardness	%	95	Method on request
Chlorine half-length value	cm	3	Method on request
Grain size distribution			Sieving analysis
> 8 mesh (2,36 mm)	%	5	
< 30 mesh (0,60 mm)	%	5	
Uniformity coefficient		max 1,7	

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Adsorbent materials for COD removal

Adsorbent materials characterization

Leaching test

Test followed the EN 12457-2:2002 for the waste characterization (liquid to solid ratio of 10 L/kg).

Concentrations are expressed as ppm in the leached solution.

	LAV1	HC	HC ATT1	HC ATT4	HC ATT5
F^-	< 0.1	54.2	0.2	0.4	< 0,1
Cl^-	2,5	44.4	62.5	26.4	1.7
$NO3^-$	0.2	1.3	< 0,1	< 0,1	< 0,1
$PO4^{---}$	3.2	38.5	< 0,1	54.3	8.4
$SO4^{--}$	32.9	147.3	143.9	110.2	103.4
COD	81	4200	< 15	< 15	< 15

- **NEED OF PRE-TREATMENT (WASHING) OF THE HC**
- **FURTHER TEST FOR ADSORPTION IN THE INTEGRATED SYSTEM (ROSIGNANO-CECINA WWTP)**

BET analysis

	LAV1	HC ATT1	HC ATT4	HC ATT5	CA1
Specific surface area (m^2/g)	6	117	449	752	1100÷1150
Specific pore volume (cm^3/g)	0.003	0.055	0.214	0.359	/
Average pore radius(Å)	50.23	13.61	15.16	16.08	/

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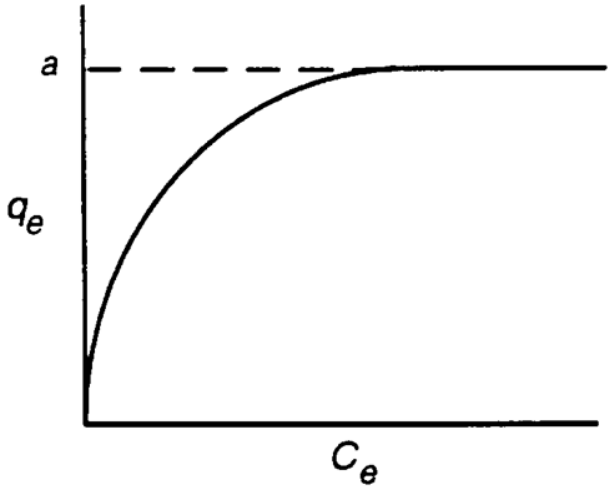
Adsorbent materials for COD removal

Preliminary adsorption tests with Methylene Blue (MB) solution

MB solutions are commonly used for comparative adsorption tests on activated carbon and they simulate chemical substances with an effective molecular diameter of 15 Å.

The Adsorption capacity (q_e) is the amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent at equilibrium conditions. It changes with the final equilibrium concentration of the adsorbate in the solution (c_e) and an 'isotherm curve' can be realized for each material tested.



This is a 'Langmuir isotherm' that describes the most common adsorption mechanism of an activated carbon.

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Adsorbent materials for COD removal

Preliminary adsorption tests with Methylene Blue (MB) solution

CPTM is currently completing these preliminary tests in order to compare the different adsorbent materials.

PRELIMINARY RESULTS >> TEST STILL ONGOING!

	c_e (mg_{MB}/L)	q_e (g/kg)
LAV1	0.6	11
ATT4	0.1 4.0	305 321
CA1	0.1 0.9	304 383

LAV1 material (Bentonite OC by-product by Laviosa) **shows a lower adsorption capacity** compared to the chemically activated HC ATT4 and to the commercial activated carbon.

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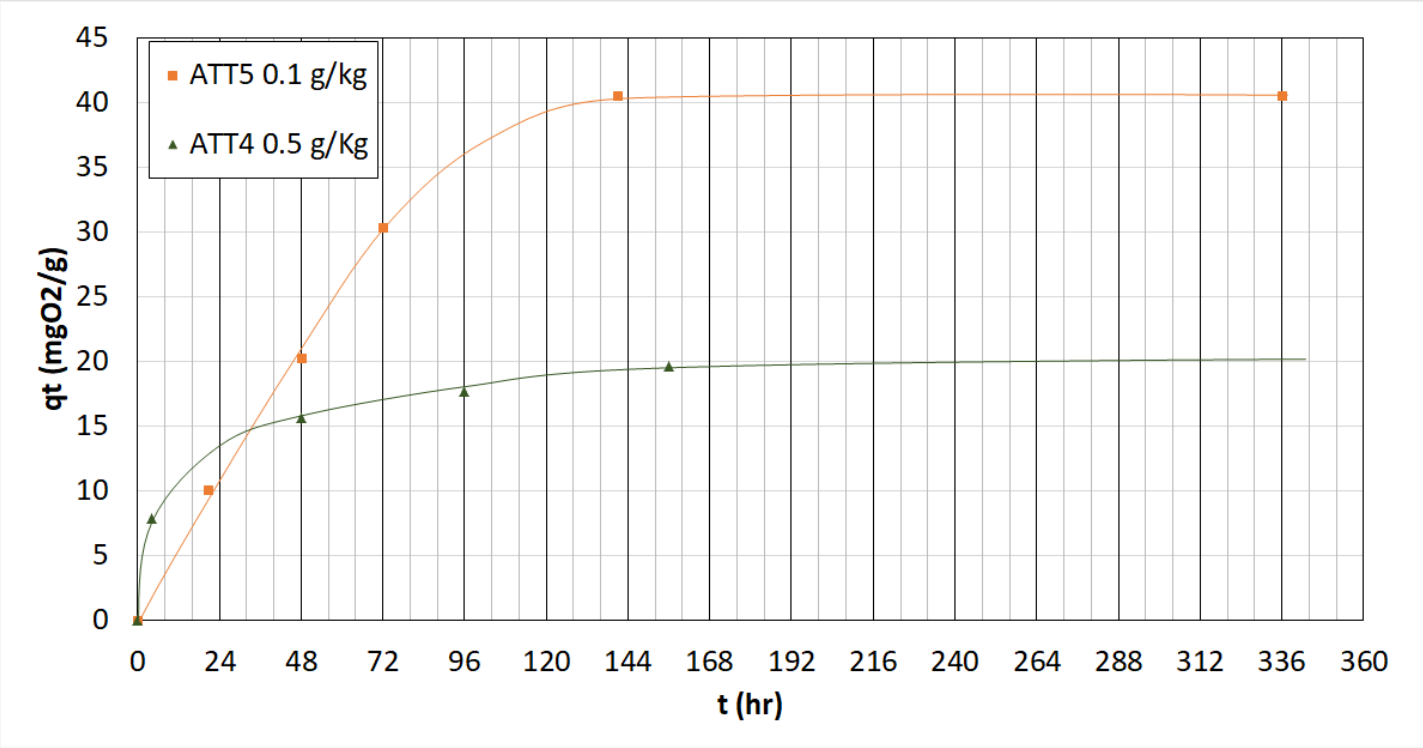
Adsorbent materials for COD removal

Adsorption tests with Aretusa water sample (COD reduction)

ARETUSA sample → **COD = ~20 mgO_2/L.**

Kinetic adsorption tests:

Here below an example of two kinetic adsorption curves: the scope of these tests is to evaluate the minimum time necessary to reach the equilibrium state and find the Adsorption capacity (qe) of the material.



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Adsorbent materials for COD removal

Adsorption tests with Aretusa water sample (COD reduction)

CPTM is currently completing these preliminary tests in order to compare the different adsorbent materials that can be used for the COD reduction in the Aretusa water.

PRELIMINARY RESULTS >> TEST STILL ONGOING!

	c_e (mgO_2)/L	q_e (g/kg)
LAV1	16	4.0
ATT4	7 17	19.6 20.0
ATT5	9 15	40.5 40.0

These tests confirmed that **LAV1 material** (Bentonite OC by-product by Laviosa) **shows a lower adsorption capacity compared to the chemically activated HC** ATT4 and ATT5.
ATT5 shows a better adsorption capacity than ATT4 probably caused by the higher specific surface area previously described (752 and 449 m2/g).

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Adsorbent materials for COD removal

Preliminary conclusions

- ✓ Both from the preliminary tests conducted with MB solutions and from those conducted with the real water sample, it can be anticipated that the adsorption capacity of LAV1 is much lower than that of activated HCs and unfortunately does not probably justify its possible use as an adsorbent material.

- ✓ The different activated HCs will be compared with the commercial activated carbon.

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Softening tests

HARDNESS (mg_{CaCO3}/L)	
Direct measure*	Aretusa-Solvay contractual limit
520	340

*Direct measure with EDTA complexometric titration

Hardness overcome the contractual limit requested by SOLVAY !

Specific analyses have shown that about 50% of the total hardness is temporary hardness essentially due to Ca(HCO3)2 while the remaining part of 50% is due to the permanent hardness which is mainly composed of chloride, sulphate and nitrate of Mg.

SOFTENING TECNIQUES: *lime and the lime-soda ash process.*

- ✓ "Precotto": granulated limestone rocks only partially calcinated and slacked, with a declared content of $Ca(OH)_2$ of about 9%.
- ✓ Na_2CO_3 "Soda Solvay® Light" product that resulted to be out of specification.

Solvay Chimica Italia SpA by-products tested

SOLVAY

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

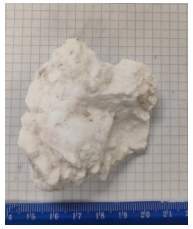
Softening tests

Solvay by-product and OOS were compared to pure laboratory lime and soda ash.

Lime process

$Ca(OH)_2$	Pure product	'Precotto' Solvay
Concentration (mg/L)	583	1074
pH after the reagent addition	10.8	10.5
Final total hardness measured	277	238
Total hardness reduction	**46%**	**54%**

Lime - Soda ash process



$Ca(OH)_2$	Pure product	'Precotto' Solvay
Concentration (mg/L)	622	1349
Na_2CO_3	Pure product	'Soda Light' OOS
Concentration (mg/L)	631	1419
pH after each reagent addition	11.0 – 11.2	11.0 – 10.7
Final total hardness measured	69	71
Total hardness reduction	**87%**	**86%**

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Softening tests

Preliminary conclusions

- ✓ Solvay annual production of ‘Precotto’ and of out-of-spec ‘Soda Light’ is absolutely sufficient to treat the total Aretusa water output.
- ✓ The preliminary tests conducted shows a very good total hardness reduction.
- ✓ Specific tests will be carried out to optimize the exact dosage of the two reagents and to evaluate the generated sludge amount.

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