



Advancing Sustainability of Process Industries through Digital and Circular Water Use Innovations

AquaSPICE

Final Conference

CS#6 Tüpras (Turkey)

12th December 2024

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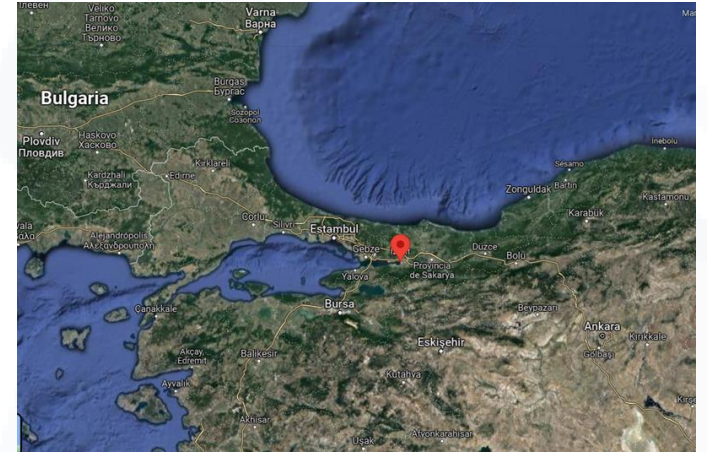
The AquaSPICE project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958396.

Tüpras is the first producer in Turkey's refining sector and the largest industrial enterprise of the country, operating four oil refineries with a total annual processing capacity of 30 million tons crude oil.

Oil and gas refining industry is highly water intensive consumer, requiring huge amounts of water, used as: cooling water, service water, firefighting water, demineralization water and for steam production.

Nowadays, Tüpras Izmit Refinery is consuming:

- fresh water from a nearby lake
- treated wastewater from its own wastewater treatment plants

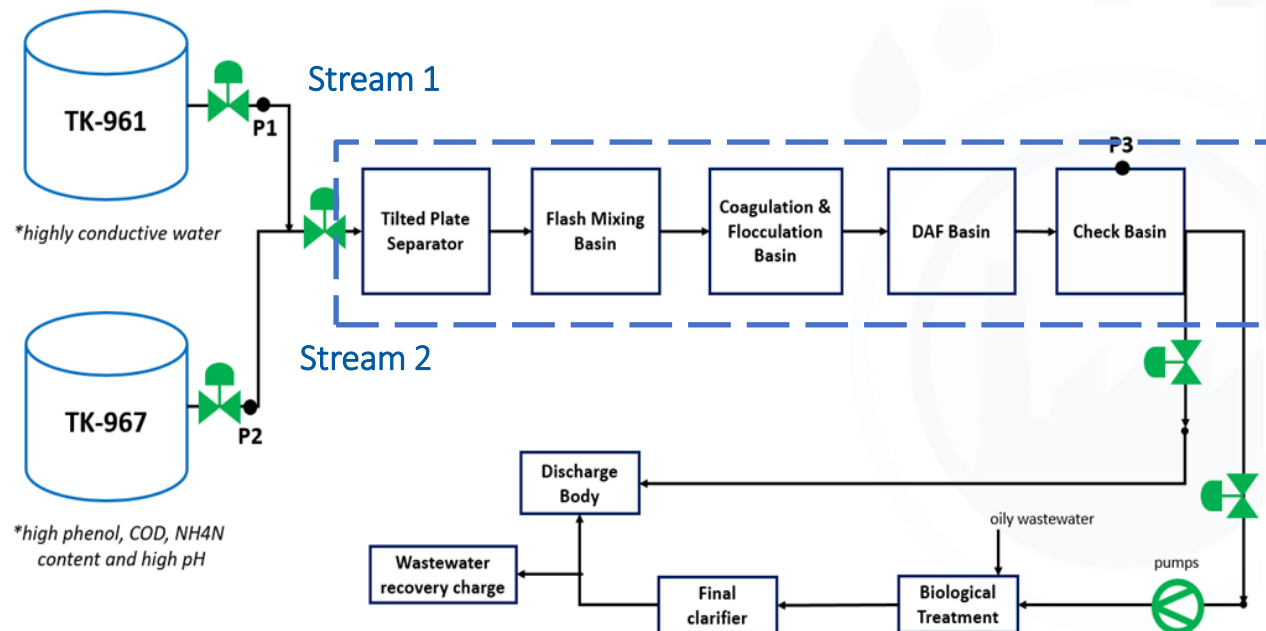


BALLAST WATER TREATMENT PLANT

The wastewater treatment system that is studied in the scope of AquaSPICE project is **ballast water treatment system**.

2 different streams are involved in the scope of the AquaSPICE Project:

- **Stream 1:** It is not rich with pollutants
- **Stream 2:** It is highly polluted with high levels of COD, phenol, $\text{NH}_4\text{-N}$ and S^{-2} and high pH.



BALLAST WATER
TREATMENT PLANT

OBJECTIVES

- ✓ To minimize the damage to the environment (sea)
- ✓ To comply with discharge legal regulations
- ✓ To recover and reuse water in the refinery (cooling water)

KPI	Current status	With AquaSPICE	Relative priority
The percent number of days to keep discharge water in limits	None	90% of the year	High
Water recycle ratio of the water charged to pilot plant	None	At least 50%	Medium

AQUASPICE PROPOSAL PILLARS



WATER

- ACTIONS

- To implement innovative water treatment technologies → pilot plant

- EXPECTED RESULTS

- To decrease the amount of water discharge to the sea.
- To increase the amount of water reused in TÜPRAS facilities.
- To decrease the freshwater intake



MONITORING

- ACTIONS

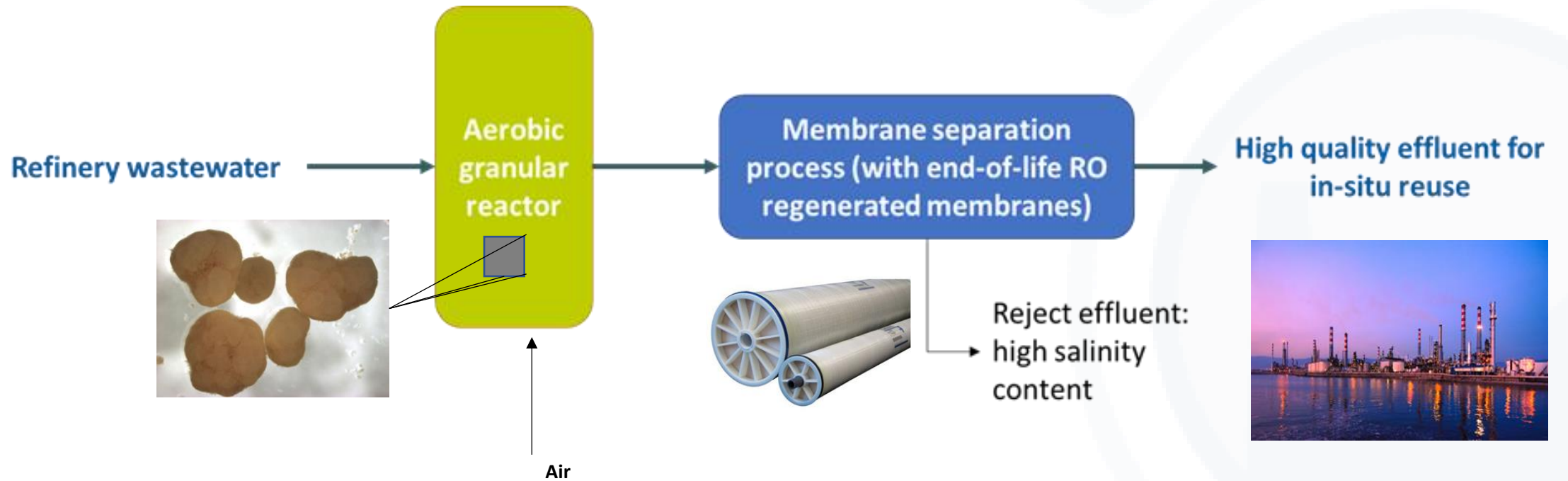
- To implement online sensors to measure water quality in real time.

- To implement monitoring tools used to decide whether the contaminated water will be used for the subsequent processes or discharged to the sea.

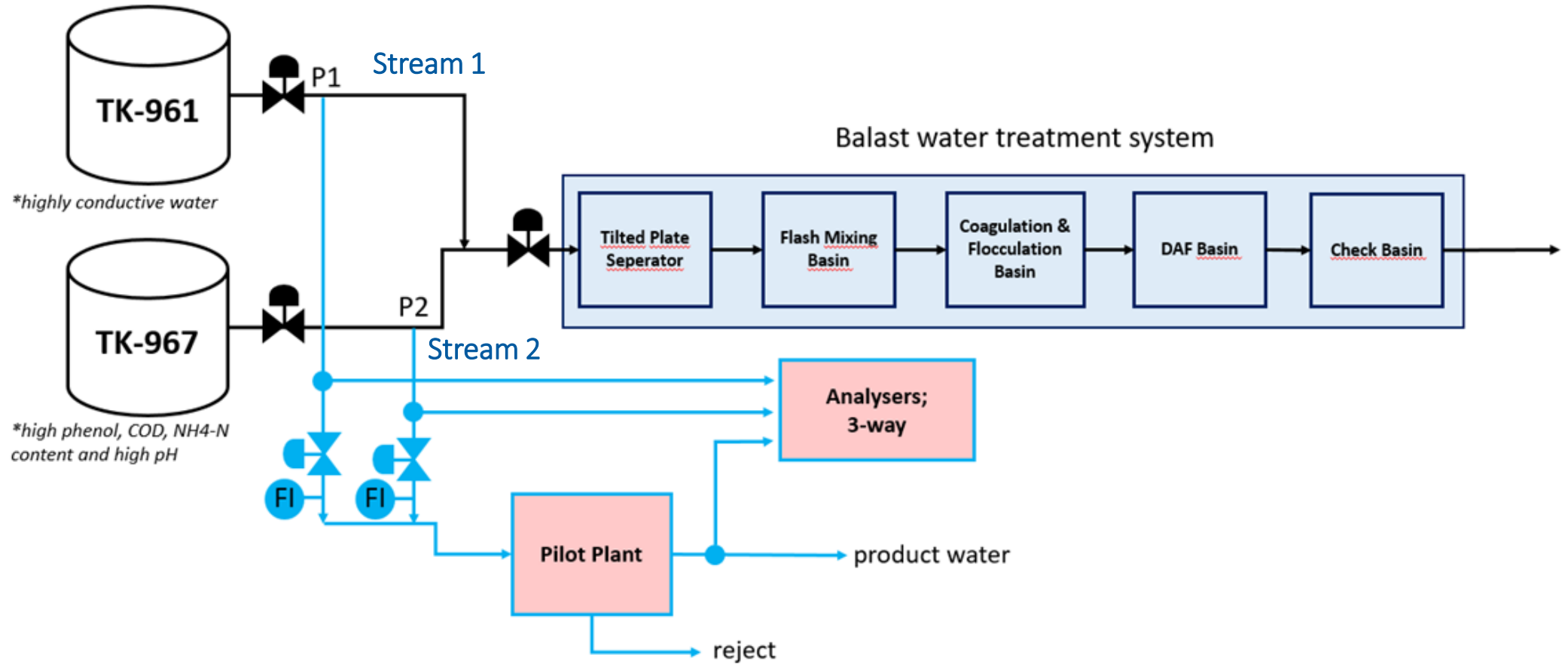
- EXPECTED RESULTS

- - To optimize the blending operation of Stream 1 and Stream 2.
- - To know in real time water quality before being treated or discharged.

AQUASPACE PROPOSAL APPROACH



AQUASPACE PROPOSAL APPROACH

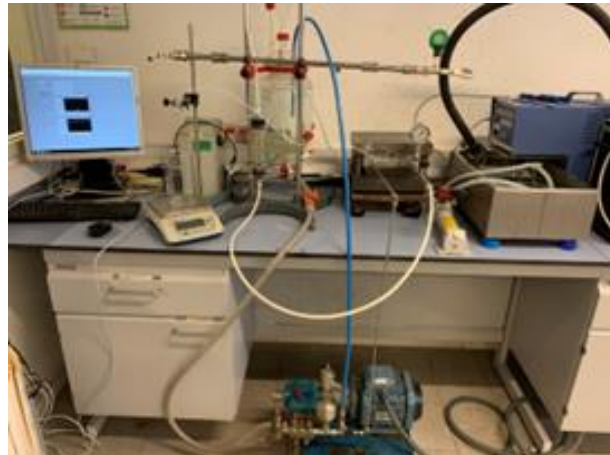


PHYSICAL SYSTEM

Treatments to be investigated within AquaSPICE: P&ID



GRANULAR BIOLOGICAL REACTOR



REVERSE OSMOSIS
(REGENERATED MEMBRANES)

LAB
SCALE



PILOT PLANT
SCALE
(since Nov.2023)



GRANULAR BIOLOGICAL REACTOR



ULTRAFILTRATION + REVERSE OSMOSIS
(REGENERATED MEMBRANES)

PHYSICAL SYSTEM

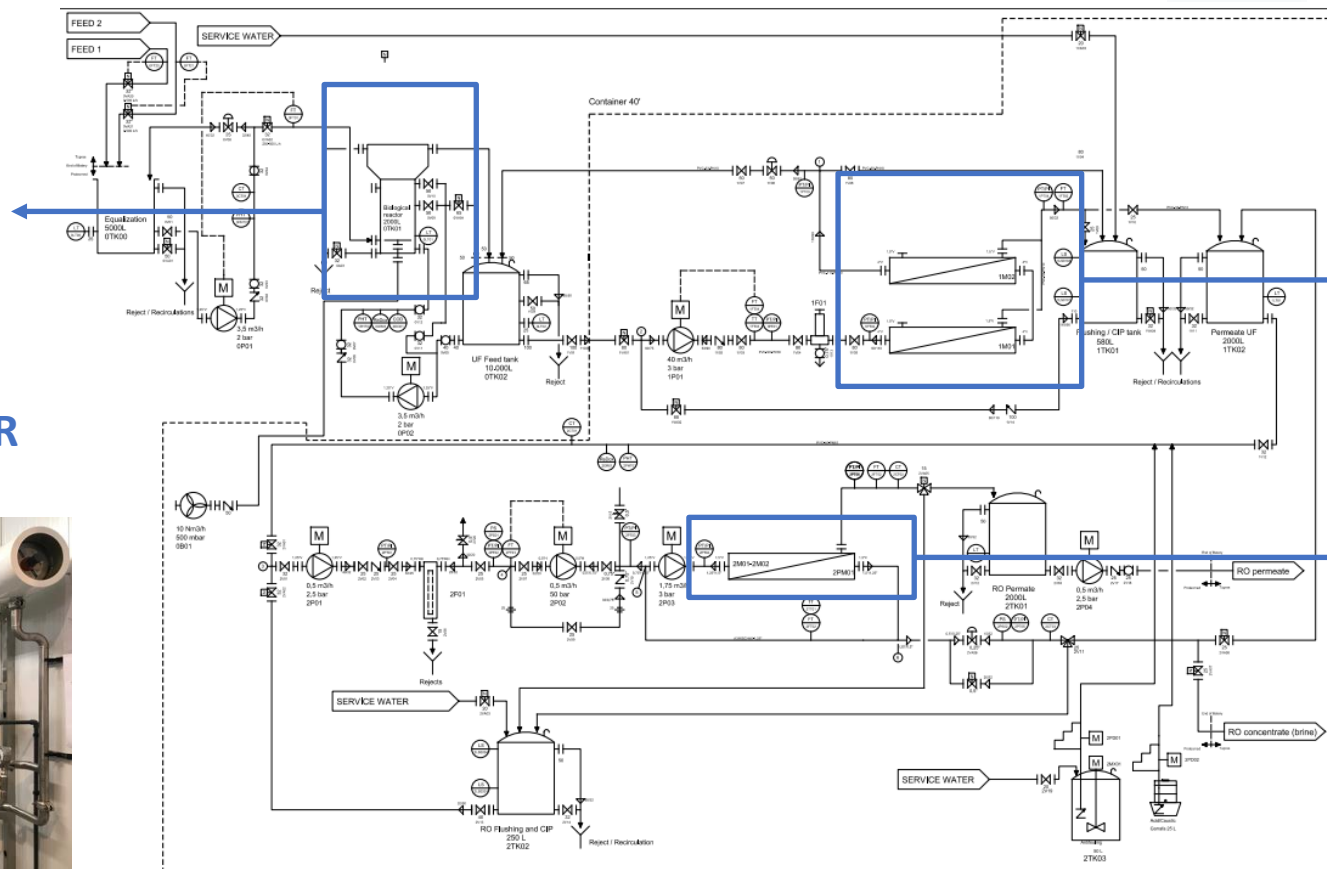
Treatments to be investigated within AquaSPICE: P&ID



GRANULAR BIOLOGICAL REACTOR (AIRLIFT)



GLOBAL OVERVIEW



ULTRAFILTRATION



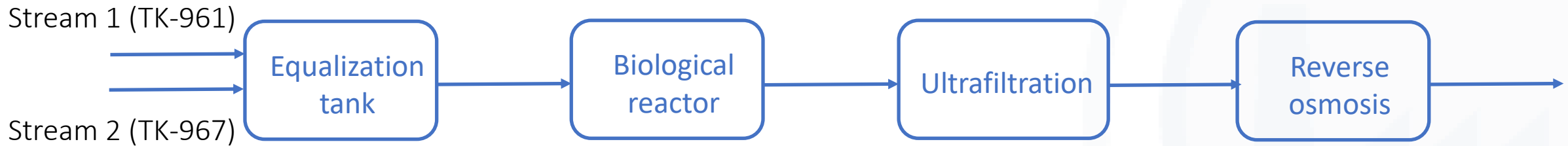
REVERSE OSMOSIS (REGENERATED MEMBRANES)

PHYSICAL SYSTEM

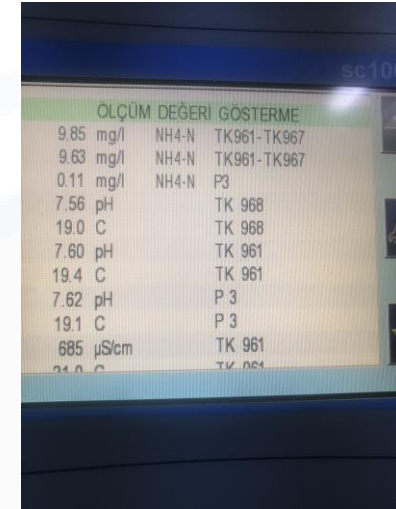
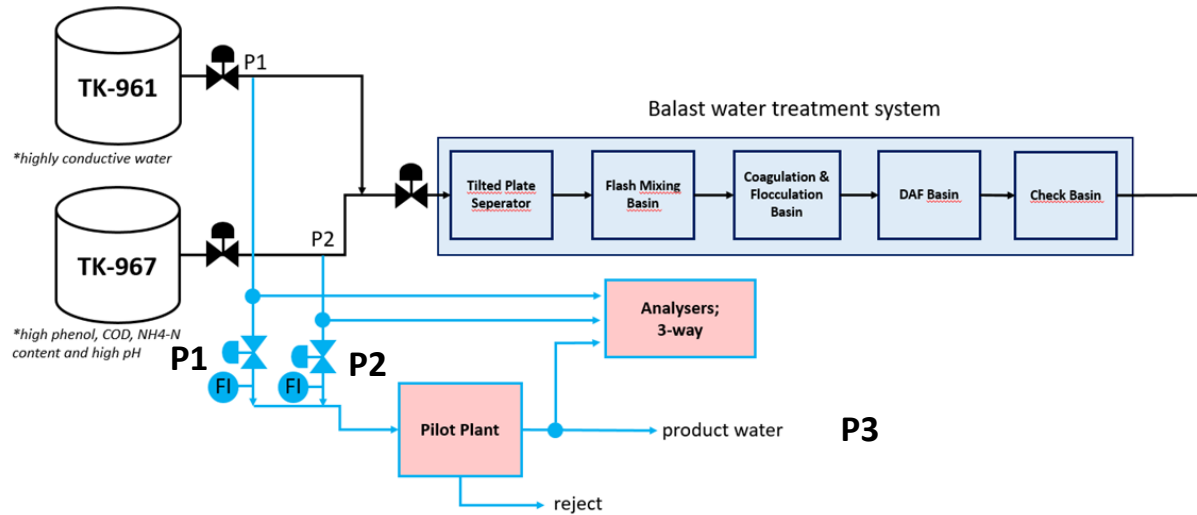
Pilot plant sensors (SCADA)

OPERATION PARAMETERS

Flow rate	Water level	Inlet flow rate Water level	Inlet pressure Inlet flow rate Permeate pressure Permeate flow rate Concentrate pressure	Inlet pressure Inlet flow rate Permeate pressure Permeate flow rate Concentrate pressure
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<p>pH</p> <p>Conductivity</p> <p>TOC</p> <p>Ammonium</p> <p>Sulfide</p>	<p>pH</p> <p>Conductivity</p>	<p>pH</p> <p>Temperature</p> <p>Conductivity</p> <p>Dissolved oxygen</p> <p>ORP</p>	<p>pH</p> <p>Inlet conductivity</p> <p>Permeate conductivity</p> <p>Temperature</p>	<p>pH</p> <p>Inlet conductivity</p> <p>Permeate conductivity</p> <p>Temperature</p>
ANALYZER	ANALYTICAL PARAMETERS			



Parameter	Measurement range		
	P1 – TK-961	P2 – TK-967	P3
pH	0-14	0-14	0-14
Conductivity, uS/cm	0 – 2,500,000 uS/cm	0 – 2,500,000 uS/cm	0 – 2,500,000 uS/cm
Ammonium, mg/L	0 – 20 mg/L	0 – 1000 mg/L	0 – 20 mg/L
TOC (COD), mg/L	0 – 10,000 mg/L (0-30,000 mg/L)	0 – 10,000 mg/L (0-30,000 mg/L)	0 – 10,000 mg/L (0-30,000 mg/L)
Sulfide, mg/L	0 – 100 mg/L	0 – 100 mg/L	0 – 100 mg/L



WATER STREAMS ANALYTICAL CHARACTERIZATION

Analytical results from off line measurements (Nov. 2023-July 2024)

Parameter	Units	Stream 1 (TK-961)	Stream 2 (TK-967)	Biological reactor inlet limits	Discharge limits	Cooling water quality
pH	upH	3.5-9.9	7.4-9.7	9	6-9	7.5-8.5
Conductivity	mS/cm	382-2086	34-37890	<2500		200-250
COD	mg/L	9.8-927	1212-24100	700	200	
TOC	mg/L	64	404			0-4
TSS	mg/L	30	n.a.		60	
Phenol	mg/L	0.1-0.7	12-38.6	50	1	
Ammonium	mg/L	0-67.4	24-6538	20	20	
Sulfide	mg/L	0-172	189-10230	10	1	

Stream	Biological reactor inlet limits	Discharge limits	Cooling water quality
1 (TK-961)	¿?	¿?	X
2 (TK-967)	X	X	X

High variation in several analytical parameters in both streams, mainly in stream 2 (conductivity, COD, ammonium, sulfide)



a) Water stratification in tanks?

TK-961 (stream 1)=3175 m³, TK-967 (stream 2)=4275 m³

b) Tanks refilled periodically with wastewater from refinery processes

Higher sulfide concentration in stream 2 than initially expected



3-way analyzer cannot measure stream 2 because of safety reasons (high sulfide concentration inside the analyzer cabinet)

OPERATION PARAMETERS

Parameter	Units	Test 1	Test 2	Test 3	Test 4
Operation time	day	30	95	48	68
Blending ratio	L stream1/L stream2	1.7	1.7-6	6-13	6.5-16
VER	%	3.9	4.7	32.8	50
HRT	h	104.1	64.5	36.6	24
Flow rate	L/cycle	65.9	78.5	785.4	1610
Cycles	cycles/day	7.3	8	2	2
OLR	kg COD/m ³ /day	0.3-0.5	0.1-3.7	0.9-12.2	0.2-14
Cycle time	h	3.5	3	12	12

High variability in equalization tank water quality at the same blending ratio (reactor feed)



OLR not stable, getting more difficult biomass granulation



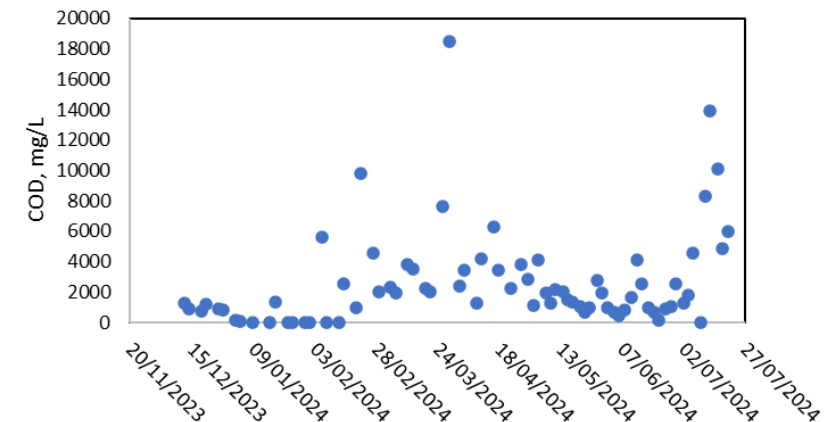
- 1) To increase blending ratio (increase dilution)
- 2) To increase VER to promote water mixing and renewal

POLLUTANTS REMOVAL, % (average values)

Parameter	Test 1	Test 2	Test 3	Test 4
COD	10	11	61	59
Phenol	72	19	77	60
Ammonium	52	15	27	30



COD in equalization tank (AGR inlet)



PHYSICAL SYSTEM

Biological reactor SBR tests: Test 4

Aerobic granular reactor stopped since end July 2024 due to a failure in the pilot plant PLC software

Date	Removal %		
	COD	Phenol	N-Ammonium
14.05.2024	71%	83,55%	7,0%
16.05.2024	47%	-7,69%	-152,3%
18.05.2024	-23%	50,00%	-52,8%
21.05.2024	79%	95,17%	13,9%
25.05.2024	-47%	17,03%	-0,7%
28.05.2024	72%	73,73%	11,6%
30.05.2024	65%	69,00%	2,8%
1.06.2024	68%	73,27%	15,2%
4.06.2024	78%	68,75%	99,0%
6.06.2024	16%	-20,00%	99,6%
8.06.2024	79%	47,37%	100,0%
11.06.2024	85%	39,53%	16,4%
13.06.2024	88%	15,52%	-9,1%
15.06.2024	94%	92,31%	49,8%
18.06.2024	70%	91,95%	25,6%
20.06.2024	93%	97,26%	37,3%
22.06.2024	23%	-1114,29%	100,0%
25.06.2024	88%	69,51%	24,5%
27.06.2024	88%	96,11%	92,8%
29.06.2024	28%	91,91%	13,8%
2.07.2024	36%	73,17%	35,4%
4.07.2024	73%	29,75%	3,3%
6.07.2024	30%	-3,23%	38,9%
11.07.2024	-20%	6,32%	3,0%
13.07.2024	-17%	13,64%	0,8%
16.07.2024	28%	84,23%	-68,9%
18.07.2024	2%	26,32%	11,8%
20.07.2024	-1168%	-10,00%	8,5%

Re-inoculation, Test 4 started

Highest NH4 removal %

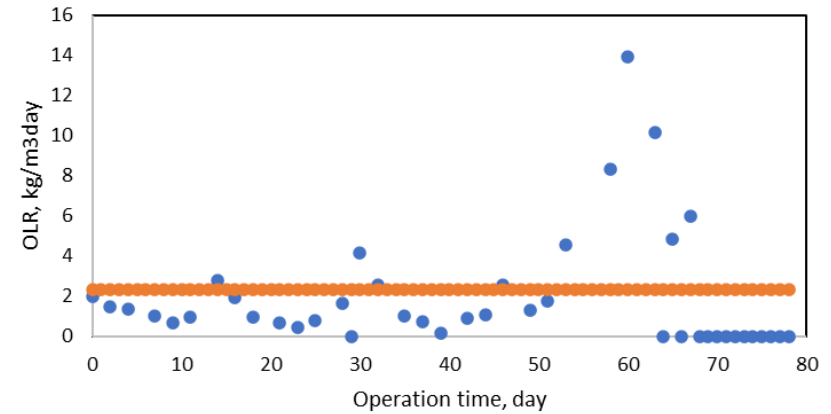
Highest COD removal %

Highest phenol removal %

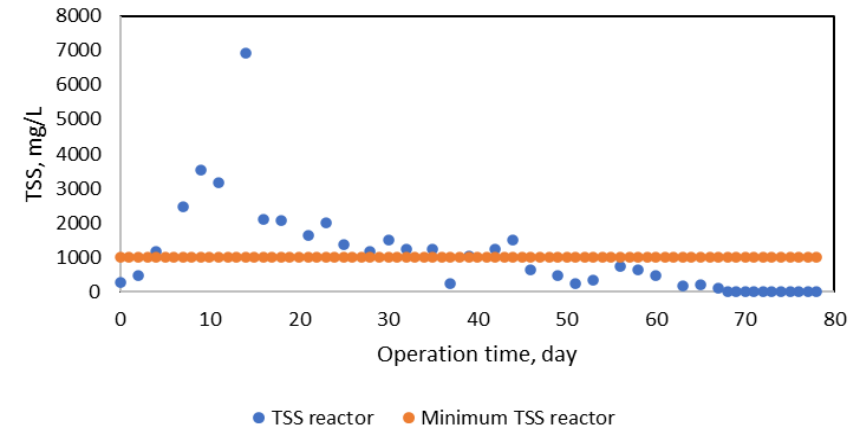
Reduced in performance after tank filling system logic was malfunction

Wash-out

OLR- Test 4 SBR



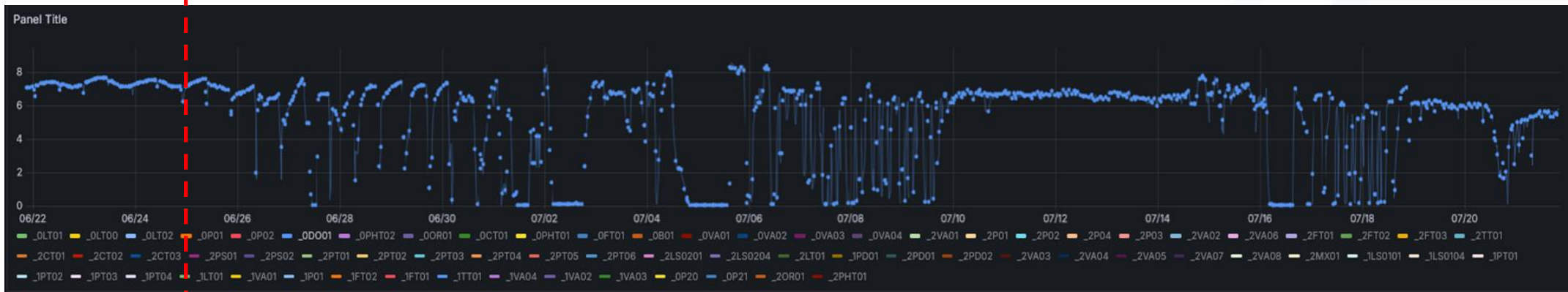
TSS reactor- Test 4 SBR



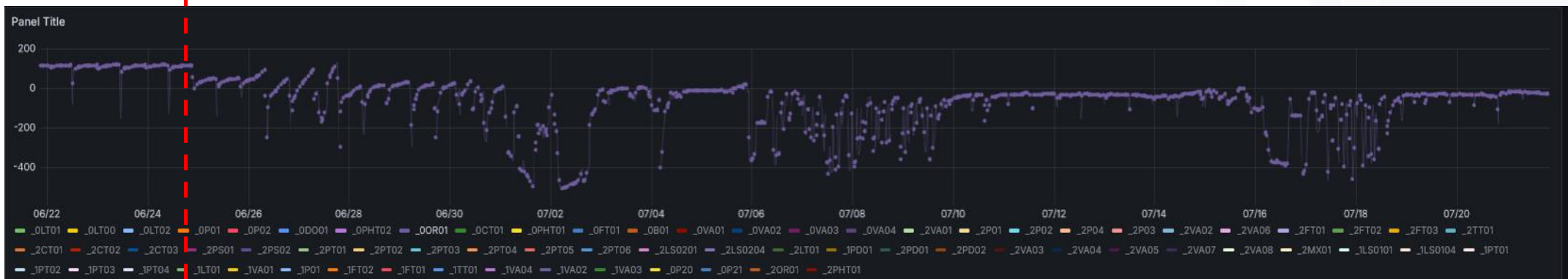
● TSS reactor ● Minimum TSS reactor



Reactor pH



Reactor DO



Reactor ORP

ULTRAFILTRATION AND REVERSE OSMOSIS PRELIMINAR TESTS

- UF and RO tests with clean water (September 2024)
- Preliminary UF and RO tests with refinery-treated water (october 2024)

Parameter	Units	UF inlet	UF permeate	RO permeate	Cooling water	Discharge limits
TSS	mg/L	38	2.8	0.4		60
COD	mg/L	55	-	<15	0-4	200
pH	upH	7	6.7	3.8	7.5-8.5	6-9
Temperature	°C	24	23	23		
NH4-N	mg/L	8.80	-	3.45		20
Sulfur	mg/L	0.59	0.19	-		1
Oil	mg/L	7.1	-	-		

- More UF and RO tests are required to assess operation parameters and to study fouling issues and optimize cleaning procedures.



AEROBIC GRANULAR REACTOR RESTART (NOV.-DEC. 2024)

- On 23rd-24th October, pilot plant PLC and HMI software were updated by pilot plant supplier technical staff.
- During November/December 2024 biological reactor was reinoculated several times to start Test 5 but some issues took place:
 - Stream 2 more polluted than expected → reactor washout
 - Broken pH probe in equalization tank
 - Broken pump and valve between equalization tank and biological reactor due to clogging.



Clogged pump and valve 27/11/2024

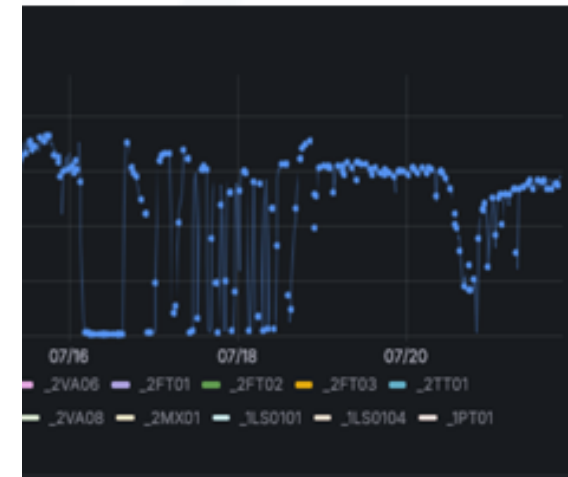
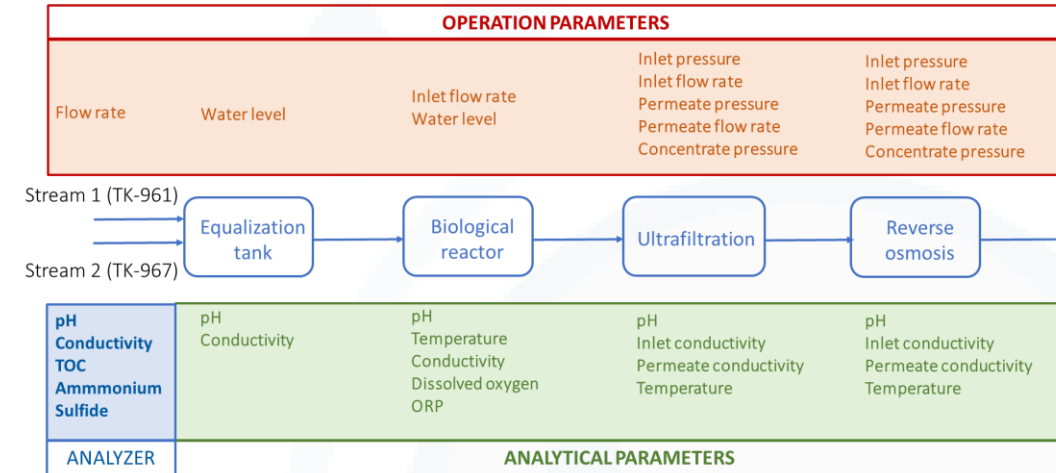
UF is operated, uf inlet and outlet shown below.



UF test on 29/11/2024

WATER CPS

- **RTM Platform:** deployed and collecting data from pilot plant.
- **Digital Twins platform:** deployed, connected to RTM, integrated WaterCPS Services.
- **Modelling:** An operational simulation scenario regarding the water treatment technologies of the pilot plant was developed. Aerobic granular reactor, Ultrafiltration and Reverse osmosis process models were developed and incorporated.
- **Optimisation:** Decide on the optimal flows for TK-961 & TK-967 with respect to quality requirements and flowrate capacities.
- **Analytcs:** Developed a predictive model estimating parameters at the bioreactor outlet of the biological reactor using historical data.
- **LCA:** Model developed, linked to data from the operational simulation scenario developed by TUC.



Reactor DO

ANALYTICS

- 3 way analyser sampling point has been decided, it will be in the following weeks
- DAF inlet turbidity analyser is broken right now, outlet turbidity analyser is working but it is out of range right now, thats why we cannot see data → Replace DAF inlet turbidity analyzer

OPERATION

- Reinoculate biological reactor and restart granular reactor operation.
- UF and RO tests

DIGITAL

- Test the digital services (models, optimization, analytics and LCA) with good quality real time data from Tüpras (once operation issues are fixed).

PUBLICATION

- Scientific article in progress (AGR lab scale results)



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