FROM SHARED RESOURCES
TO JOINT SOLUTIONS

D.4.6.1. and D 4.6.2 Feasibility study with all results critically evaluated and reported-SWOT analysis-and new reference model as analytical tool evaluated and reported

February 2022
Version n.1

PROJECT AdSWiM

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Phase Leader:	**UNIVERSITA' POLITECNICA DELLE MARCHE**
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PART 1: INTRODUCTION

Due to the transboundary nature of the marine environment, impacts on the marine environment in the Croatian territorial part of the Adriatic Sea may extend to other countries in the Adriatic region and vice versa. Therefore, good cross-border cooperation in the management of the marine environment and in the management of activities that can significantly affect the state of the marine environment is crucial for improving the state of the marine environment in the Adriatic Sea.

AdSWIM project creates a professional and technical basis for drafting proposals and selecting the most favorable solution for wastewater drainage and treatment (with respect to existing projects, technical studies and other documentation). This basis is technically and operationally harmonized with existing Croatian and EU legislation, economically and commercially viable and socially acceptable in Croatian conditions. The ultimate goal is to create an effective system for ecosystem preservation and environmental protection.

PART 2: THE STATE OF IMPLEMENTATION OF THE MULTIANNUAL PROGRAM FOR THE CONSTRUCTION OF WWTP ON COASTAL AGGLOMERATIONS

The multi-annual program for the construction of municipal water structures for the period until 2030 (hereinafter: the 2021 Program) is one of the most important planning documents for water management. It is also an act of strategic planning related to conditions enabling the implementation of EU funds in the period from 2021 to 2027. I s adoption is prescribed by Article 43 of the Water Act (Official Gazette, Nos. 66/19 and 84/21), and by decision of the Government of the Republic of Croatia it was placed on the list of strategic planning acts on October 2020.t

Water resources law stipulates that multi-annual construction programs must be in accordance with other water management planning documents (Water Management Strategy, Water Areas Management Plan). This ensures that the 2021 Program is in line with the strategic commitments and water management policies as well as the adopted European Union standards for water policy, in particular those of Directive 2000/60 / EC of the European Parliament and Council, designed on the 23rd of October 2000. establishing a framework for Community action. Water Policy (Water Framework Directive) (OJ L 327, 22.12.2000), was last amended by Commission Directive 2014/101

/ EU on the 30th of October 2014., amending Directive 2000/60 / EC of the European Parliament and of the Council establishing a framework for Community action in the field of water management.

The Republic of Croatia became a full member of the European Union on the 1st of July, 2013. It should be emphasized that in the process of accession to the European Union, the Republic of Croatia had to harmonize its national legislation with the legislation of the European Union in the field of environmental protection and water management. Consequently, the obligation to meet all the requirements arising from alignment with the acquis Communautaire was apparent. As a member state of the European Union, the Republic of Croatia has the right to access funds from the Structural Funds and the Cohesion Fund of the European Union. The main purpose of the mentioned funds is to provide financial assistance in meeting the requirements arising from the European Union legislation that Croatia has transposed into its national legislation i.e., accession treaty signed upon accession to the European Union.

As set out in the Marine Strategy Framework Directive, three important steps in implementation were taken in 2012:

(1) Member States submitted reports on the initial assessment of the current marine waters environmental status (Article 8 of the Marine Strategy Framework Directive);

(2) Member States have identified what good environmental status (GES) means for the marine waters of the relevant marine regions and sub-regions (Article 9 of the Marine Strategy Framework Directive);

(3) Member States have set environmental targets and related indicators to guide their progress towards achieving good environmental status by 2020 (Article 10 of the Maritime Strategy Framework Directive).

- Below, Reports review document Current DP management with SWOT analysis and operating mode cost-benefit for Split Katalinića brig & Split Stupe:

Split Katalinića brig plant (Croatia)

Wastewater treatment plant Katalinića brig is located near Bačvice beach in Split, and it is designed to receive and treat the wastewater from southern basin of Split, with a capacity for 122.000 population equivalents. The average flowrate around 35.000 m^3/day with some oscillations during the year.

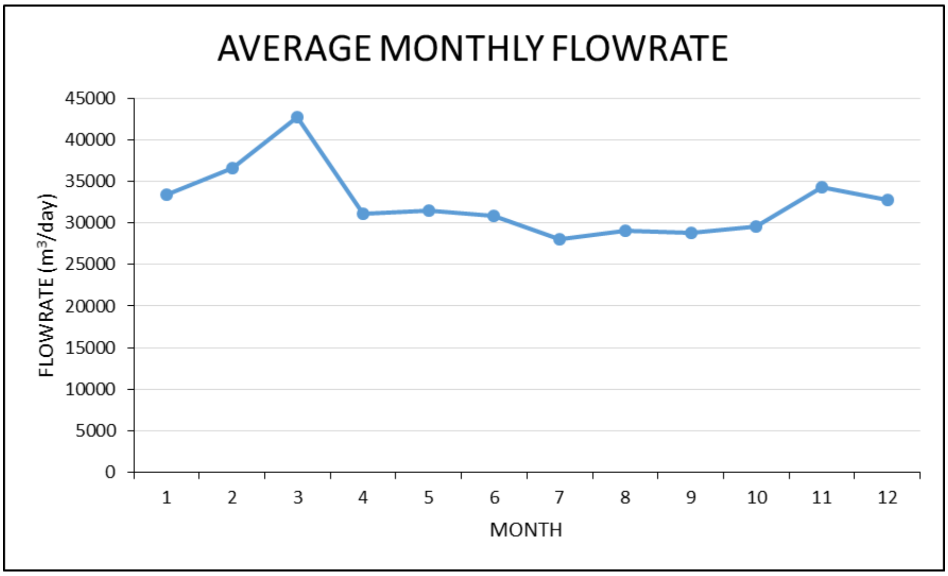

Figure 1: Average monthly flowrate (m^3/day) for year 2018. (Katalinića brig)

Wastewater inflow to the plant is a mixed type – combined urban wastewater and rainfall runoff. Treatment consists of only automatically cleaned coarse grid with a screen hatch of 50 mm, and a fine grid with screen hatch of 7 mm.

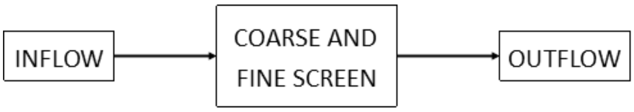

Figure 2: Technological scheme of Split Katalinića brig plant

The treated wastewater is discharged by a pumping station through submarine outfall with a diffuser. The total length is 1570 m (100 m on land, 1470 m underwater), with a discharge depth of 43 m. Submarine discharge pipe is 800 mm in diameter. Maximum allowed discharge quantities according to water permit are 17.005.400 m^3 per year.

In Table 1., main strengths and weaknesses are shown for wastewater treatment plant Katalinića brig. Strengths are related to good recipient characteristics, large depth of submarine outfall and the fact that there is no industrial or agricultural load. The weaknesses are related to poor treatment technology with no biological treatment and no nutrient or sludge removal. In addition, the system is combined of rainfall runoff and sewage wastewater. There is no entrance monitoring which makes it impossible to determine the wastewater inflow parameters.

Table 1. Strengths and weaknesses of Split - Katalinića brig plant

WEAKNESS	STRENGHT
Combined system – rainfall runoff and sewage wastewater	Good recipient characteristics
Poor depuration technology, no biological treatment or nutrient removal	Submarine outfall at large depth (44 m)
No sludge removal	No industrial or agricultural load
Lack of monitoring on depuration plant entry	

On Figure 3, exit outflow measurements are displayed. Parameter COD has the highest concentration, especially during summer (900 mg/L) thus exceeding allowed concentrations of endpoint outflow (plant to nature). Unfortunately, the wastewater is not analyzed at the entry of the plant so it is impossible to determine the removal rate.

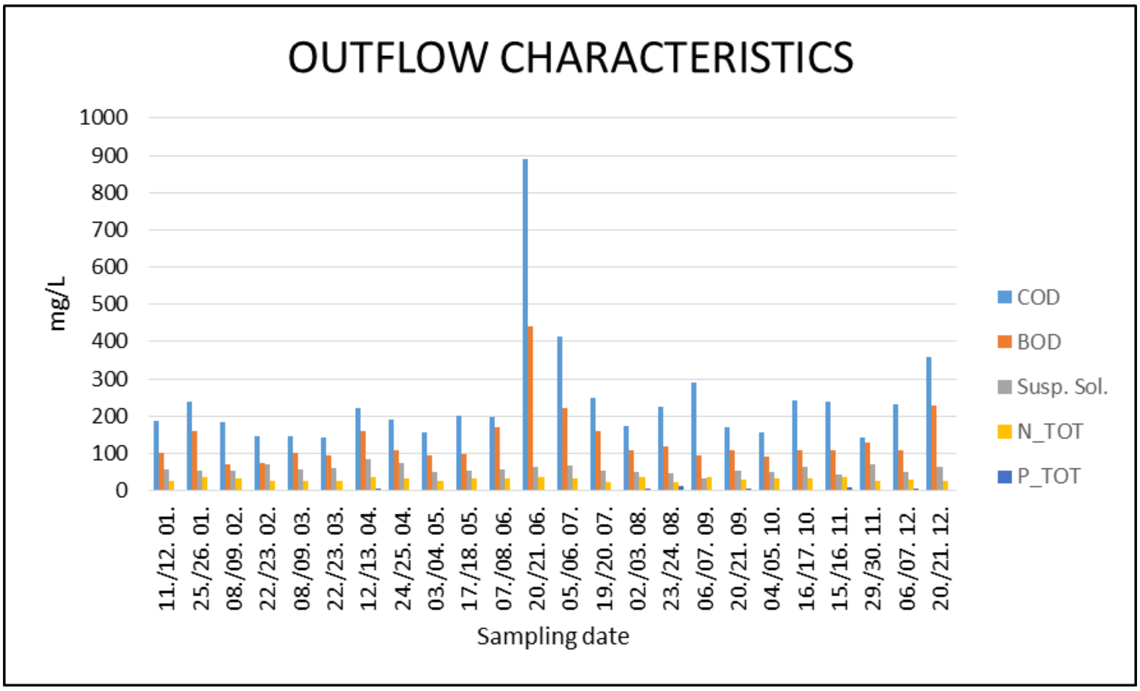

Figure 3: Effluent characteristics at Split Katalinića brig plant

Split Stupe plant (Croatia)

Wastewater treatment plant Stupe is located in the eastern part of Split, and it is designed to receive and treat the wastewater coming from north-eastern part of Split as well surrounding municipalities (Solin, Podstrana, Klis, Dugopolje). Design capacity is equal to 138.000 population equivalents. Average inflow is equal to approximately 30.000 m^3/day with significant oscillations.

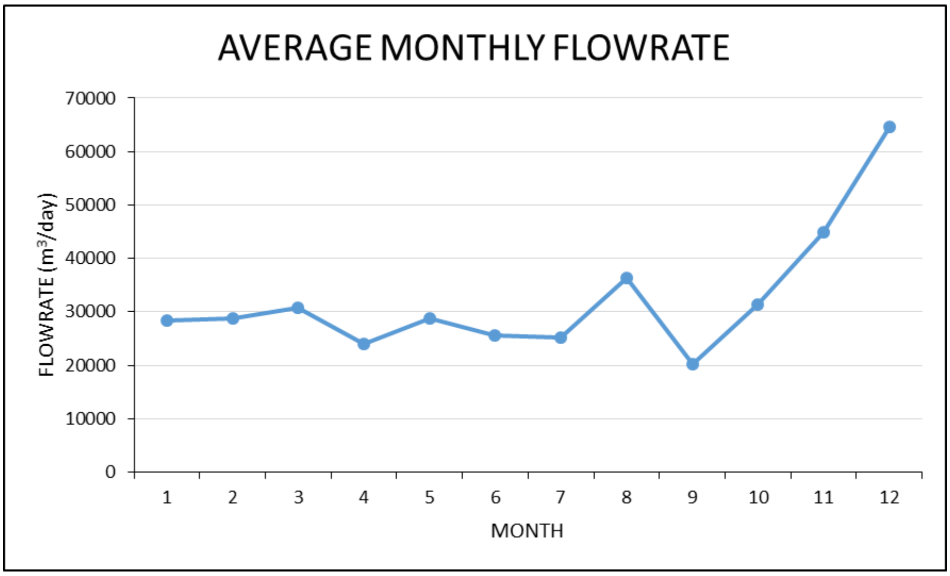

Figure 4: Average monthly flowrate (m^3/day) for year 2018. (Stupe)

Wastewater is treated with two automatically cleaned coarse grids (screen hatch of 10 mm), two fine grids (screen hatch of 2 mm), aerated sand and grease filter, with sand classifier as well as oil and grease separator. In addition, within this wastewater treatment plant exist a facility for septic tanks wastewater collection. Maximum discharge according to water permit is 11.000.000 m^3 per year. The treated wastewater is discharged through submarine outfall with a diffuser, total length is 2750 m (1850 m on land, 900 m underwater), discharge depth 37 m.

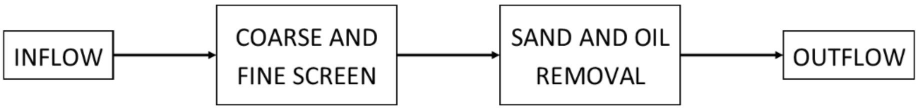

Figure 5: Technological scheme of Split Stupe plant

In Table 2., main strengths and weaknesses are shown for wastewater treatment plant Stupe. Similarly, to Katalinića brig, main strengths are related to good recipient characteristics, large depth of submarine outfall and the fact that there is no industrial or agricultural load. The weaknesses are related to poor treatment technology with no biological treatment as well as non-existent nutrient or sludge removal. There is no entrance monitoring which makes it impossible to determine the wastewater inflow parameters. In addition, wastewater coming from septic tanks with undetermined contents is received at the facility.

Table 2. Strengths and weaknesses of Split - Stupe plant

WEAKNESS	STRENGHT
Poor depuration technology, no biological treatment or nutrient removal	Good recipient characteristics – auto purification capacity
No sludge removal	Submarine outfall at large depth
Lack of wastewater monitoring on DP entry	No industrial or agricultural load
Septic tanks sewage reception	

On Figure 6, endpoint outflow parameters are displayed. Parameter COD has the highest concentration (900 mg/L) exceeding allowed endpoint outflow concentrations (plant to nature, in this circumstance -the sea). Unfortunately, wastewater is not analyzed at the entry so it is impossible to determine the removal rate.

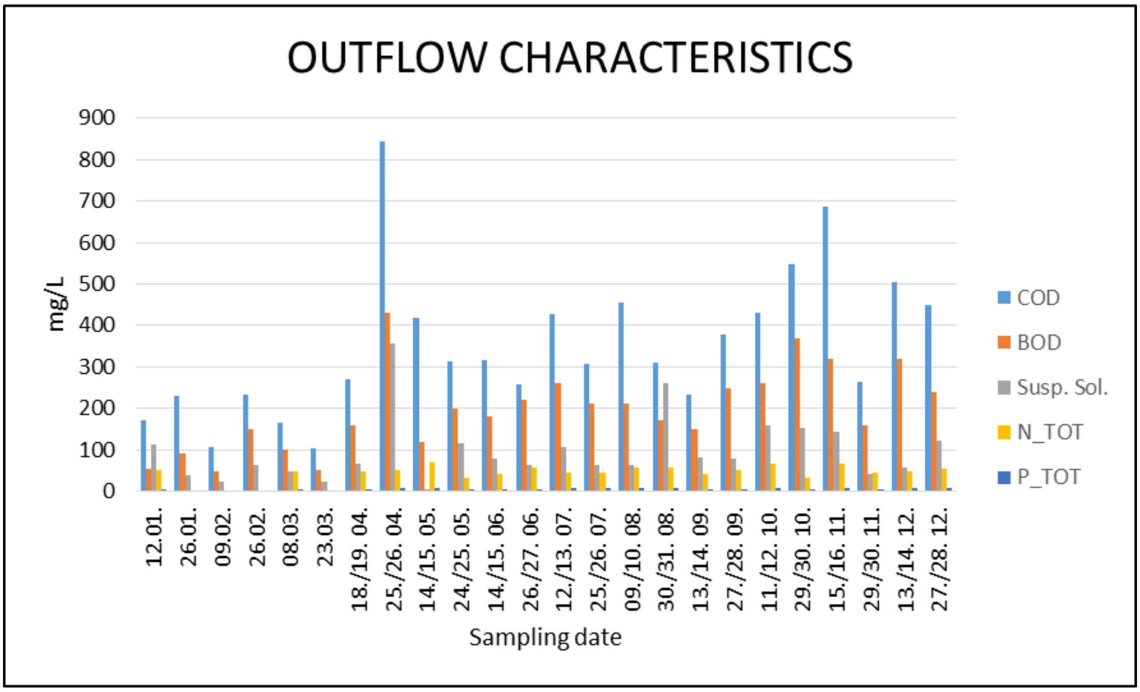

Figure 6: Outflow characteristics at Split Stupe plant

Split Stupe and Katalinića brig plants

For plants located in Split there is no data available about the inflow characteristics so it is impossible to determine the removal rate and estimate environmental as well as monetary benefits from wastewater treatment. The total operational costs for Stupe and Katalinića brig are shown in Table 3. and Table 4.

Table 3. Summarized costs and benefits for current operational mode of Split Stupe plant (year 2018.)

PARAMETER	COD	BOD	Susp. Sol.	P_TOT	N_TOT
Outflow load (kg/year)	3.702.004	2.075.512	1.021.500	59.888	531.993
Total operational costs (€/year)	**492.200**				

Table 4. Summarized costs and benefits for current operational mode of Split Katalinića brig plant (year 2018.)

PARAMETER	COD	BOD	Susp. Sol.	P_TOT	N_TOT
Outflow load (kg/year)	2.894.692	1.647.319	689.330	49.549	365.905
Total operational costs (€/year)	**250.480**				

PART 3: ECOLOGICAL CONDITION OF THE MARINE ENVIRONMENT CLOSEST TO WWTP

Monitoring the ecological state of the marine environment near the WWTP provides necessary information and assessments needed for developing sustainable management and use of water near and connected to the European seas. The system creates a knowledge base needed to monitor Europe's progress towards good environmental status for freshwater and marine environments.

The Marine Environment Monitoring Program also determines and monitors the efficiency of public sewerage system, determines operational flow and efficiency of WWTPs and implements necessary technological upgrades and reconstructions.

In the case of the Croatian coast, published results of the coastal sea quality for tourism purposes are of utmost importance as well as raising public awareness on importance of maintaining high sea quality.

The amount of nutrients in marine environment is cumulatively affected by existing discharges of municipal and industrial wastewater combined with nutrient impact of the tourist-laden coast. Likewise, there is an issue of unregulated water leaks in hinterland region, illegal discharges from vessels and a significant anthropogenic factor such as dumping waste and non-degradable packaging into the sea.

To determine ecological state of the marine environment closest to DPs, chemical parameters from the water column were presented and analyzed. Parameters were chosen according to European directives applied to Croatian legislative regarding eutrophication in marine environment. Estimation of the ecological state in the water column at the Croatian part of the Adriatic Sea (as in other EU members) is governed with Marine Strategy Framework Directive, MSFD (2017/848/EU) through Descriptor 5 Eutrophication and Water Framework Directive, WFD (2000/60/EU).

According to MSFD (2017/848/EU), primary criteria parameters were: For Criteria D5.C1 Nutrients in the water column: Dissolved Inorganic Nitrogen (DIN), Total Nitrogen (TN), Dissolved Inorganic Phosphorus (DIP), Total Phosphorus (TP); for Criteria D5.C2 Chl alpha concentration and for criteria D5C5 Bottom water oxygen concentration. Accordingly, in this Report, marked parameters inside the primary criteria are taken into consideration.

As for some of the indicators within the primary criteria (DC51 - Nutrients in the water column) (concentrations of total inorganic nitrogen and orthophosphate and total phosphorus) there are no threshold values defined at the level of region or subregion, in line with a recommendation by EC Decision (2010/477/EU), for the assessment (the existing national criteria for water bodies in the Republic of Croatia adopted in accordance with the WFD (2000/60/EC) (OG 96/2019) will be applied. For Croatian part of the Adriatic, threshold values were defined as within limits of the Biological Element of Quality (BEQ) of Phytoplankton (OG 96/2019). [1]

According to the EU decision 2018/229 on reference conditions and boundaries of ecological status classes for different parameters for Type II A of the Adriatic coastal waters, the trophic index TRIX according to Vollenweider et al., (1998) is evaluated as a degree of eutrophication. [2] The evaluation of the ecological status of the water column according to the TRIX index is applied to the Adriatic Sea and is included in the official Ministry of Environment and Energy of the Republic of Croatia reports (http://jadran.izor.hr/azo/). TRIX index as a parameter was also calculated for the investigated sites.

Review and analysis of available “historical” sets of chemical data on sites closest to Croatian DPs in Zadar and Split area (ZD-REF, KB-REF and ST-REF) included concentration of nutrients (dissolved inorganic phosphorus and nitrogen forms, total nitrogen and total phosphorus), organic carbon, chlorophyll a concentrations, dissolved oxygen and pH. Besides the concentrations, as their bioavailability, N/P ratios were calculated as well as ecological TRIX index to estimate the ecological state of the marine environment.

Parameters were chosen according to European directives applied into Croatian legislative regarding eutrophication in marine environment. Estimation of the ecological state in the water column at Croatian part of the Adriatic Sea (as in other EU members) was governed with Marine Strategy Framework Directive, MSFD (2017/848/EU) through Descriptor 5 Eutrophication and Water Framework Directive, WFD (2000/60/EU). Where it was possible, interpretation of data was obtained by using existed threshold values adopted in accordance Directives and introduced into Croatian legislative ((OG 96/2019).

Furthermore, for the purpose of better monitoring and estimation of the ecological state of the seawater in the proximity of DPs, monitored chemical parameters should be harmonized with EU Directives regarding eutrophication in the marine environment (2017/848/EU2000/60/EU) already applied into Croatian legislative (OG 96/2019).

PART 4: INNOVATIVE TECHNOLOGIES OF WASTEWATER TREATMENT - AEROBIC GRANULAR BIOMASS AND PHOTO-DISINFECTION

By conventional process, biological treatment of wastewater is achieved by using activated sludge (AS) process which requires large land footprint for bioreactors and secondary clarifiers. AS is a mixed microbial community feeding on the biodegradable substrates present in the wastewater. Negatives regarding conventional AS technology are complex process design, requirement of large land footprint and biomass and wastewater recirculation energy usage.

Its focus was technological solutions based on newly developed bioprocesses for wastewater treatment using selected microbial cultures in free or granular form. Such bioprocesses are intended for targeted pollution removal using bacterial biosensors. Said technology is suitable for treating both municipal wastewater and industrial wastewater. One of innovative methods for wastewater treatment for the protection of marine and coastal surface waters is AGS technology (Aerobic Granular Sludge Technology - AGS Technology).

The AGS is advantageous over the conventional AS process in numerous ways. Experience up to date has shown an upgrade of nitrification efficiency and process stability as well as improved toxic load resistance. What's more, AGS technology has exhibited significant sludge reduction and improved sludge settling. Correspondingly, it has shown enhancement via additional micropollutants removal as well as reduction of activated carbon. Targeted application domain for the AGS technology are new WWTPs or complete reconstruction of WWTP.

The method is based on binding selected microorganisms or activated sludge in solid form of flakes of naturally produced biopolymers (exopolysaccharides). Polysaccharides, in addition to importing microorganisms, also contribute to the stability of granular biomass. Granulation of microorganisms, which ensures systems strength and stability, occurs in specific process conditions, which facilitates the excretion of microbial biopolymers used for micro granulation of selected microorganisms. Micro granulation ensures that all selected microorganisms present in the granules, are held together, eg nitrification and denitrification of microorganisms and microorganisms for biodegradation or detoxification of certain industrial wastewaters. In the next stage, the microgranules are translated into granules. Compared to conventional bio flakes, granular biomass has a strong structure and excellent deposition properties. AGS technology uses an optimized batch cycle structure with three main cycle phases: charging, reaction, precipitation. Phase duration is defined by sludge characteristics, flow, and required effluent. Its robust granular structure withstands chemical fluctuations jumps, loads, salts, pH, and toxic shocks. Due to single reactor tank design, the required number of tanks and mechanical equipment is lesser than the conventional AS process. There is no need for secondary precipitators, selectors, separate swimming pools or sludge recovery pumping stations. Moreover, AGS has proven enhanced removal of biological nutrients Ingredients (BNR) and deals with deposition properties at all values from 3050 ml / g allow an MLSS concentration of 8000 mg / l or larger. With side stream granular biomass preparation, a controlled process without disturbances is achieved. Various substrates for cultivation can be used (influent WW, mineral substrates, industrial effluents, digestor centrate etc.) making it a versatile and broadly applicable process.

The specific AdSWIM objectives are to improve the environmental quality of the Adriatic Sea through planned use of treated wastewater, collect biological parameters, use analytical devices and innovative treatments to protect water bodies, set and exchange management models and assess regulatory effectiveness.

Clean unpolluted water is necessary to improve ecosystem resilience. Both can be achieved with integrated and sustainable water resource management. This would require more robust implementation of the Water Framework Directive (EU, 2000).

Given the above, AGS process is a promising method due to advantages such as lower land footprint, effective nutrient removal, and lower sludge production, compared to AS technology. It has shown to be a significant cost savings upgrade for existing plants as well as new plants (smaller nitrification, sedimentation tanks). Moreover, AGS technology has enhanced nitrogen and organic compounds removal, higher tolerance on shock loads and better settling properties compared to AS.

In spite of issues with respect to granulation and stability, such technology could be beneficial to improvement of water quality and the ecological condition of marine and coastal ecosystem. Even so, it is not applicable to the specific case mentioned above.

PART 5: CONCLUSION

It should be emphasized that in the process of accession to the European Union, the Republic of Croatia had to harmonize its national legislation with the legislation of the European Union in the field of environmental protection and water management. This way, the obligation to meet all the requirements arising from alignment with the acquis Communautaire was apparent. As a member state of the European Union, the Republic of Croatia has the right to access funds from the Structural Funds and the Cohesion Fund of the European Union.

The ultimate goal is to create an effective system for ecosystem conservation and environmental protection. One of the proposed possible technological solution options (AGS, photodesinfection) should be taken in consideration among alternative technical solutions with regard to cost effectiveness.

Mutual cooperation of all subjects of environmental protection and the inclusion of environmental issues in everyday life and business activities as well as policy of sectoral development and development in general, is necessary for sustainable development of each agglomeration. Only in this way is the preservation of the environment achieved.

Progress in achieving good environmental status will depend on progressive pollution removal, i.e., the ability to maintain the presence of pollutants in the marine environment and their biological effects within acceptable limits, to ensure that they do not have significant impacts and do not pose risks to the marine environment.

LITERATURE

- *Economic Valuation of Wastewater, The Cost of Action and The Cost of No Action*, The Global Programme of Action for the Protection of the Marine Environment from Land-based Activities (GPA), through the Global Wastewater Initiative (GW2I), UNEP (2015)
- Multi-year program for the construction of municipal water structures for the period up to 2030, September 2021

List of Directives used in the Report:

COMMISSION DECISION (EU) (2017/848/EU) laying down criteria and methodological standards on good environmental status of marine waters and specifications and standardized methods for monitoring and assessment, and repealing Decision 2010/477/EU

WFD (2000/60/EC) Directive of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy

EC Decision (2010/477/EU) 2010/477/EU on criteria and methodological standards on good environmental status of marine waters

OG 96/2019 Official Gazette of Croatia, No96/2019 Water Quality Standard Regulation

EC Decision (2018/229) establishing, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, the values of the Member State monitoring system classifications as a result of the intercalibration exercise and repealing Commission Decision 2013/480/EU

D.4.6.1 and D4.6.2

Document of evaluation of the devices obtained

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PART 6: BIOSENSOR for TOXICITY and DEVICE TRL
Next steps for commercialization

The biosensor prototype developed and realised within the frame of the AdSWiM Project, in collaboration with the Company Biosensor s.r.l., though the Contract n° 1249024 (CIG ZAC2C3A591), is an analytical platform customized for photosynthetic algae as biological recognition element to detect pathogens and herbicides in wastewater.
The instrument (Figure 1) is a portable prototype consisting of a module cell for the insertion of screen-printed electrodes (SPEs) hosting the biological material. The cell is equipped with a LED system (of 350 µmol photons m-2 s-1 of red light at a 650 nm wavelength) which provide algae illumination and measure the fluorescence emission at 680 nm by a photodiode, automatically calculating the fluorescence parameters (F_V/F_M and $1\text{-}V_J$) according to the recorded chlorophyll fluorescence profile (Kautsky curves). The red light covers a surface of 1 cm^2, resulting in highly reproducible measurements averaged over 1000 points. The electrochemical set-up is constituted of a DC voltage supply, which provide a bias potential in the range of ±0.800 V between the working and the reference electrodes, and an amperometer to detect the current intensity variation deriving from the algae oxygen evolution process. The biological module, perfectly sealed, hosts the samples under test. Both static and dynamic operations are allowed thanks to an automatically controlled fluidic system equipped of inlet and outlet connections for the electrolytic/washing solution and sample flow.

Figure 1. Dual electro-optical transducer prototype for the measurement of the chlorophyll a fluorescence and for the measurement of the current signals of algae under light illumination.

The main characteristics of the instrument are:

1. A biologically relevant whole-cell biosensor for the detection of pollutants
2. Integration of microfluidic elements and appropriate microelectronics into the multi cell type biosensor to provide simple robust autonomously operating sampling and analysis modules.
4. Integration of pre-charged biosensor cartridges in an online autonomously operating system.
5. This product presents the platform for different whole cell biosensors, targeting several pollutants that can be further developed and incorporated into the diagnostic instrument.

Compared to existing products and competitors, this approach provides not only quantitative, but also qualitative information of treatment process, by giving information of the presence and concentration of pollutants as well as monitoring the potential process blockage these substances could provoke. This approach provides a dynamic diagnostic system, comparing with conventional punctual information. Based on these facts, it is expected to reach in the future a leading position on the market, as a specialized bio-diagnostic platform.

Concerning the TRL reached, we have passed:

Level 1 – Basic Principles Observed and Reported
Level 2 – Potential Application Validated
Level 3 – Proof-of-Concept Demonstrated, Analytically and/or experimentally
Level 4 – Component Laboratory Validated.

We now started work to pass TRL 5 Technology validated in (industrially) relevant environment, but more work must be performed in this step.

Despite the described advancements in the stage of development, the device still needs to work in the consolidation of the business models. During our feasibility study carry out in the project, we detected the necessary actions to take our product for current TRL 4 to a TRL 9 for the future.

Thus, we foresee technical and commercial activities to reach the market (Figure 2):

✓ Technical activities

- Improve stabilization of bioreceptors as well as develop new biomaterials or raw materials in house.
- Industrial development of different analysers adapted to end-user needs including functionalities such as automatic, online, remote and easy friendly.
- External Validation of the analysers and kits of bioreceptors carrying out PoP (Proof of Performances) including Commutability with other technologies.
- Certifications to be fully compliant to the current legislation.

✓ Commercial activities

- Dissemination activities such as brochures, web sites, videos and press campaigns in orderto get visibility.
- Communication activities address to Water Treatments Plants to reveal directly the scientific, technical and commercial validity of our products. It will include seminaries, exhibitions, demonstrations and involvement of end-users.
- Setup a distribution network in the target countries and train the possible collaborators involved in the products distribution.

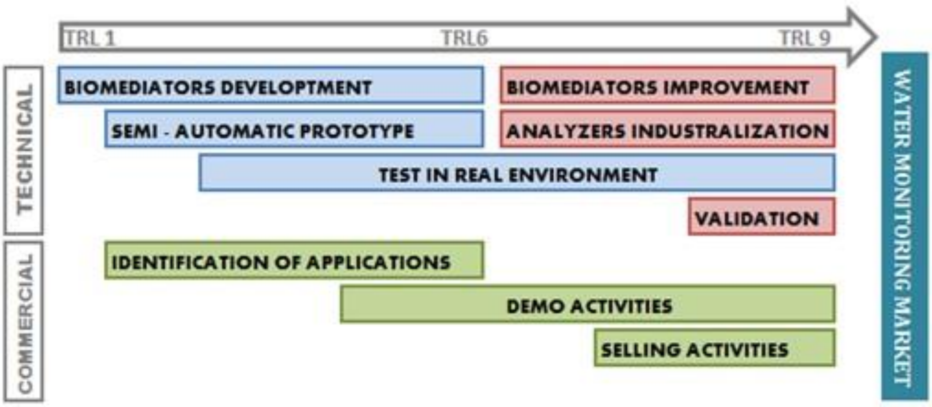

Figure 2. Next Development Activities.

D 4.6.1 and D 4.6.2 Document of evaluation of thedevices obtained

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PART 7: NUTRIENT ANALYZER (D4.2) AND SENSORS FOR ORTOPHOSPHATE ANALYSIS (D 4.3)

The literature survey highlights that phosphate analysis is performed by ionselective electrode in which the sensitive tip of the electrode is obtained by using selectively binding ion for phosphate detection (DL about 1 to 10 mM). To improve the sensitivity and reduce the interferences from the samples (either environmental of biological) enzymatic biosensors have been optimized. The improvement of the sensitivity was generally reported (0.1 to 1 mM as DL) but the drawback of the interferences from the samples is still reported as well as the fragility of the enzyme stability in some samples, particularly from the environment, is observed. These sensors and biosensors were intended to implement the instrumental approach aiming to transfer the analysis in field. In fresh water or samples of low salinity ion chromatography is offering a DL of about 50 nM, but in sea water more sample treatments are required due to the interfering effects of the other anions highly concentrated and with very unbalanced ratio. However, nutrient analyzer offers good performance with a DL of about 20 nM in sea (saline) water and the application of this instrumentation was performed by UNIVPM. The samples collection procedure, preservation and analysis was performed in these years and the reliability of the results was confirmed vs standard marine water as well. In this task the TRL of 9 was gained, in fact the total analytical procedure was optimized and tested in samples of sea water and of treated waste water. Moreover, metal ions were detected. In parallel, to transfer the analysis in filed, the optimization of a sensoristic approach for the electrochemical detection of phosphate was faced.

The designed analytical tool developed in the framework of Adswim project consists of a cost-effective carbonaceous electrode, which surface is purposely customized to electrochemically detect low amounts of orthophosphate eventually present in oligotrophic waters as the case of the Adriatic Sea. This chemical sensor was validated as a proof-of-concept for the reliable and highly sensitive quantification of phosphate ions in both standard solutions and relatively complex water samples. The technology developed here is based on the so-called “plastic electrodes” recalling their fabrication protocol using a combination of plasticizer and PVC polymer. This homemade and straightforward protocol showed a number of merits compared to other technologies present in the market, including the ease of formulation’s customization using chemical additives. Indeed, thanks to the embedment of octamolybdate anions, the sensor surface was tuned to recruit phosphate ions from the solution and form a new electroactive complex (phosphomolybdate) based on a chemical affinity mechanism. Another advantage of such technology is its scalability i.e. Larger carbon films could be fabricated to produce more electrodes/sensors from the same batch, which reduces remarkably the fabrication time. The DL gained was of about 5nM and the reliability of the results produced a peer-reviewed paper. The formulation was modified, over project duration, by adding mesoporous nanoparticles (POM) purposely prepared with different features to improve the DL offered by this sensor.

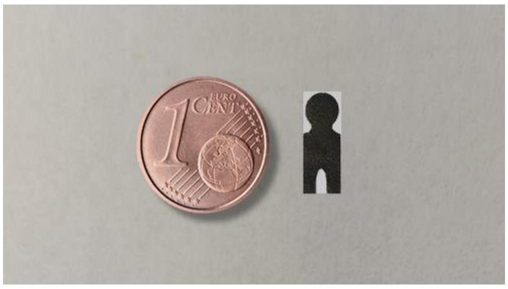

Figure 1. Photo of the phosphate sensor developed based on miniaturized plastic electrode showing its actual dimensions compared to a one-cent coin.

A classical electrochemical workstation was used for the experiments, implying a Gamry potentiostat, a classical glass cell equipped with conventional Ag/AgCl reference, and a platinum wire as the counter electrode. Competitive analytical performances were obtained, particularly in terms of detection limit recorded to be less than 1nM for the first time regarding phosphate detection. These encouraging outputs incite escalating the technological ladder further and making the device available for on-site routine analysis.

Nevertheless, further investigations are still needed to design a commercial prototype of the device by integrating the modified carbon-based electrodes in a portable electrochemical cell along with suitable formats of reference and counter electrodes. The engineering of the electrical part of such monitoring devices is already well known in the literature, especially since the detection technique relies on amperometric measurements that can be run using a miniaturized and straightforward set-up.

Another interesting option is to study the feasibility of microfluidic chips that enables the real-time monitoring of phosphate nutrient via continuous records of the redox signals.

Overall, the developed tool could be affected to the 4th level of technology readiness (TRL) for a commercial use since it passed the proof of concept, yet additional efforts should be conducted to bring the technology from level 4 (actual) to level 9 (according to the EU TRL designation) resorting to specific project supporting the development in research.

Level 1 – Basic Principles Observed and Reported.

Level 2 –Technology concept formulated.

Level 3 – Proof-of-Concept Demonstrated, Analytically and/or experimentally.

Level 4 –Technology validated in laboratory.

Level 5 – Technology validated in relevant industrial environment (e.g., WWTPs).

Level 6 – Technology demonstrated in relevant environment.

Level 7 – System prototype demonstration in operational environment.

Level 8 – System complete and qualified.

Level 9 – Actual system proven in operational environment with competitive manufacturing.

PART 8: CONCLUSIONS

This Wp 4 focus on the optimization of innovative solutions for chemical, microbiological control, and for treating urban wastewater. It emerged a very different degree of technological maturity among the research activities performed by PPs. Photodisinfection denotes high costs deriving from the preparation of the photoactive material and experimentation has failed to overcome the laboratory environment. More efforts in optimisation are required and devoted projects are desirable. The use of granular biomass appears to be interesting and more advanced as a technology of microbiological treatments of wastewater. To highlight a weakness, it emerged the difficulty in defining a general operating protocol as the efficacy of the treatment is very sensitive to the characteristics of the wastewater and of the plant features (see also D 5.1.1 and 5.1.2 and 5.2.1.).

both analytical (instrumental analysis) and microbiological (molecular tests) methodologies, conventional, have been successfully optimized and applied to the analysis of samples of both seawater and treated wastewater, confirming that they are robust technologies and indeed indicating that their application (in particular PCR analyzes for the characterization of bacterial populations emerging from wastewater) is strongly recommended to increase the detail of the knowledge of the wastewater composition (Waste water Based Epidemiology). The sensors and biosensors have been optimized for validated measurements with respect to reference samples and in particular, the biosensor for global toxicity algae-based have a good level of technological advancement and its engineering is already being defined. Surely a great variety of results emerged which suggest further research and study activities to tackle.