LIFE Project Number

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DELIVERABLE D.B.1.1: REPORT OF THE DESIGN OF BOTH PROTOTYPES (PLANS AND COMPONENTS).

ADNATUR: Demonstration of natural coagulant use advantages in physical & chemical treatments in industry and urban waste water.

CONTENTS

1. INTRODUCTION

ADNATUR project aims to validate, assess and industrially demonstrate a new innovative and environmentally friendly technology. This technology is based on products derived from natural extracts, for its use in the primary treatment of wastewaters, at urban and industrial level.

Some of the advantages offered by this new technology derives in energy and resources save and the removal of hazardous chemical waste production during the physical-chemical treatment of industrial or urban wastewater. In order to demonstrate these advantages two wastewater treatment industrial-scale prototype plants will be designed, assembled, and put into operation in different real end-users facilities.

During this task two prototypes, specifically adapted to treat wastewater coming from different sectors, will be designed and constructed. First prototype is mainly focused on feeding industrial water, in particular textile and ceramics sector. Second prototype is exclusively focused on feeding urban water.

Current report presents design plans and components description of these prototypes. In addition to that, further technical details focused on the treatment procedure are also included.

2. INDUSTRY WASTE WATER.

2.1 Facilities.

The characteristics of each kind of waste waters coming from industrial sectors are very different, for this reason the problems derived from its treatment are very diverse and specific. During the development of this new technology, two kinds of waste water coming from industrial sectors (ceramic and textile sector) will be treated. The characterization of different waters will be shown in the next points.

a. Ceramic sector.

In the ceramic industry many wet processes are given, which implies high consumption of water. Companies included in this sector, carried out manufactured ceramic tiles finishes. This means chamfering and/or polishes the surface to achieve different finishes. For this purpose, highly abrasive grinding wheels made with substances that are consolidated by inorganic salts and resins are used.

In this process, water is used for cooling both the grinders and cutting and polishing saws and for dragging the eroded particles from the ceramic pieces. The main characteristics of this kind of water are:

- High salinity caused by continuous supply of salts from the abrasive used in the polishing process and a minor fraction from inorganic coagulants used in their treatment. However, this water does not have problems of organic matter, heavy metals and boron.
- High conductivity values cause corrosion and fouling problems on facilities and pipes and, for instance, greatly reducing the average life of them.

In this type of water is essential establishing an appropriate system of purges in the circuit in order to keep the salt content between appropriate values.

The samples of the ceramic sector used for the study of the new technology based on natural coagulants are from two different processes. The first sample is from ceramic grinding. A complete characterization of that sample is shown in Table 1.

PARAMETER	Method	Units	Result
pH	ELM/001	u pH	8,2
Conductivity 20 ºC	ELM/004	µS/cm	2210

Chlorides	VOL/005	mg/l	319
Turbidity	NEF/001	NTU	800
Chemical Oxygen Demand (COD)	EAM/006	mgO_2/l	32
Suspended solids	GRA/001	mg/l	2939
Sulphates	EAM/011	mg/l	460
Calcium	VOL/002	mg/l $CaCO_3$	1225

Table 1. Ceramic grinding wastewater characterization.

The second sample is from ceramic glazes. A complete characterization of that sample is shown in Table 2.

PARAMETER	Method	Units	Result
pH	ELM/001	u pH	7,0
Conductivity 20 ºC	ELM/004	µS/cm	2520
Chlorides	VOL/005	mg/l	390
Turbidity	NEF/001	NTU	800
Chemical Oxygen Demand (COD)	EAM/006	mgO_2/l	1905
Suspended solids	GRA/001	mg/l	10000
Sulphates	EAM/011	mg/l	150
Calcium	VOL/002	mg/l $CaCO_3$	830

Table 2. Ceramic glazes wastewater characterization.

In the Tables 1 and 2, the parameters analysed in water samples used in this study are indicated, as well as, the internal laboratory method.

b. Textile sector.

The textile industry consumes large quantities of water and produces large volumes of wastewater from different steps such as tanning, dyeing and finishing processes. For this reason, wastewater treatment represents an important environmental issue. Consequently, correct management is necessary for water reuse in the textile industries. Wastewater from textile industry is often rich in color, containing residues of reactive dyes and chemicals, high COD and BOD concentration, high values of conductivity as well as much more hard-degradation materials.

The sample collected for the study of the new technology base in natural coagulant is from tanning industry. The tanning industry is of a considerable pollution load in terms of both organic and toxic parameters. A complete characterization of the sample from textile sector, more specifically from tanning is shown in Table 3.

PARAMETER	Method	Units	Result
pH	ELM/001	u pH	7,3
Conductivity 20 ºC	ELM/004	µS/cm	5080
Chlorides	VOL/005	mg/l	532
Turbidity	NEF/001	NTU	> 1000
Chemical oxygen demand (COD)	EAM/006	mgO_2/l	3145
Total nitrogen	EAM/010	mg/l	150
Suspended solids	GRA/001	mg/l	2515

Table 3. Textile wastewater characterization.

In the Table 3, the parameters analysed in water samples used in this study are indicated, as well as, the internal laboratory method.

2.2 Prototype scheme.

Main scheme of the prototype designed for wastewater coming from ceramic and textile sectors is presented below. It is based on lamellar decantation physics-chemical procedure.

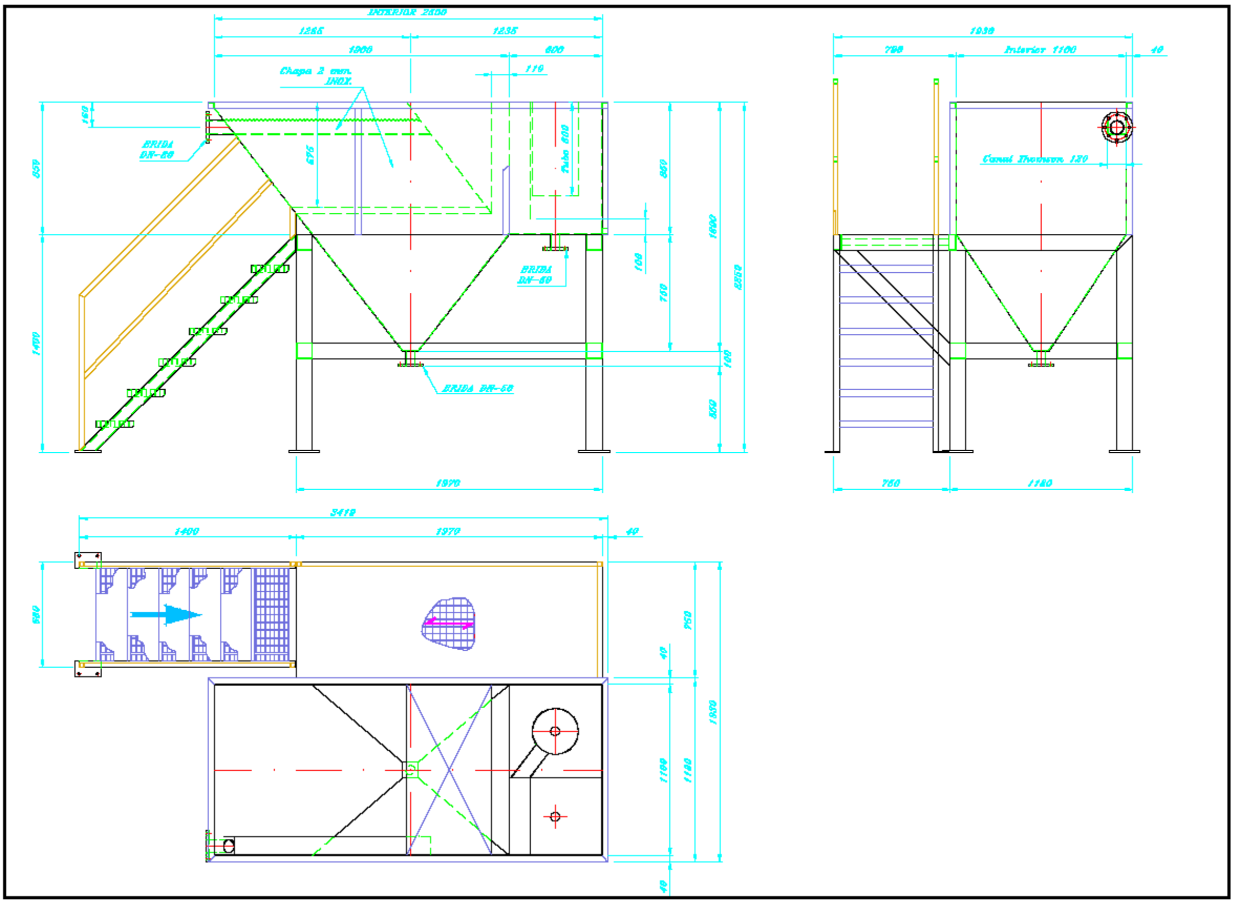

Figure 1. Scheme for industrial wastewater prototype.

Most relevant properties of the current prototype are presented below:

- Flow rate: 1 m^3.
- Coagulation tank capacity: 100 liters.
- Coagulation stirrer rate: 150 rpm.
- Coagulant flow rate: 0,2 liters.
- Flocculation tank capacity: 100 liters.
- Flocculation stirrer rate: 100 rpm.
- Flocculant flow rate: 0,15 liters/hour.
- Decanter capacity: 2 m^3.
- Decantation surface: 1,2 m^2.
- Sludge outflow: 75 liters/hour.
- Flocculant mixer capacity: 100 liters.
- Flocculant mixer stirrer rate: 50 rpm.

2.3 Prototype components.

Main components of the developed prototype, focused on wastewater coming from ceramic and textile sectors are deeply described bellow:

1. Coagulation tank.

After coagulant dosage, treated water need some time to react. In the coagulation tank suspended and dissolved matter are conveniently destabilized in order to generate colloidal particles. These particles are invisible by glance, but present a high speed transport and specific contact area. Therefore, they are more sensitive to surface interactions than gravitational forces.

2. ADNATUR dosing system.

Natural based coagulants present a great number of advantages previously reported. However, reaction time limits its coagulant efficiency. To avoid this issue current system present a specific dosing system where coagulant and water are simultaneously injected in order to dramatically reduce reaction time of natural based coagulant. This way it is competitive compared to currently used inorganic coagulants, maintaining its environmentally friendly properties.

3. Flocculant mixer.

Current decantation system use a solid anionic polyacrilamide based flocculant. Pilot plant contains a small deposit where the flocculant needs to be previously dissolved in water. The preparation procedure is not automatic and recommended flocculant/water ratio is 1/1000.

4. Flocculation tank.

After flocculant dosage, treated water need some time to react. In the flocculation tank previously generated colloidal particles are aggregated in order to form flocs which are easily separated from water by a sedimentation process.

5. Decantation tank.

When flocs are well formed decantation procedure occurs. Current pilot plant presents a lamellar system where decantation is favoured. This way, with smaller pilot size decantation surface is exponentially increased in order to accelerate solid-liquid separation.

6. Outlet water.

Treated water does not contain high levels of suspended solids or turbidity and needs to fit technical requirements in some physico-chemical properties. If requested, samples of treated water must be picked up from this point. In order to ensure correct treatment, physico-chemical parameters of incoming and treated water should be conveniently compared, confirming reduction percentages.

7. Sludge extraction.

Solid matter, once separated, is extracted from the lower part of the system in sludge form. The dewatering properties of the generated sludge really depend on the chemical treatment. This way, using natural based coagulants generated sludge does no contain metals and could be used in specific applications.

2.4 Operating procedure.

Chemical treatment in the current plant is based on a combination of different reaction mechanisms. Most important processes are described bellow:

- Cross-linking: Suspended particles are agglomerated and efficiently removed, forming floc structures by three different direction lines.
- Adsorption: Colloidal particles interact physically with formed flocs, being adsorbed in the surface, increasing floc size and reducing its stability in solution.
- Destabilization of charges: Before coagulant dosage, suspended particles are stable in solution. This way, a negative charge excess is present in the media and avoids particles interaction. Coagulant dosage introduces positive charges that rapidly react with negative cloud and permit suspended particles interaction.
- Complexation: ADNATUR technology, based on the chemical treatment, is able to form complexes with some divalent metals present in water, like Zinc or Nickel, easily removed by liquid-solid separation procedures.

3. URBAN WASTE WATER.

3.1 Facilities.

In most Urban Wastewater Treatment Plants (WWTP) the main problematic parameter are the suspended solids and the colloidal particles that remain stable in inlet water. These particles are the main visible contamination parameter because they add turbidity, colour or pollutants, among others. In order to eliminate these solids, primary treatments or physicochemical treatments are used. Physicochemical treatments consist in the addition of coagulant reagents in order to remove 80 – 90% of the total suspended matter, 40 – 70% of BOD_5 and 30 – 40% of COD. In other cases, chemicals are used to remove specific contamination. For instance, in the WWTP case of our study, ferric chloride is used in the secondary decanter, after biological treatment, in order to remove phosphates as a specific pollutant.

The samples for the study are coming from an Urban Wastewater Treatment Plant which scheme is described bellow:

Most important components/treatments are defined in the following lines:

Wastewater Pre-treatment

- *Homogenization Tank*: Inlet wastewater is homogenized and provisionally retained, thus heavy solids settle to the bottom and other solids like oil, grease and lighter solids, float to the surface. The settled and floating materials are removed and liquid is discharged to secondary treatment.

Secondary Treatment

- *Biological Reactor*: In this treatment, dissolved and suspended biological matter is removed. Microorganisms in a managed habitat degrade biological matter and form a sludge that is disposed of and recycled.
- *Secondary sedimentation*: Suspended particles settle in these basins. Some of these settled microorganisms are recirculated into the activated sludge process in order to maintain a high microbiological concentration. In order to remove phosphates and improve settling time, ferric chloride is added.

Tertiary Treatment

- *Coagulation and flocculation process by flotation*: In order to remove specific pollutants and remain suspended solids, an additional flotation chemically based treatment is required.

Disinfection

- Ultraviolet system: Ultraviolet is used to disinfect treated water.

The sample of the WWTP comes from the biological reactor. A complete characterization of that sample is shown in Table 4.

PARAMETER	Units	Result
pH	u pH	7,4
Conductivity 20 ºC	µS/cm	1571
Suspended solids	mg/l	3335
Chemical Oxygen Demand (COD)	mgO_2/l	4005
Turbidity	NTU	1448
Total phosphorus	mg/l	92,4
Iron	mg/l	117,8
Aluminium	mg/l	7,07

Table 4. Characterization of the sample from biological reactor.

3.2 Prototype scheme.

Main scheme of the prototype designed for wastewater coming from urban sector is presented below.

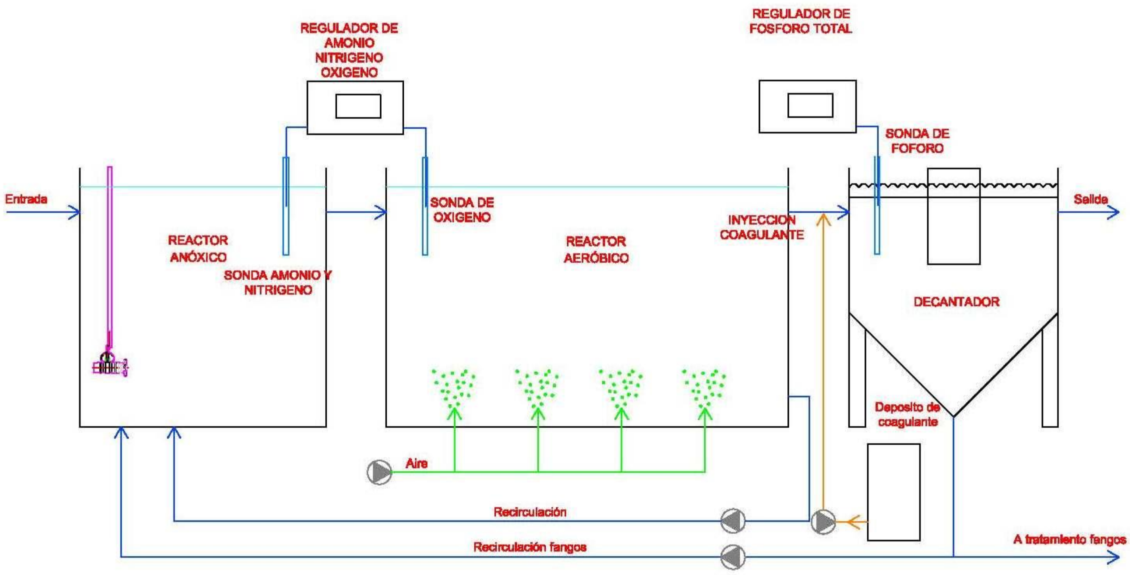

Figure 2. Scheme for urban wastewater prototype.

Most relevant properties of the current prototype are presented below:

- Flow rate: 1 m^3.
- Anoxic reactor capacity: 3000 liters.
- Anoxic stirrer rate: 1200 rpm.
- Aerobic reactor capacity: 3000 liters.
- Coagulant flow rate: 0,2 liters.
- Decanter capacity: 2 m^3.
- Sludge outflow: 150 liters/hour.

3.3 Prototype components.

Main components of the developed prototype, focused on urban wastewater, are deeply described bellow:

1. Wastewater inlet.

Proposed prototype is designed to fit the end user requirements. In this case, industrial scale biological treatment is based on two different treatments, one for COD removal and another for Nitrogen and Phosphorus removal. Accordingly, in the proposed pilot plant, inlet wastewater comes from the first industrial reactor where COD levels are dramatically reduced.

2. Anoxic tank.

In the anoxic tank, the nitrification-denitrification process is produced. This process occurs in anoxia conditions, accordingly without the presence of oxygen. Its function is reducing the quantity of nitrogen in order to reach values of discharge. This reduction is carried out for the current bacteria that transform ammonium to nitrogen gas which is released to the atmosphere.

3. Anoxic mixer.

The anoxic tank is stirred but not aerated (no oxygen is generated). Accordingly, a good homogenization of the tank is absolutely necessary for a proper process of nitrification-denitrification.

4. Biological reactor.

Biological treatment is carried out inside this reactor that is specifically designed to focus on Nitrogen and Phosphorus removal, increasing the treatment efficiency. In this point of the process, activated sludge is generated and partially returned from the second stage, based on decantation.

5. Blower.

The biological reactor needs good aeration in order to have a proper contend of dissolved oxygen, so inside the biological reactor an aeration system is conveniently included. Microbial content need to live and grow in this media so dissolved oxygen is absolutely necessary. Accordingly, blower generates microbubbles to reach homogeneous and complete distribution of oxygen in the reactor.

6. Aeration system.

The aeration system is the equipment, located outside the biological reactor, that generates the air to be distributed through the blower. Start and stop of the aeration system is controlled by the dissolved oxygen level currently present in the biological reactor.

7. Dissolved oxygen electrode.

In order to fit bacteria requests and correctly control its grown, dissolved oxygen detector is included in the biological reactor. This way, aeration system activation is directly managed by the detector measures.

8. Ammonium-Nitrate probe.

In the nitrification process, that is previous to the denitrification, the ammonium is transformed into nitrate. Accordingly, in order to control both species an Ammonium-Nitrate probe is absolutely necessary. This way, Ammonium-Nitrate levels help us to determine current efficiency of the process.

9. ADNATUR dosing system.

Natural based coagulants present a great number of advantages previously reported. However, reaction time limits its coagulant efficiency. To avoid this issue current system present a specific dosing system where coagulant and water are simultaneously injected in order to dramatically reduce reaction time of natural based coagulant. This way it is competitive compared to currently used inorganic coagulants, like ferric chloride, maintaining its environmentally friendly properties.

10. Decanter unit.

Designed prototype contains a physico-chemical unit where formed flocs are separated by decantation. ADNATUR products are previously injected in order to improve solid-liquid separation and increase Nitrogen/Phosphorus elimination.

11. Equipment for phosphorus determination.

In order to control the phosphorus removal rate after the treatment, a specific equipment for phosphorus determination is introduced in the physico-chemical decantation stage. Current equipment is able to determine phosphorus content through an in situ colorimetric procedure.

12. Activated sludge return system.

Generated sludge in the physico-chemical decanting process is partially returned to the biological reactor as an activated sludge. This way, microbial population is maintained between specific levels and could be easily controlled.

13. Water outlet.

Treated water is also separated in the physico-chemical decanting process and then discharged. For that reason, outlet water must fit very strict levels, mainly physico-chemical and microbiological parameters like COD or Phosphorus content.

14. Sludge extraction system.

Generated sludge in the physico-chemical decanting process is partially extracted and sent to the sludge dewatering system. In this case, generated sludge will be dewatered in a centrifugal system.

3.4 Operating procedure.

In order to obtain the most improved efficiency of the proposed treatment, final optimization of the operating procedure was necessary. Two different stages of the pilot plant were slightly modified in order to maximize the efficiency.

i) Adjustments on the dosing point of ADNATUR technology.

Several points of dosage for ADNATUR products were tested. The dosage before the biological reactor was rejected, because the sludge settles in the reactor and this is detrimental for the activity of the activated sludge. Thus, the best point of ADNATUR technology application is in the outlet of the biological reactor, before of the settler. At this point, ADNATUR technology achieves the proper sludge settling, obtaining clarified water without suspended solids. Although the active sludge is partially returned in order to maintain a high microbiological concentration, biological reactor presents a residual amount of ADNATUR products. However, this amount is insignificant and does not affect the proper efficiency of the biological reactor.

ii) ADNATUR dosage management depending on the phosphorus concentration.

An equipment of phosphorus control has been placed in the outlet of the settling tank. This way, depending on the amount of phosphorus measured, ADNATUR products dosage in the settling tank inlet would be properly modified. Thus, the amount of ADNATUR products will be perfectly controlled, avoiding overdoses. Moreover phosphorus, which is a crucial parameter in this kind of facilities, will be under control all the time.

Finally, to have a proper performance of the facility, key factors in the coagulation process have to be taking into account. Accordingly, efficiency of the coagulation processes depends on the following parameters:

- **pH**. It is necessary to adjust the pH in order to precipitate the metal hydroxides present in the solutions. It is the most important parameter to control in order to get a proper coagulation. However, using natural-based coagulants adjustment is not required because coagulant mechanism and product reactivity is different.

- **Temperature**. Low temperatures affect the coagulation-flocculation process, by altering the solubility of the coagulant, increasing the viscosity of water and slowing the reaction kinetics.
- **Dissolved organic matter**. The amount of NOM present has a determining effect on the required dosage of coagulant.
- **Turbidity**. Coagulant doses are generally higher when water turbidity increases.

4. CONCLUSIONS

Two wastewater treatment industrial-scale pilot plants have been designed and assembled. First prototype is mainly focused on feeding industrial water, in particular textile and ceramics sector. Second prototype is exclusively focused on feeding urban water. To do so, during current action both prototypes have been specifically adapted to treat wastewater coming from different sectors.

Current report presents design plans and components description of these prototypes. In addition to that, further technical details focused on the treatment procedure have been also included.

The main objective of this action is the design and construction of both prototypes, for industrial and urban wastewater treatment. The development of the corresponding plans and descriptive schematics of the pilot plants have constituted a clear indicator of progress within this action.