LIFE Project Number

LIFE12 ENV/ES/000265

DELIVERABLE D.A.1.2: REPORT OF THE PRE-INDUSTRIAL ASSESSMENTS RESULTS IN URBAN WASTE WATER.

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

EXECUTIVE SUMMARY

D.A.1.2 summarizes the first studies and validation carried with wastewater from WWTP at laboratory level. It has been compared the results between the usual procedure and with different doses of the natural coagulants.

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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. The proposed technique will be demonstrated at industrial level in two Spanish companies from textile and ceramic sector and, on the other hand, at urban wastewater level.

Currently presented action is focussed on natural based coagulant validation procedure when treating urban wastewaters. In order to do so, the coagulant efficiency at laboratory scale will be tested in real wastewater samples coming from the urban wastewater. Thus, several Jar Tests using increasing dosage of natural coagulants will be carried out. The efficiency of natural coagulants will be compared with the efficiency of currently used inorganic coagulants. Raw materials used for developing natural coagulants comes from the same substrate, extracted form acacia, and is chemically modified in order to improve its coagulant efficiency. This modified coagulant, even improved after the laboratory scale tests, will be used lately in the industrial demonstration phase.

In this specific action the main advantages that will be demonstrated are, among others:

- Reduction of corrosive tendency and/or fouling of water, increasing the lifetime of the facilities in contact with treated water.
- Increase of the security of workers due to the substitution of hazardous products by eco-friendly products.
- Minimization of chemicals use, such as coagulants and flocculants, avoiding neutralizing agents in the physical-chemical treatment and controlling salt supplies.
- Improvement of biological processes and sludge dehydration.
- Reduction of costs derived from hazardous wastes management.

2. EXPERIMENTAL PROCEDURE

In order to validate the new technology based in natural coagulant a coagulation-flocculation, a great number of tests at laboratory scale will be carried out. Standard procedures are called Jar Test. In this test a specific device, called flocculator, is required. This equipment has six points of homogenization, which allows, at a controlled speed, simultaneous stirring of the liquid contained in several beakers. It is very important that during the test, water sample has approximately the same temperature than in the real treatment plant.

Jar Test method helps to determine the efficiency of coagulants, prepared in aqueous solution (5% w/w), in the specific samples of wastewater. Furthermore, with this method the minimal dosage of coagulant product to obtain an optimum clarified after treatment is determined. Each beaker contains 500 ml of water to be treated and they are located along the ascending order of coagulant concentration. After the coagulant addition, the pH value should be set to a given working value. When a natural coagulant is used, the pH value should be between 4,5 and 9. The pH value is corrected with an acid or a base such as hydrochloric acid or sodium hydroxide. The consumption of neutralizing product will be registered, since it is a crucial factor when the final result is assessed. Once the coagulant has been added, the pH value was adjusted and it reacts for 5 minutes at 120 rpm. Then, the stirrer is stopped in order to make relevant observations.

At that time, the flocs fall to the bottom of the beaker, the clarified grade is reached and the rate of settling is visually scored. After that, flocculant diluted in water is added, with a dilution of 1‰ if it is solid or 2‰ if it is liquid. For this step, the stirrer should have a speed of 60 rpm during 120 seconds.

Once all the process has been carried out and the optimum dosages have been obtained, the Jar Test is repeated with the same sample and with the same combinations of coagulants, but adding the total amount of products in one step only. When the dosage is gradual, the reaction time is longer than with one-step dosage and results could be not realistic. With this final test, the reproducibility of the treatment and the dosages of coagulants have been assessed.

3. RESULTS AND DISCUSSION

Urban wastewater treatment plants (WWTPs), receive complex mixtures of nutrients and organic/inorganic micropollutants, which are treated to reduce their concentrations in order to avoid the environmental impact. In many cases raw wastewater needs chemical treatment, either as the only direct precipitation treatment or as a tertiary treatment in order to improve treated water quality. Thus, in WWTP physical-chemical treatment are used in order to remove contaminants associated with organic matter particles, suspended matter, organic micropollutants, bacteria, heavy metals, and others like phosphates or metals. For a customized treatment, characterization of inlet water is needed in order to establish the problematic parameters and proceed to reduce their concentration down to acceptable values.

3.1 Urban wastewater characterization.

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:

<u>Wastewater Pre-treatment</u>

- *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 1.

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 1. Characterization of the sample from biological reactor.

3.2 Physical-chemical treatment procedures.

After the previous characterization, an efficiency comparison between inorganic coagulants and natural based coagulants has been carried out. The main objectives to be achieved in the current laboratory scale study are:

- Assess coagulant efficiency of ADNATUR technology in front of standard inorganic coagulants in wastewater.
- Verify that natural base coagulants reduce corrosive tendency and/or fouling of water. Lifetime of the facilities in contact with treated water will be extended because of non-toxic and environmentally friendly character of the products used in the eco-innovative technology. Moreover, security of workers will be also improved.
- Regarding its strong cationic character and its optimal coagulant efficiency in a wide range of pH, proposed technology provides a rapid flocculation and decantation, even at lower chemical dosage values.
- Control the salts supplied to the treated water to not damage the current production system. Furthermore, with non-incorporation of metallic elements as Iron or Aluminum, the next steps like biological processes or sludge dewatering processes will be clearly favoured.

As has been mentioned previously, in order to compare the different coagulants at laboratory scale, the Jar Test procedure has been used.

3.2.1 Secondary sedimentation after biological treatment.

In order to carry out the experimental tests during the secondary decantation process after biological treatment, a sample of inlet water from the biological reactor was collected. In the current procedure three coagulants were compared: an inorganic coagulant, in this case ferric chloride and two coagulants from ADNATUR technology, the coagulants named as ADNATUR K70 and ADNATUR K20.

ADNATUR K70 and ADNATUR K20 are based on tannin natural coagulant with a strong cationic character. The raw material is extracted from the bark of the Black Acacia (Acacia mearnsii), which has a strong coagulant action. The tannin extract is chemically modified in order to even improve its coagulant efficiency. ADNATUR K20, moreover, has organic additives that improve its efficiency.

In Table 2, the most remarkable results of the Jar-Test carried out have been shown. In this case coagulant is the only reagent used.

Products/ppm	1	2	2
Ferric chloride	625	-	-
ADNATUR K70	-	312	-
ADNATUR K20		-	312
Stirring speed (rpm)	100	100	100
Stirring time (sec)	20”	20”	20’’
Sedimentation (*)	L	M	M
Turbidity (**)	8	10	10

Table 2. Coagulation test result.

** S: Sedimentation → R (decanted in less than 4 seconds) M (decanted in less than 10 seconds.)*

L (decanted in more than 10 seconds) F (floats)

***T: Turbidity → Scale (1-10) of the clarified water after 20’’, 10 being the best clarified.*

It is observed that the best results are achieved by using ADNATUR technology based on natural coagulants. Clarified water with low value of turbidity and proper separability is achieved with a reduction in the coagulant dosage of 50%. With respect to the formed flocs after the use of the tested coagulants, ADNATUR K20 exhibits a higher degree of dewatering and increased resistance than with the other coagulants and floc formed has higher diameter. In the case of ADNATUR K70 the floc formed is more resistant than the floc formed with ferric chloride. Moreover, sludge volume is reduced in approximately 40% with ADNATUR technology as is shown in the following picture.

Figure 1. From left to right, Test 1 (ferric chloride), Test 2 (ADNATUR K70) and Test 3 (ADNATUR K20).

Then, the analytical results obtained from the resulting clarified water are detailed bellow:

0.- Inlet water.

1.- Outlet water.

2.- Clarified water after 625 ppm of **Ferric Chloride**.

3.- Clarified water after 312 ppm of **ADNATUR K70**.

4.- Clarified water after 312 ppm of **ADNATUR K20**.

PARAMETER	Units	0	1	2	3	4
pH	u pH	7.4	7.3	7.1	7.7	7.7
Conductivity 20 ºC	µS/cm	1571	1151	1674	1569	1239
Suspended solids	mg/l	3335	19	37	48	55
Chemical Oxygen Demand (COD)	mgO_2/l	4005	68.7	57.3	73.4	78.5
Turbidity	NTU	1448	2.1	<0.05	5	4.3
Total phosphorus	mg/l	92.4	0.687	<0.5	<0.5	<0.5
Iron	mg/l	117.8	1.02	4.99	3.11	3.42
Aluminium	mg/l	7.07	0.105	0.126	0.277	0.354

Table 3. Clarified water characterization.

REMOVAL RATE (%)	1	2	3	4
Conductivity 20 ºC	26,7	-6,6	0,1	21,1
Suspended solids	99,4	98,9	98,6	98,4
Chemical Oxygen Demand (COD)	98,3	98,6	98,2	98,0
Turbidity	99,9	100,0	99,7	99,7
Total phosphorus	99,3	100,0	100,0	100,0
Iron	99,1	95,8	97,4	97,1
Aluminium	98,5	98,2	96,1	95,0

Table 4. Removal rate.

From the results obtained it can be concluded that the coagulant ADNATUR K70 and ADNATUR K20, besides not increasing conductivity of the sample, reduces it. Furthermore, the coagulants ADNATUR with a dose reduction of 50% produce the same removal rate in problematic parameters than the inorganic coagulant, ferric chloride. Moreover, they reduce the iron in more than a 97% by not providing heavy metals as ferric chloride. Finally, as is appreciated in the photography, the clarified obtained with ADNATUR technology, do not have color. The color is a parameter to take into account in this area because there are textile industries that provide color to the inlet water.

In order to compare sludge settling time, a settling curve was carried out, the results are shown below:

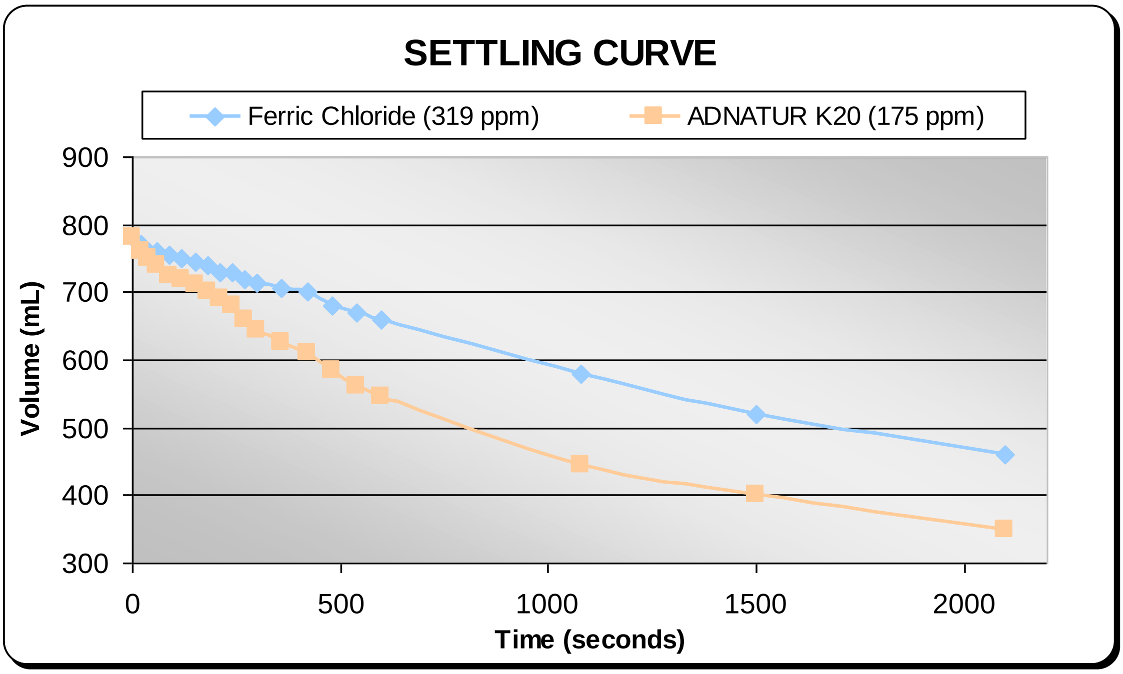

Figure 2. Settling curve comparing Ferric chloride vs. ADNATUR K20.

In Figure 2, the difference in sludge settling between treatment with inorganic coagulant Ferric Chloride and ADNATUR technology is shown. Using ADNATUR K20 as a chemical treatment, the rate of settling greatly increases. Furthermore, the sludge volume is reduced in a 41% with Ferric Chloride and in a 55% with ADNATUR K20.

3.2.2 Tertiary treatment after sedimentation by flotation system.

In order to remove specific pollutants and remain suspended solids, an additional flotation chemically based treatment was required. Currently, this treatment is not necessary and it is unused, so this part of the plant is not operative during the project period.

4. CONCLUSIONS

After the improvement of the tannin extract from Acacia mearnsii, two new products with strong cationic character and very high coagulant efficiency, called ADNATUR K70 and ADNATUR K20, has been developed and validated at laboratory scale.

ADNATUR technology is compared with the most commonly used coagulants in wastewater treatment, inorganic coagulants. For this purpose, several Jar Tests have been carried out in at laboratory scale. Current treated samples come from urban wastewater sector. The conclusions obtained after the tests are described bellow:

- ADNATUR technology is more efficient than current inorganic coagulants as ferric chloride. With this technology up to 50% of coagulant dosage has been reduced at laboratory scale.
- The strong cationic character of ADNATUR technology, gives the formed flocs a higher degree of dewatering and increased resistance.
- Additionally, corrosiveness of treated water was experimentally reduced and lifetime of the equipment in contact with treated water would be extended. In order to monitor this tendency, conductivity value of treated water has been controlled and consequently reduced with the use of ADNATUR technology.
- Substitution of hazard chemicals, as ferric chloride, for eco-friendly products like ADNATUR K20 or ADNATUR K70 would improve security of worker, reduce waste to be treated and improve next steps in water treatment, including biological processes or sludge dewatering. In this case, sludge volume has been reduced in 55% approximately.