Deliverable D1.2
Second report on project progress

Lead Beneficiary	PoliMi
Delivery Date	30 05 2021
Dissemination Level	PU
Version	1.0

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 821431

Second report on project progress

Deliverable D1.1

Deliverable name	Second report on project progress
Deliverable No.	D1.2
Dissemination Level[1]	Public
Work Package	WP1
Task	Task 1.1 & 1.2
Contributing beneficiary(ies)	PoliMi, CaptiveS, IDENER, ISQ, Gaser CNano, NTUA, RISE, AXIA, ASFIMET, Kampakas, Tecnochimica
Due date of deliverable	31/05/2021
Actual submission date	28/06/2021
Lead beneficiary	PoliMi

Document Information

Author	All partners	
Version number	1.0	
Date	28/06/2021	
Reviewed by		
Comments		
Status	✓	Submitted
		Accepted
Action requested		To be revised

[1] PU = PUBLIC
PP = Restricted to other programme participants (including the Commission Services)
RE = Restricted to a group specified by the consortium (including the Commission Services)
CO = Confidential, only for mbers of the consortium (including the Commission Services)

Document history

Version	Date	Beneficiary	Author
0.1	07/05/21	PoliMi	Chrysavgi Kostoula
0.2	10/05/21	CaptiveS	Ruggiero Pesce
0.3	12/05/21	IDENER	Jesus Buzon, María Tripiana Serrano, Ana Lara
0.4	17/05/21	ISQ	Cristina Matos
0.5	21/05/21	ASFIMET	Elena Travaini
0.6	28/05/21	AXIA	Cristina Onorato
0.7	02/06/21	NTUA	Chrysa Panagiotopoulou, Dimitra Kosmidi, Lefki Sakellariou
0.8	10/06/21	RISE	Anwar Ahniyaz, Abhilash Sugunan
0.9	14/06/21	CNano	Alexandros Karathanasis
1.0	28/06/21	Gaser	Alessio Carminati

Publishable Executive Summary

Deliverable 1.2 "Second report on project progress" gives an overview of the status of the project covering all the tasks foreseen after the first reporting period on M18.

By month 24, the PureNano project has defined data on the overall specifications and requirements of the materials and components that will be developed as well as of the overall demonstration activities. The MNPs production line has been optimized and validated after the first runs with different types of MNPs. Thorough MNPs characterization has been performed and partners implemented activities regarding the functionalization of MNPs with biopolymers that will provide new types of MNPs with higher acidic stability. Moreover, the design of the purification plants for both Gaser and CNano pilot lines were finalized and partners are finalizing the installation of the plants in their premises. Activities to assess the recycling routes of the used MNPs as well as studies on sustainability of the MNPs production and wastewater purification processes are ongoing. Market assessment as well as ecological, financial and social evaluation of the proposed technology are taking place. Finally, safety, training and standardization activities are also under development and aim to ensure an easier acceptance of the technology from the targeted market and society.

This document summarizes all ongoing Tasks and gives a detailed view of the milestones achieved, the pitfalls encountered and the progress of the project.

Table of Contents

List of Tables

List of Figures

Abbreviations and acronyms

WP	Work Package
MNPs	Magnetic Nanoparticles
Mo	Months
SM	Social Media
KER	Key Exploitable Result
IPR	Intellectual Property Rights
D&C	Dissemination & Communication
PEDR	Plan for the Exploitation and Dissemination of Results

1. WP1 - Management & Coordination

1.1 Overview of activities in WP1

1.1.1 Task 1.1: Administrative and financial project management

Administrative and financial project management are ongoing with PoliMi being the contact point for the EC and the partners providing regular updates on project status to the EC.

Three consortium meetings and a review meeting were organized:

- Kick-off meeting, Athens, 12-13 September, 2019
- 9Mo consortium telematic meeting, 1-2 April, 2020
- 18Mo telematic consortium meeting, 4 December 2020
- 1st telematic Review meeting, 1-2 February 2021

During these meetings, partners presented the progress of the activities, identified issues and defined tasks to be completed. Moreover, during the review meeting, project activities were assessed by the reviewer and an external expert with positive feedback on the overall progress of the project.

PoliMi was responsible for the interim payment received after the periodic report and all project partners monitor continuously the expenses and personnel effort according to the budget allocated.

COVID-19 emergency has led to some delays in the technical activities of the project and has postponed visits to partners facilities important for the implementation of some activities. Moreover, all meetings during the last 12 months have been done remotely due to the health emergency. All partners are dedicating effort on monitoring eventual delays in their activities and on identifying mitigation actions and implementation strategies.

1.1.2 Task 1.2: Technical project management

PoliMi in close collaboration with the Technical Manager and the Work Package Leaders, has been managing the technical part of the project. Technical risk management has been updated and delays have been taken into account.

During the last 12 months no physical technical meetings were carried out by the partners due to the health emergency.

PoliMi provided support and revision of deliverables before their submission and the progress of the project was presented during the review meeting.

1.2 Achievements and results of WP1

1.2.1 Task 1.1: Administrative and financial project management

Administrative and financial project management led by PoliMi is currently running and has allowed to:

- identify issues and implement actions
- successful revision of the project
- define strategy to overcome delays due to the health emergency
- budget transfers to PureNano partners
- continuously monitor of costs and effort

1.2.2 Task 1.2: Technical project management

The technical project management allowed PureNano consortium to:

- submit all deliverables specified in the Grant Agreement in M01-M18
- achieve all milestones scheduled in M01-M18
- successfully implement activities and identify delays

Table 1. WP1 Deliverables submitted

Deliverable Number	Deliverable Description	Date
D1.1	First report on project progress	30/05/2020
D1.2	Second report on project progress	28/06/2021

Table 2. WP1 Milestones

Milestone Number	Milestone Description	Date
MS1	Kick off meeting	12-13/09/2019

2. WP2 - Generation of Specifications & Requirements

2.1 Overview of activities in WP2

5.1.1 Task 2.1: Specification on materials to be used

The raw materials used within the project for the production of aggregates of magnetic nanoparticles (MNPs) have been defined and specifications along with Safety Data Sheet were provided by all partners involved in the production and functionalization of MNPs as well as in the two plating lines to be treated. The technology that will be used for the purification of spent baths and wastewater is based on the use of magnetic-nanoparticles with specific functionalizations. The core of the particles is iron oxide, while the outer coating is selected according to the type of pollutant that needs to be removed. Three different categories of specific coating were defined: anionic, cationic and nonionic. The selection of the chemicals to be used for the functionalization was done avoiding the ones inserted in the SVHC list in order to propose a safe and green solution.

5.1.2 Task 2.2: Specification on purification systems

The main goal of task 2.2 is the identification and data collection for both processes to be studied, electroplating and electroless systems. Information collected at this task was essential for the design of the purification system. A thorough investigation has been carried out, taking into account all the involved streams, the main inputs, intermediate flows and outputs o in each process. Different points have been studied for Ni-P, NiP SiC, Zn and Cu electroplating processes, as well as for Ni electroless process. A top view of the processes taking into account the main parts of the system to provide a complete list of the involved streams has been provided. Moreover, information on the subprocesses of each plating process has been gathered together with data related to the equipment and information on the available equipment in the tow pilot lines. The gathered information has been fundamental for the development of activities in other WPs, especially in WP5 and WP6.

5.1.3 Task 2.3: End users' requirement

A detailed description of the plating processes has been provided by the end users along with information on the working parameters of the plating baths. Such information has been used for the functionalization of the MNPs, the design of the purification processes and the methods for MNPs reuse and safe disposal. Details on the process parameters of the plating baths such as pH, temperature, volumes and concentration of the undesired species and by-products were shared amongst partners. Importantly, the physicochemical properties of the species and the characteristics such as the charge and the type of additives used were also collected. End users' requirements were used for the production and functionalization of MNPs in order to increase their capturing efficiency.

5.1.4 Task 2.4: Update of Specification deliverables

With the aim to track the progress and deviations of the technical aspects of the project, an update of the specification deliverables has been performed. Information of the concentrations and type of undesired species as well as the developments of purification system design and equipment and the MNPs functionalization process were continuously shared among partners. This resulted in the optimization of the purification system design and the functionalization of the MNPs. Finally, the involved partners continuously provide updates on the progression of MNPs functionalization, contaminants characterization, process parameters and quality tests to verify the re-usability of plating baths.

2.2 Achievements and results of WP2

2.2.1 Task 2.1: Specification on materials to be used

The main achievement of this Task are summarized below:

- Materials selected of the MNPs functionalization correspond to the needs of the end users for the removal of metal species and organic compounds.
- MNPs production process has been optimized and the raw materials chosen do not require modifications of the already established synthetic route.
- Availability and cost of raw materials for MNPs production was verified and sustainability was achieved by selecting raw materials not present in the SVHC list.

2.2.2 Task 2.2: Specification on purification systems

Essential inputs were collected for the design and optimization of the purification system as well as the mathematical model developed in WP5. Specific aspects of each process have been identified such as:

- the different streams involved
- all the necessary chemical solutions in the process, taking into account capacity volume, concentration of the chemicals, final concentration needs, temperature and pressure as operating values

- pH needs and other operational parameters
- other details on each sub process

Different configurations of the purification system have been proposed and final designs have been selected for the final purification system in electroless and electroplating process.

2.2.3 Task 2.3: End user requirement

All aspects of the purification process and the mechanisms present in the spent plating baths were investigated. Parameters, types and concentrations of undesired compounds were also defined and work on the design of the purification system has been implemented. Moreover, studies on the MNPs functionalization, to adapt nanoparticles to the extraction of specific pollutants and their use in specific environment were carried out according to the inputs of this Task.

2.2.4 Task 2.4: Update of Specification deliverables

New information and updates related to materials and products, equipment and processes, recyclability and demonstration and validation activities were collected aiming to have a reference point for project implementation, including deviations and additions that came up during the last period.

Table 3. WP2 Deliverables submitted

Deliverable Number	Deliverable Description	Date
D2.1	Report on materials to be used	18/11/2019
D2.2	Report on equipment and purification system	29/10/2019
D2.3	Report on end user requirements	03/12/2019
D2.4	Updated report on PureNano Specifications	01/12/2020

Table 4. WP2 Milestones

Milestone Number	Milestone Description	Date
MS2	Delivery of plating line data to IDE and Kampakas	27/01/2020

3. WP3 - Magnetic NPs development

3.1 Overview of activities in WP3

3.1.1 Task 3.1: Modification of the MNPs production line

The main objective of WP3 was the setup of a pilot production plant with an enhanced production capacity and capable of producing different types of MNPs, such as anionic, cationic and non-ionic.

The formation of aggregates of magnetic functionalized nanoparticles is a one-step process, where chemical co-precipitation is combined with *in situ* surface functionalization with specific molecules. Particles can be synthetized from nanometer range to micrometer. The final dimension of aggregates is controlled by the parameters set during the production and by the type and percentage of outer coating. Mainly due to the safety and operational issues related to working with nano-materials, it was decided to set-up the production parameters in order to obtain micron-aggregates of functionalized magnetic nanoparticles.

The design of the new production plant was done in collaboration with partners Polimi, IDENER and Kampakas, taking into account the need of obtaining a well-controlled process capable to guarantee the optimal size and functionalization of the final aggregates of MNPs. The pilot plant has a versatile layout that makes it possible to produce MNPs according to the new synthetic routes (bio-based coated MNPs) that are under development. The output of the plant is a dispersion of MNPs in water with a concentration of 10% w/vol. The possibility to process further the product in order to obtain dried particles for static application was also explored. For safety and management reasons, it was decided not to proceed with this step due to the safety issues concerning handling micron-powder materials.

3.1.2 Task 3.2: Optimization of MNPs production

The core of the production plant is the static mixer in which the co-precipitation reaction, that leads to the formation of aggregates of functionalized magnetic nanoparticles, takes place.

The set-up of the parameters involved in this step is essential since it influences the final dimension of the aggregates. It is important to have a turbulent regime in the tube in order to have an efficient mixing of the reagents. During the scaling up of the production plant, the design of the plant was done in order to guarantee a minimum of turbulent regime in the tube.

Different runs, in collaboration with Polimi, were done in order to verify that the production guarantees standard products with reproducible characteristics.

3.1.3 Task 3.3: Optimization of the MNPS aggregation process

The final dimension of the aggregates of magnetic nanoparticles is strictly dependent of both on the process and on the formulation parameters. The pumping rate, the mixing efficiency and geometry of the static mixer influence the dimensions and the shape of the final aggregates. Moreover, differences in the coating and its percentage can lead to aggregates with difference sizes. In this Task, the characteristics of the final MNPs aggregates in relation to the chemical formulation of the reagents were investigated.

The first tests for optimizing the aggregation process were done changing the types of the coating and its percentage respect to the ferromagnetic core. It was decided to fix the process parameters (pumping velocity, mixing efficiency and geometry of the static mixing) while changing the chemical composition of MNPs. MNPs were produced using three types of coating: anionic, cationic and non-ionic. Moreover, for each type of coating, three different amounts were used. Subsequently, each set of MNPs produced was analyzed by IR-spectroscopy in order to check the presence of the coating on the surface and by particle size analyzer in order to assess the particle size distribution.

Currently, similar tests are ongoing, by producing MNPs with new functionalizations. In addition, bio-based polymeric coating, the development of which is led by RISE, is also being explored for anionic, cationic and non-ionic functionality. This part is being tested in a lab scale by partner RISE and the pilot production facility will be modified accordingly.

3.1.4 Task 3.4: Characterization of MNPs

The objective of Task 3.4 is to ensure that the developed MNPs will be properly characterized since their properties are of great importance for the quality of these materials. Firstly, studies verified that all the listed properties are actually the properties of interest for both the developers and the users. Next, partners defined the characterization capacity of each one of the entities in this Task in order to define which characterizations are necessary and who can provide them. The first MNPs produced with the pilot plant were characterized in detail by the partners RISE, NTUA, PoliMi and CaptiveS.

3.2 Achievements and results of WP3

3.2.1 Task 3.1: Modification of the MNPs production line

The modification of the MNPs production line resulted in:

- A pilot plant with a production capacity of 50 Kg per day was built.
- A layout that guarantees the production of different types of MNPs.

Additionally, the possible use of a decanter, hydrocyclone with combination of magnetic bars or a centrifuge as tools for dehydrating the MNPs solution and the possible use of spray-drying, freeze-drying and controlled evaporation as techniques for drying the MNPs were evaluated. It was decided that powdered particles will not be produced for safety reasons, unless necessary.

Figure 1. *Pilot Production Plant.*

3.2.2 Task 3.2: Optimization of MNPs production

In this Task, the capacity of the pilot plant of guaranteeing a standard production was verified as well as its correct operation. The different set of runs of the MNPs production resulted similar in terms of the size distribution of the aggregates (verified by master sizer analysis) and regarding the presence of the coating on the surface (verified by FT-IR and XRD analysis) thus verifying a correct operation of the new pilot production plant.

3.2.3 Task 3.3: Optimization of the MNPs aggregation process

The main results of this Task are:

- The final dimension of the MNPs aggregates depends on the type of chemical used as coating.
- The final dimension of aggregates of MNPs with a certain type of coating depends on the amount of chemical used.
- A method for obtaining a targeted size distribution of the final aggregates by changing the types and amount of coating was developed.
- Aggregates with a size distribution from few micron-meter to hundreds of micrometers were obtained.

- The presence of the coating on surface was validated by IR the results and the size distribution of the MNPs aggregates shows a low polidispersity indicating a narrow size distribution of the MNPs aggregates.

RISE, within WP4, is developing a series of standard operating procedures (SOPs) for the production of bio-based polymeric coatedMNPs. The SOPs have been drawn up strictly taking into consideration the equipment of the pilot production plant. The SOPs for the production of anionic (starch) and non-ionic (lignin) bio-based MNPs have been successfully tested on the pilot plant. The SOPs regarding the production of bio-based cationic (chitosan) MNPs are under development and will be tested on the pilot plant in the following months.

3.2.4 Task 3.4: Characterization of MNPs

The main MNPs characterization results are presented below:
FTIR (Figure 2), SEM (Figure 2), TEM,EDS analysis, BET test, thermo-gravimetric analysis, size distribution (Figure 4), stability in acidic media and efficiency of the MNPs in removing different pollutants of interest.

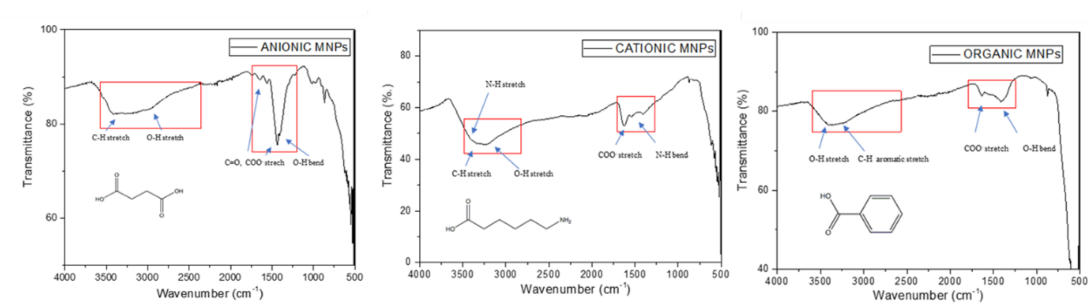

Figure 2. *FT_IR spectra of different MNPs produced with the pilot plant.*

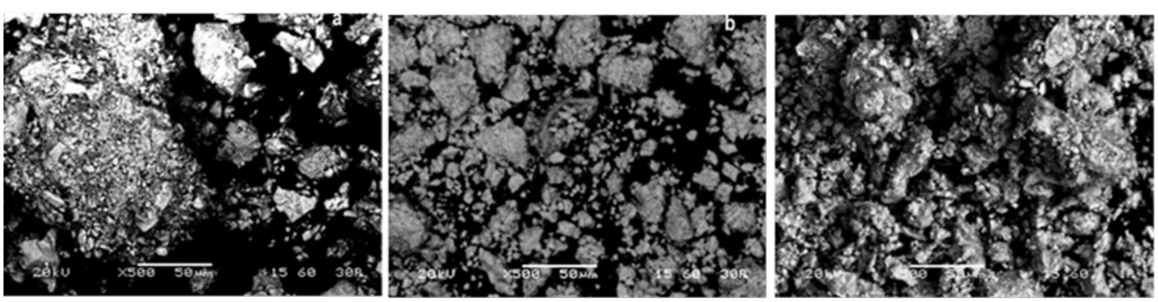

Figure 3. *SEM photos of anionic (a), cationic (b) and non-ionic (c) MNPs. Scale: 500x.*

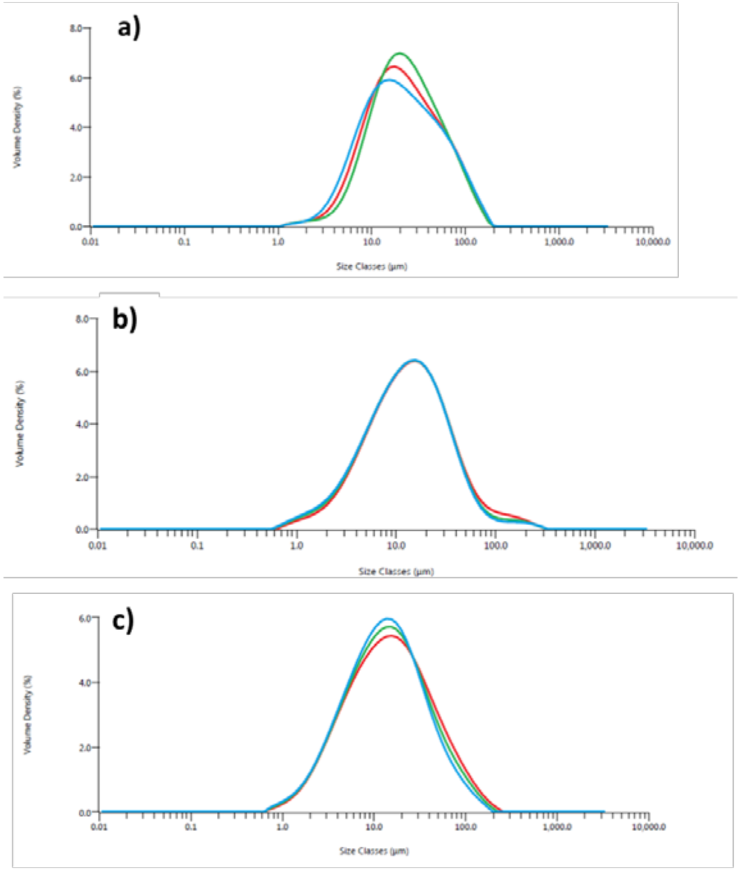

Figure 4. *Size distribution of anionic (a), cationic (b) and non-ionic (c) MNPs.*

The deep characterization above mentioned, is currently being performed by the partners on the new bio-based coated MNPs under development in WP4.

Table 5. WP3 Deliverables submitted

Deliverable Number	Deliverable Description	Date
D3.1	Pilot line for production of MNPs with mixing equipment and magnetic separation	30/03/2020
D3.2	Definition of baths formulations and process parameters for MNPs	26/05/2020
D3.3	Protocol for MNPs surface area and efficiency measurements	08/12/2020
D3.4	Protocol and equipment for drying MNPs	30/11/2020

Table 6. WP3 Milestones

Milestone Number	Milestone Description	Date
MS3	First successful operation of the upscaled MNPs production line	17/02/2020

4. WP4 - Functionalization of MNPs

4.1 Overview of activities in WP4

4.1.1 Task 4.1: Development of Cationic Coating for MNPs

The objective of this task is to develop a cationic polymeric coating on the magnetic particle aggregates in order for the final magnetic beads to be able to remove anionic species from the spent electrolytic bath. The outcome of this task would be a standard operating procedure (SOP) for lab-scale synthesis developed by RISE and shared with partners for implementation at a pilot scale.

4.1.2 Task 4.2: Development of anionic Coating on MNPs

Similar to Task 4.1, the objective of this task is to develop an anionic polymeric coating on the magnetic particle aggregates for the removal of anionic species from the spent electrolytic bath. In this case as well, the outcome would be a standard operating procedure (SOP) for lab-scale synthesis developed by RISE and shared with partners to implementation at a pilot scale.

4.1.3 Task 4.3: Development of non-ionic Coating on MNPs

The last functionalization of the MNPs foresees the development of a non-ionic polymeric coating that is able to capture non-ionic compounds from the spent paling baths. In line with what developed in Tasks 4.1 and 4.2 RISE has been working on the development of a SOP that will be then used for the upscaling of the non-ionic MNPs production by partner Captive.

4.1.4 Task 4.4: In depth characterization of functionalized MNPs

The objective of this task is to provide the characterizations needed for the functionalised MNPs, taking into account the crucial properties that would best describe the MNPs. As a result, it was necessary to define these properties as well as to determine the capacity of each partner involved in this task. To this end, NTUA created a questionnaire for the partners, aiming to define which properties need to be measured as well as which partner can contribute measuring each

property. The distribution of activities regarding properties measuring, took place based on the data gathered by this questionnaire.
In a virtual meeting that took place in September (Month 16), it was decided that in order to evaluate the functionalisation of MNPs and the effect on their properties, the best approach is to measure the morphological, chemical and thermal characteristics as well as the crystallinity and particle size of the MNPs, both before and after the functionalisation. The distribution of the performed measurements per partner will be the same as in WP3. In the following table, the work distribution per partner is presented.

Table 7. Characterization activities to be performed by each partner

	NTUA	RISE	PoliMi/CaptiveS	Cnano
FTIR				X
Raman		X		
XPS		X		
TGA			X	
SEM/EDS	X			
TEM	X			
Size distribution			X	
BET	X			
AFM		X		
Dispersion stability		X		
XRD		X		
GDOES			X	
Collection time		X		
VSM		X		

4.2 Achievements and results of WP4

4.2.1 Task 4.1: Development of Cationic Coating for MNPs

After consultation with PoliMi and Captive Systems, the cationic bio-polymer chitosan was chosen for its metal ion chelating properties at low pH. Furthermore, selection of a bio-degradable biopolymer lowers the possible environmental impact of the magnetic beads, by avoiding synthetic polymers.

First few batches of chitosan coated magnetic beads have been prepared (Figure 5).

The magnetic chitosan beads were initially found to dissolve under acidic conditions of the electrolytic bath, and presently work is also focused on crosslinking the chitosan with counter charged biopolymers to improve its stability in acidic environments.

The chitin derived polysaccharide chitosan exhibits interesting properties, largely due to that the saccharide rings are substituted with primary amine groups. Under acidic conditions, protonation of the amine groups render the amines positively charged, which makes chitosan an interesting alternative for ion exchange purposes, e.g., for pH responsive catch-and-release of negatively charged ion species in from a solution.

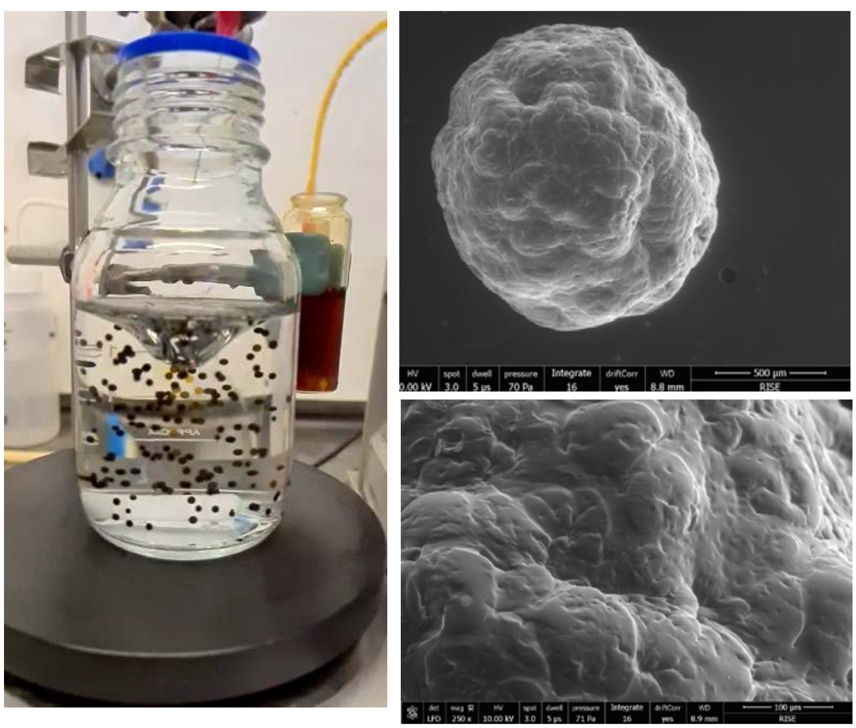

Figure 5. *Chitosan coated magnetic beads synthesis and SEM images of a single bead and its surface roughness.*

For use under low pH conditions, a challenge is to keep the chitosan in the solid phase, as the solubility of chitosan increases with decreased pH due to the repulsive forces induced by the protonated (positively charged) amines, while at the same time preserving the ion-exchange capacity. For finding practical use of chitosan at low pH, it is therefore essential to find a way of stabilizing the polymer and slowing down the dissolution propensity.

Several methods have been proposed and demonstrated to stabilize chitosan – whereof the majority incorporate some way of crosslinking the polymer chains, either by covalent bond formation or by electrostatic interactions.

Covalent crosslinking normally provides the most stable bonds, but forming e.g., amide or imide bonds normally require harsh conditions or very reactive (and thereby toxic/carcinogenic) reagents – especially in water-based solvent systems. The project team therefore decided to focus the efforts on crosslinking via electrostatic interactions (ionotropic gelation). Whereas beads made from chitosan readily dissolves at pH 2, tripolyphosphate (TPP)- or Surfactant-Complexed (e.g., SDS) chitosan beads displayed considerably higher stability at low pH [1] compared to pure chitosan. In addition, polyphosphoric acid (PPA) has been shown to improve the stability [2]. Another promising strategy for improving the overall stability of chitosan beads is by combining chitosan with an oppositely charged polymer to for a polyelectrolyte complex (PEC) [3, 4]. Several different polymers bearing carboxylic functional groups are available (e.g., alginate, carrageenan, carboxymethylated starch or carboxymethylated cellulose). For the purpose of ensuring commercial availability and a low price point, carboxymethylated cellulose (CMC) was chosen for the project.

Bearing three carboxylic acids, citric acid has the potential of working both for aiding dissolution of chitosan, and to work as an ionotropic crosslinker [6]. Citric acid was therefore tested as an alternative to acetic acid for preparing chitosan solutions.

Beads/particles of chitosan materials (pure chitosan/crosslinked chitosan/chitosan PECs) are formed by adding the respective dissolved chitosan formulation to an anti-solvent. The antisolvent can be a solution of higher pH (NaOH solution) or a solution of a crosslink inducing agent (TPP, SDS, PPA).

The activities towards crosslinking chitosan for improved acid stability can be summarized in figures 6, 7, 8. These are overviews of the experiment design which eventually led to identifying the appropriate crosslinking conditions. We have now obtained chitosan magnetic beads that are stable at pH 2.

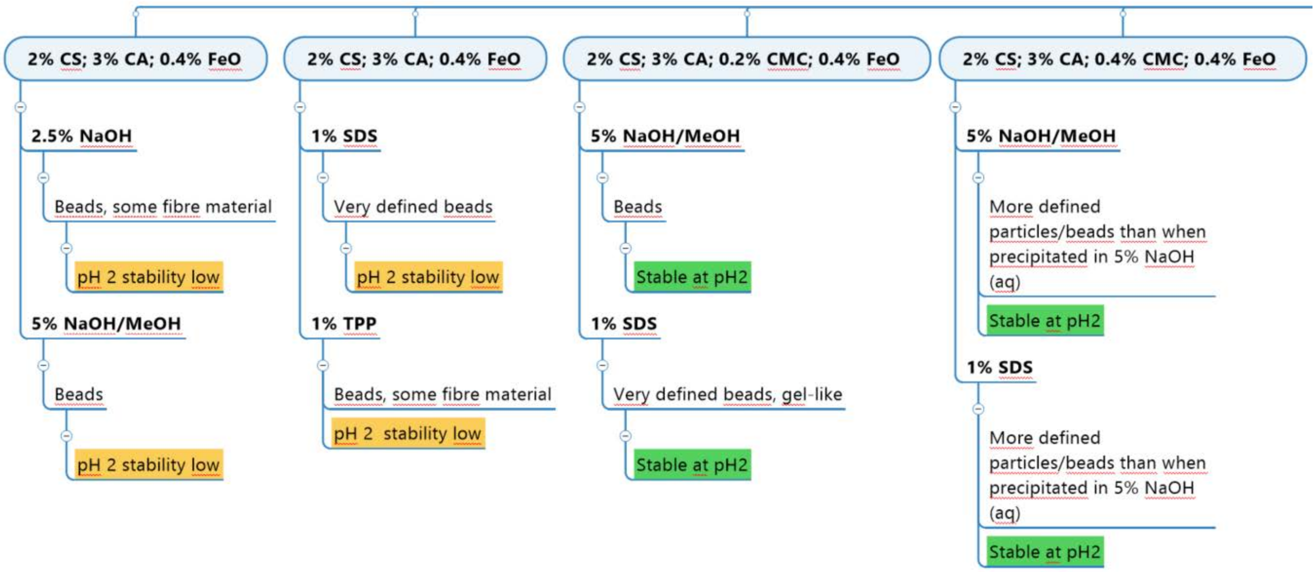

Figure 6. *Overview of experimental conditions and observations for the initial trials attempting to identify a viable cross-linking mechanism.*

Figure 7. *Overview of experimental conditions and observations for the trials using the PEC strategy for stabilization.*
The first column shows the test with citric acid for dissolution of chitosan, for the rest, AcOH was used. The CMC ratio increases from left to right, and the iron oxide ratio increases from top to bottom.

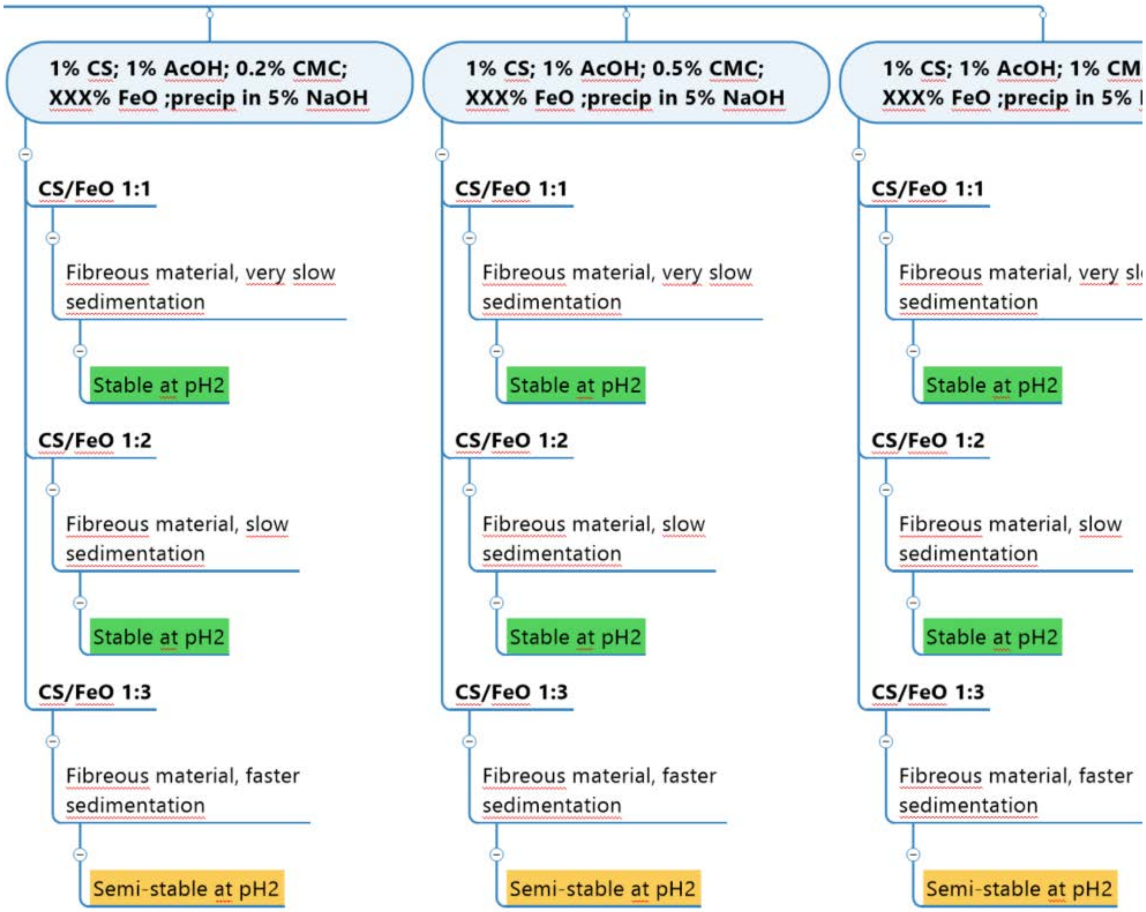

Figure 8. *Overview of experimental conditions and observations for the trials using the PEC strategy for stabilization.*
As in Figure 2, the CMC ratio increases from left to right, and the iron oxide ratio increases from top to bottom.

Many properties interplay and have an impact on the results when observing properties like particle size, pH stability, reproducibility etc. Crosslinking of the chitosan polymer chains have a positive effect on improving the stability at low pH. However, at such low pH as pH 2, the stabilizing effect from crosslinking with citric acid, TPP or SDS is not sufficient for the intended use. The attempts of achieving a stabilizing effect from the formation of a polyelectrolyte complex were more successful. By PEC formation between chitosan and CMC, a significant increase in pH 2 stability could be obtained. Using citric acid instead of acetic acid to benefit from additional crosslinking had no observed effect, therefore acetic acid was chosen for dissolution of chitosan.
The ratio between chitosan and CMC was varied from 10:1 to 1:1, but there was no apparent difference in stability between the different ratios. Therefore a 10:1 ratio is preferred; both because a lower CMC ratio decreases the risk for precipitation during the PEC solution preparation, and because the number of free amines from

chitosan, and thereby the accessible sites for ion-catching (in the electrolyte bath) increases.

It was viewed as desirable to maximize the iron oxide-to-chitosan ratio in order to maximize the magnetic strength of the particles, but at such low pH as pH 2, the stability of the particles started to decline when a chitosan-to-iron oxide of over 1:2 was passed. pH 2 was set as the lower threshold for the stability evaluation to validate a worst-case-scenario, and the only thorough evaluations were carried out at pH 2, but based on the literature examples reviewed, considerably higher stability of the chitosan-based particles can be expected already at pH 3.

Establishing the particle size of the chitosan/CMC/iron oxide precipitate proved more challenging than anticipated, mainly because the pH plays a vital role in aggregate formation for the formed beads/fibrous material/particles. Generally, larger aggregates were formed upon precipitation in the antisolvent (for most trials 5% NaOH). When lowering the pH for the formed material, gradually the attractive forces between the aggregates decreased, and particles/aggregates of considerably smaller sizes started to dominate. If aiming for a certain particle size range, it is therefore vital to measure the size distribution at the pH of the intended use conditions.

As seen in the overview of the results from the experiments where different conditions were tested, a selection of viable choices can be made. When comparing the results from the different crosslinking mechanisms, PEC formation (chitosan:CMC PEC) stands out as a promising way of improving the stability of chitosan at low pH without utilizing covalent bond formation. It is apparent however that increasing the CMC ratio of the chitosan:CMC PEC over 10:1 does not seem to provide any significant advantage in terms of stabilizing/protecting the iron oxide particles.

Obtaining stabilization at pH 2 appears challenging for FeO content over 1:2 (chitosan:iron oxide). If a higher pH threshold would be set, it is assumed that the ratio would be possible to increase considerably.

References:

1. Gels (Supramolecular Strategy Effects on Chitosan Bead Stability in Acidic Media: A Comparative Study) 2019, 5, 11
2. Frontiers in Bioengineering and Biotechnology (Stable Chitosan-Based Nanoparticles Using Polyphosphoric Acid or Hexametaphosphate for Tandem Ionotropic/Covalent Crosslinking and subsequent Investigation as Novel Vehicles for Drug Delivery) 2020, 8, Article 4, 1-21
3. 3. Procedia Technology (Preparation of Chitosan- CMC Blends and Studies on Thermal Properties), 2016, 24, 721 – 726
4. 4. J. Phys.: Mater.(Effects of reaction pH on self-crosslinked chitosan-carrageenan polyelectrolyte complex gels and sponges), 2019, 2, 015003

5. Colloids and Surfaces B: Biointerfaces (The pH sensitive properties of carboxymethyl chitosan nanoparticlescross-linked with calcium ions), 2017, 153, 229–236
6. Reactive and Functional Polymers (Citric acid crosslinked natural bi-polymer-based composite hydrogels: Effect of polymer ratio and beta-cyclodextrin on hydrogel microstructure) 2020, 154, 1046822

4.2.2 Task 4.2: Development of anionic Coating on MNPs

After consultation with PoliMi and Captive Systems, anionic modified Starch was chosen. Furthermore, selection of a bio-degradable biopolymer lowers the possible environmental impact of the magnetic beads, by avoiding synthetic polymers.
First few batches of starch coated magnetic beads were also prepared and characterized (Fig 3). Stability test demonstrated a good stability at pH = 2 for 24hrs with a negligible dissolution of iron oxide.

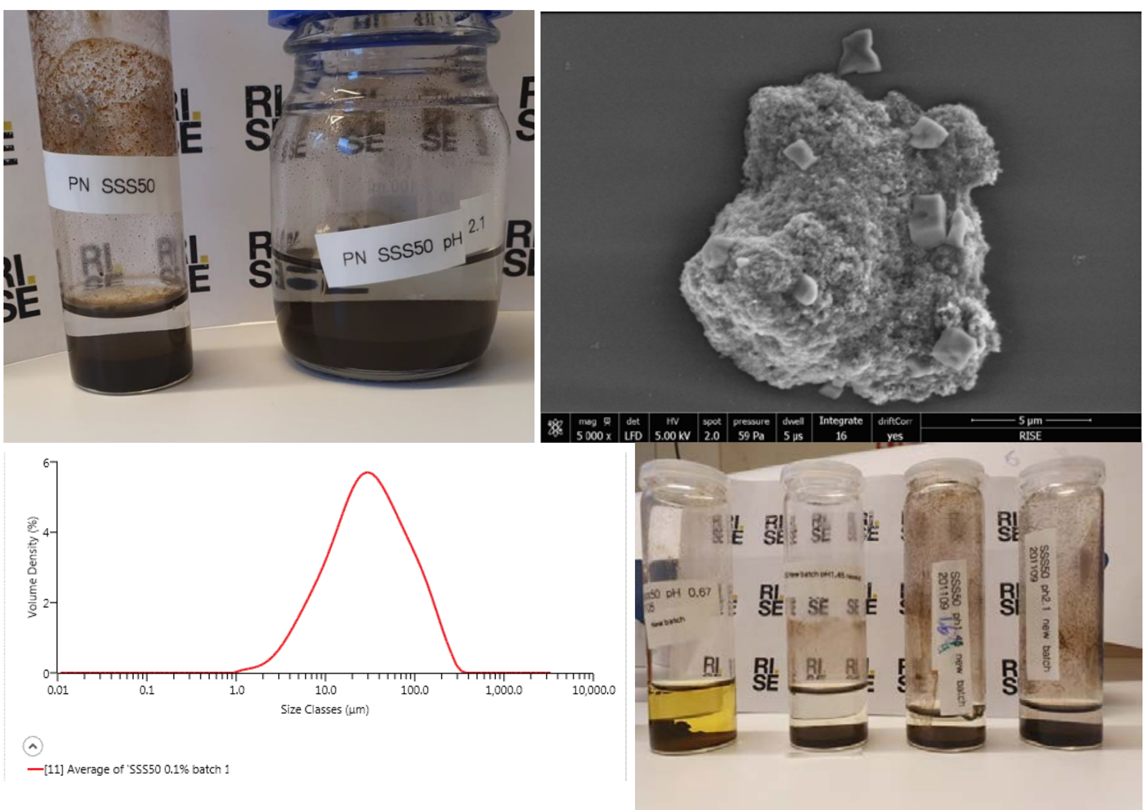

Figure 9. *Top left-Digital photos of starch stabilized magnetic beads dispersion;*

Top right-SEM image of a single bead; Bottom left-size distribution from master sizer; Bottom right-Acid stability under various low pH conditions.

In the pH stability tests, a standard operating procedure was developed. In brief, a known weight of the particles were dispersed in a pH 2 aqueous solution and the supernatant was monitored periodically via UV-Vis spectroscopy to detect the presence of Fe(II) or Fe(III) ions. Figure 3 shows the clear supernatant after an overnight dispersion in a pH 2 aqueous solution.
This indicates negligible dissolution of the iron oxide core into the supernatant. Adsorption tests to determine their absorbent capacity respect to pollutants of interest are ongoing. Moreover, the work is focused on scaling up these samples for delivery to other partners. This will be carried out during the next period.
An SOP was developed for this synthesis and shared with Captive systems for implementation at a pilot-scale.

4.2.3 Task 4.3: Development of non-ionic Coating on MNPs

In close coordination with PoliMi and Captive Systems, RISE is developing non-ionic biopolymer coated magnetic beads, based on Lignin. The lignin-based magnetic beads are prepared by flocculation of lignin-modified iron oxide with cationic polymers (presently using Polydiallyldimethylammonium chloride, PDADMAC).

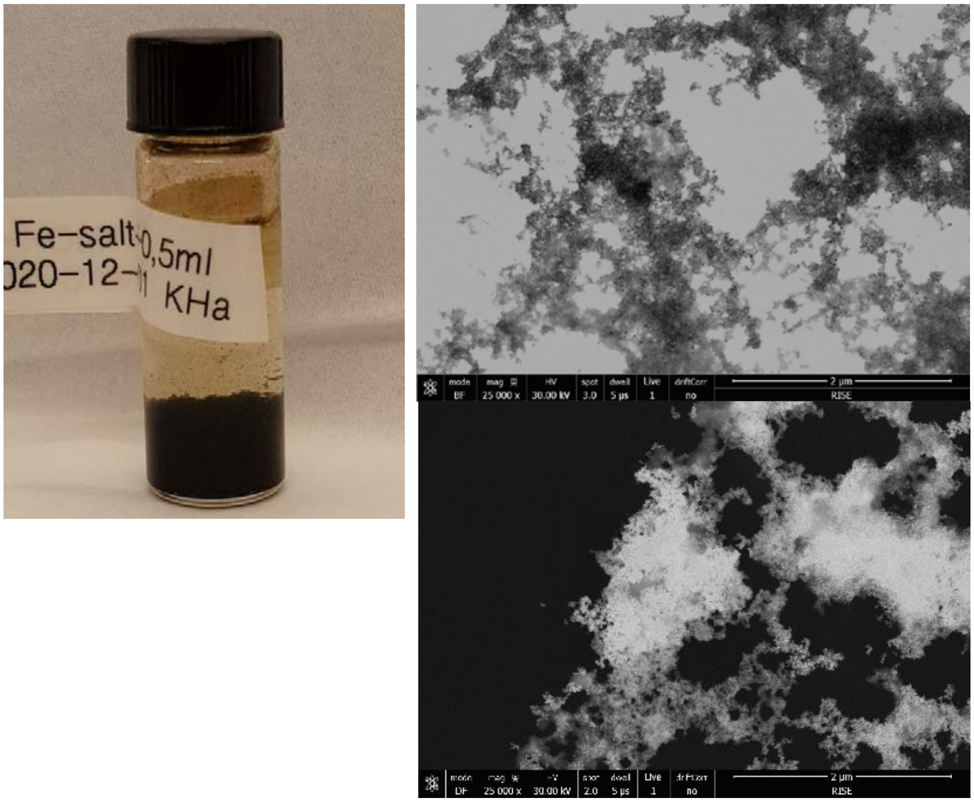

Figure 10. *Left-Digital image of the lignin coated Magnetic beads dispersion; Top right-SEM image of the lignin-coated beads; Bottom right-SEM image of the dispersion after few hours in pH 2.*

This approach also has the flexibility of varying the ratio of Lignin and cationic polymer to tailor the final charge and surface chemistry of the magnetic beads.
The first few batches have been prepared and characterized (Fig. 4). The lignin-coated beads were also found to be stable under acidic conditions (pH2 for example) for several hours. The present work is focused on scaling up the system and tailoring the surface charge/chemistry of the beads.
An SOP was developed for this synthesis and shared with Captive systems for implementation at a pilot-scale.

4.2.4 Task 4.4: In depth characterization of functionalized MNPs

The final in depth characterizations of the functionalized MNPs is pending and will be concluded in the following months once all types of functionalized MNPs have been produced.

Table 8. WP4 Milestones

Milestone Number	Milestone Description	Date
MS4	Anionic coating Functionalization of MNPs and formulations established	31/08/2020

5. WP5 - Integration of purification system and safe disposal of MNPs

The WP5 is focused on the development of the purification system for the electroplating and electroless processes in the Purenano project at Cnano and Gaser facilities.

Within the activities of this WP5, a mathematical model including the plating processes and all the necessary unit operations for the purification process is being developed. Moreover, detailed engineering steps have been investigated and are to be implemented in the purification lines. A set of documents related to the integration of the purification system have been generated. The documentation will be updated according to the final installation in the pilot lines. The modelling activities are pending to be updated in relation to MNPs efficiency, other results and their behavior.

Part of WP5 is also the safe disposal of MNPs after their use in removing different types of pollutants. A three-way approach was investigated for this purpose: 1. Metals recovery and MNPs reuse; 2. Water treatment; 3. Integration in concrete formulation.

5.1 Overview of activities in WP5

5.1.1 Task 5.1: Process model formulation and process optimization

The aim of task 5.1 is to develop a model of electroplating and electroless plating processes, which will be used as a base for carrying out an optimization analysis to minimize capital cost and energy demand.

The elaborated models account for mass and energy balances in order to provide information to develop an economic analysis. Problem formulation and implementation have been carried out using EES and Python to obtain a simplified model able to use for the optimization process.

At this stage in the project, the simulation and optimisation of the different units involved in the processes (the plating tanks, mixers, adsorption tanks, pumps, and magnetic filters) have been carried out.

Five different plating tanks have been modelled according to the pilot lines of Gasser and Cnano facilities:

- Electroless Ni-P plating (Gasser)
- Zn electroplating (Gasser)
- Ni & Ni-P electroplating (Cnano)
- Ni-P/SiC electroplating (Cnano)
- Cu electroplating (Cnano)

The input data required in the plating tank model development, such as the operating conditions of the tanks or the reactions involved in each process, have been provided to IDENER by Gasser and Cnano.

By contrast, the pumps and the magnetic filters have been modelled with some input data provided by the suppliers, while literature data have been used to develop a first preliminary model of the adsorption tanks. Once final information from WP3 and WP4 about the functionalisation of MNPs is available, these models will be updated, and current assumptions will be validated.

An economic analysis has also been performed. The capital cost and the operating cost of the pilot plants have been estimated, and the NPV (Net Present Value) has been calculated. This parameter is a widely used economic indicator. Its value will be significant to determine the project cost-effectiveness since the highest the NVP the more profitable the project is.

Regarding the optimisation process, the brute force search method has been implemented in Python. Firstly, a sensitivity analysis is developed to identify the model parameters with a significant role in controlling the processes behaviour. Then these parameters are ranged and sorted from most to less profitable (always considering the restrictions imposed by the processes).

Thus, several scenarios and options of the purification processes have been examined, and the one with the highest NPV has been chosen as the optimum scenario.

5.1.2 Task 5.2: Conceptual and basic engineering

The work on this task has been centralised in the definition and basic design of the purification system to be implemented in both electroless and electroplating processes. Some possibilities were studied to find the optimal solution in order to purify the lines at Gaser and Cnano facilities.

The preliminary designs and the collected information from WP2 as well as partners' inputs during the task execution have concluded in a basic configuration of the lines that has been further updated until finding the most suitable design. Thus, mass balances of the processes was done, and drawings as block diagrams was configurated. These data were the primary input for task T5.3.

According to each pilot plant characteristics, the global idea and necessary equipment for the purification were established at this task, focusing on achieving the optimised results in each involved stream of the purification plants. The main goal is to minimise the contaminants in the plating baths, using the required amount of MNPs for this purpose during the purification and allowing the regeneration of the plating solutions.

5.1.3 Task 5.3: Detailed engineering design

Based on the development in task T5.2, a more exhaustive design has been done. All units operation in the purification processes has been defined. In this sense, a detailed design was done for each piece of equipment of the pilot line. Datasheets of necessary equipment for the pilot plant assembling as tanks, pumps, magnetic traps or filters has been specified, specifying dimensions, materials and other operational specifications.

In this sense, in D5.2 engineering documents such as P&ID (Piping and Instrumentation diagrams) can be consulted, where all the required material or mechanical elements for the purification implementation are included. Other drawings such as Process Flow Diagrams (PFD), recommendations about the instrumentation or pipes specifications and the mass balance development in combination with the modelling activities can be also consulted in that document. Efficiencies or yield on the unit operations, especially in absorption and magnetic filtration units, will be updated when piloting activities results are available. The mass balance will be updated according to these results in order to precisely reproduce the real behaviour of the pilot lines.

5.1.4 Task 5.4: Sub assembly manufacturing and installation

Cnano System

Task 5.4 is an on-going task. Based on the designs delivered in Task 5.3, Kampakas and Gaser proceeded in the manufacturing and installation of the purification system in the premises of Cnano and Gaser respectively.

For the system of Cnano, Kampakas carried out a revision of the designs of Task 5.3 in collaboration with the personnel of Cnano. Dimensioning of the equipment as well as various other details (e.g. type of pumps, capacity of magnetic traps, components of purification reactors such as motors etc.) have been defined and the final orders have been given to manufacturers. Kampakas company was in charge of following the progress and responsible for the quality inspection of the various components during the delivery. For all metallic components (reactors, magnetic traps) high quality 316 grade stainless steel was used. Moreover, the personnel of Kampakas carried out the integration of the various components to the final sub-assembly system. Despite the COVID-19 emergency, personnel of Kampakas carried out frequent visits to Cnano, following all necessary protection measures, in order to ensure proper in-situ modifications (drilling, connections etc.) and integration of the various equipment.

Gaser System

For the Gaser system, some modifications on the design of the purification plant provided by IDENER were made. These were mostly related to the addition of an accumulation tank for stocking the exhaust bath, the addition of a recirculation system for further treatment of the bath and of a filter press before the magnetic filter. Moreover, the treatment tank has been decided to be manufactured in Polypropylene homopolymer (PP-H) and all pumps are controlled by programmable-logic controllers (PLC) commands. In Gaser's case, valves, PP tanks, pumps and PLC has been purchased from external suppliers. Reactor tank, piping and some chemical reagents tanks were build inside Gaser's manufacturing department. Finally, the purification system has been tested with two different trials in order to check for eventual leak out, malfunctioning of valves and pumps and the correct implementation of the PLC parameter and to simulate the good functioning and compatibility of all the instrumentation installed.

5.1.5 Task 5.5: Safe disposal of used MNPs

The disposal of the exhaust MNPs after the treatment process is a critical aspect to be taken into consideration. To promote a treatment in line with the directives of zero waste treatment, three different routes for an effective recycling of the MNPs were investigated:

Subtask 5.5.a Metals recovery and MNPs reuse

A series of preliminary tests were done to verify the possibility of extracting the absorbed metals from the surface of the MNPs through a low cost electrolytic process. The goal of this process will be to regenerate the MNPs that can be reintroduced again in the treatment process and to recover metals that are valuable secondary raw materials (e.g. Nickel, Zinc, and Copper). These preliminary tests concerned the electrochemical characterization of coated MNPs in both supported and dispersed configuration, polarization test on supported MNPs followed by microstructural analysis and electrochemical characterization of coated MNPs with absorbed metal cations. Next, activities will focus on the polarization tests on supported MNPs with absorbed metal cations in order to recover the adsorbed metals and on microstructural analysis of the regenerated MNPs to verify their morphology after the regenerating process.

Subtask 5.5.b Water treatment

The MNPs used for the removal of cationic species such as orthophosphite, have these pollutants attached on the surface in the form of radicals species. Moreover, the MNPS have an intrinsic lipophilic nature, which is preserved after the removal of anions, and cations, that can be exploited for the treatment of wastewater polluted with organic species. The subsequent use of the MNPs after the removal of cationic species was tested in a series of batch treatment experiments.

The re-use of particles for the removal of ionic species was not further investigated due to the poorly efficient results obtained. After the removal of cationic species, the overall amount of negative charges the surface of the MNPs is too low to allow an efficient application of them for removing ionic species.

Good results were instead obtained by re-using the MNPs after the removal of anionic species for remediation of water polluted with organic compounds, mainly dispersed of emulsified hydrocarbons (Figure 11).

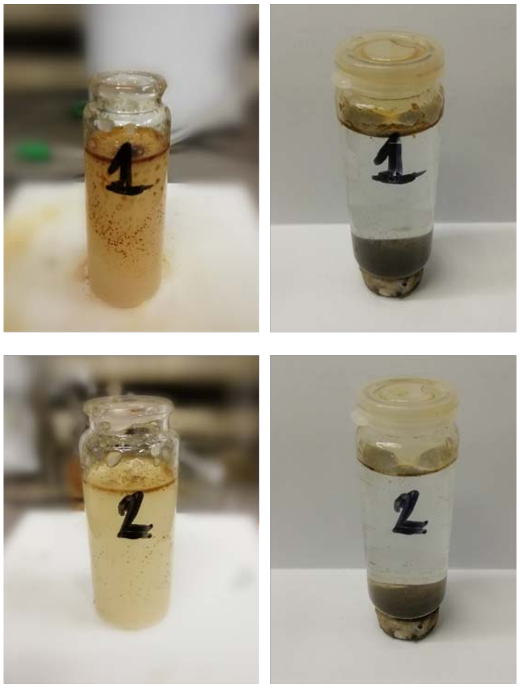

Figure 11. *Samples of water polluted with organic compounds before (right) and after (left) treatment with exhaust MNPs.*

Further experiments are ongoing to establish a correct procedure to re-use the MNPs for the treatment of water polluted with hydrocarbons and for establishing the limits of these applications.

<u>Subtask 5.5.c Integration in concrete formulation</u>

The objective of this subtask is to integrate safely the exhaust MNPs into concrete formulation. The MNPs were incorporated initially into cement pastes and mortar formulations, in the NTUA lab, in order to investigate MNPs' effect on smaller-scale samples concerning compressive strength and rheological properties. During this experimental campaign, the process for the integration of MNPs in concrete formulations was also assessed and the best mixing process were identified.
The raw materials used for the synthesis of both pastes and mortars are cement Portland type II 42.5, tap water, silica sand and two different types of MNP solutions. The investigated MNPs originate from Ni^{2+} ions removal process (type A) and Zn^{2+} ions removal process (type B). In this experimental campaign, the effect of the addition of the MNPs as well as their percentage in relation to cement was investigated. The properties evaluated are spread value (flow table test) and compressive strength.

5.2 Achievements and results of WP5

5.2.1 Task 5.1: Process model formulation and process optimization

The process model formulation leads to some interesting achievements and results. The model simulations provide information about the electrodeposition of the desired metal in the treated pieces and the mass and heat balance in the plating tanks.

Mass and energy balances of the complete processes have been solved, and some results about each unit involved in the purification systems are available, but, as mentioned before, only preliminary results have been obtained since they will be updated when more information is available.

Nonetheless, these preliminary output parameters provided by the simulations have been used as inputs in the optimisation process, obtaining the optimum values of the processes optimisation parameters.

5.2.2 Task 5.2: Conceptual and basic engineering

The development of a conceptual and basic design has been advantageous during the whole pilot design. Partners' feedback helped in the final configuration of the purification lines, and progress was achieved in order to get the final design in details. Preliminary versions of the design were generated.

5.2.3 Task 5.3: Detailed engineering design

With the help of previous engineering steps and results obtained in the modelling activities, the apparatus for the baths purification was designed. Since the capacities in Gaser and Cnano pilot lines are different (800L Ni electroless process at Gaser; 120L Ni-P SiC electroplating process and 40L Cu electroplating at Cnano facilities), and the operation mode is also done in a different way, two different configurations have been adopted. The design results have been reflected in deliverable D5.2, presenting specifications for all the involved equipment in each purification process and the system configurations. Some pieces of equipment have been manufactured under exhaustive control, and in other cases, a commercial solution has been adopted, adapting to the Purenano project case studies. The assembling of all parts is the result of the design phase, and it is currently being executed in Cnano and Gaser facilities according to the generated specifications. Such operations represent a significant milestone for baths purification with the developed MNPs.

5.2.4 Task 5.4: Sub assembly manufacturing and installation

Cnano System

Until now, most of the components have been manufactured and integrated in the premises of Cnano. The overall system consists of two main reactors with integrated stirring systems. The electrolyte is transferred via the utilization of diaphragmatic pumps. The magnetic nanoparticles are captured in customized magnetic traps. The whole system configuration is versatile and can be easily adopted to any electroplating line. In the following images, the main components of the purification system are shown:

Figure 12. *Integrated main reactor systems of the CNano treatment plant.*

Figure 13. *Interior of purification of reactor of the CNano treatment plant.*

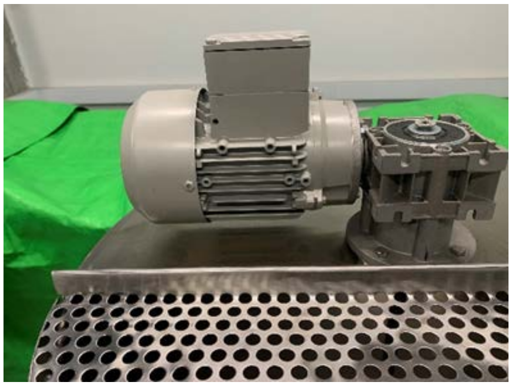

Figure 14. *Stirring motor of reactor of the CNano treatment plant.*

Figure 15. *Holder of dampener of the CNano treatment plant.*

Figure 16. *Magnetic traps with holders of the CNano treatment plant.*

Figure 17. *Platform of magnetic traps and pumps of the CNano treatment plant.*

The system will be fully integrated and tested in the last 2 weeks of June 2021.

<u>Gaser System</u>

All components have been manufactured and the system has been place in Gaser premises. The systems consists of an accumulation tank that is connected with a piping system of the production line and allows the storage of exhaust nickel electroless bath before treatment. This way production continues even in the case that more nickel solution needs to be treated. The plan contains a treatment and separation tank that allow the treatment of large volumes of bath and a filter press that allows the removal of a large quantity of magnetic nanoparticles. The magnetic filter was maintained as last filtering step, to allow the fine removal of the particles escaped from the filter press. Moreover, a recirculation system was installed to allow the re-treatment of the spent solution even after all purification steps are done or to allow a supplementary filtering step.
In the following images, the main components of the purification system are shown:

Figure 18. ***Accumulation and reactor tanks with level indicators of the Gaser treatment plant.***

Figure 19. ***Separation tank with level indicators of the Gaser treatment plant.***

Figure 20. *Piping and valve system of the Gaser treatment plant.*

Two different trials were made in order to evaluate the treatment plant.
A first run using water was done to verify any leak, malfunctioning of valves and pumps and the correct implementation of the PLC parameter.
A second run was made directly with spent electroless nickel solution from the production line in order to assess the functioning and compatibility of all the instrumentation installed. During this run, the use of chemicals such as flocculants that change the pH of the spent bath and produce some sludge, were also tested to ensure the good functioning of the filter press.
Both runs were successfully carried out and helped setting optimally all the equipment of the purification pilot plant.

5.2.5 Task 5.5: Safe disposal of used MNPs

Subtask 5.5.a Metals recovery and MNPs reuse

The main results of this subtask are summarized below:

- A process of extracting the metals adsorbed on the surface of the MNPs by an electrochemical process was established.
- A series of cyclic voltammetry experiments in order to identify the surface potential at which the redox reactions occurred showed that the ions absorbed on MNPs particles interact electrochemically in an effective way with the electrode's surface.
- The reduction of metal ions on the electrode surface, which will allow both the recovery of metals and the regeneration of particles, is possible through this method.

Subtask 5.5.b Water treatment

The main results of this subtask are summarized below:

- The MNPs, after the removal of orthophosphite, still preserve a lipophilic nature that is useful for the treatment of wastewater pollutant with organic compounds.
- Treatment of wastewater samples with used MNPs, showed a reduction of the organic species present in the samples when the pollutants were mostly dispersed or in emulsion organic compounds.
- On the other hand, a poor reduction of COD was obtained in the treatment of samples wastewater in which the organic pollutants were solubilized.
- The water treatment route for MNPs reuse could be used only for wastewater containing organic pollutants dispersed or in emulsion.

Subtask 5.5.c Integration in concrete formulation

Some interesting results came up from the integration of MNPs in cement pastes and mortar formulations. The flow table tests showed that the cement pastes with both type A and type B MNPs have similar and good workability. Mortar mixtures, on the other hand, were less workable than pastes, with type B-MNP mortars having a slight better workability than type A. The MNP/cement ratio seems to affect only the workability of type B-MNP mortars.
The compressive strength of the samples was measured after 28 days of curing. Overall, the compressive strength measurements of all the samples were satisfactory. The compressive strength for pastes and mortars is presented in the figures below.

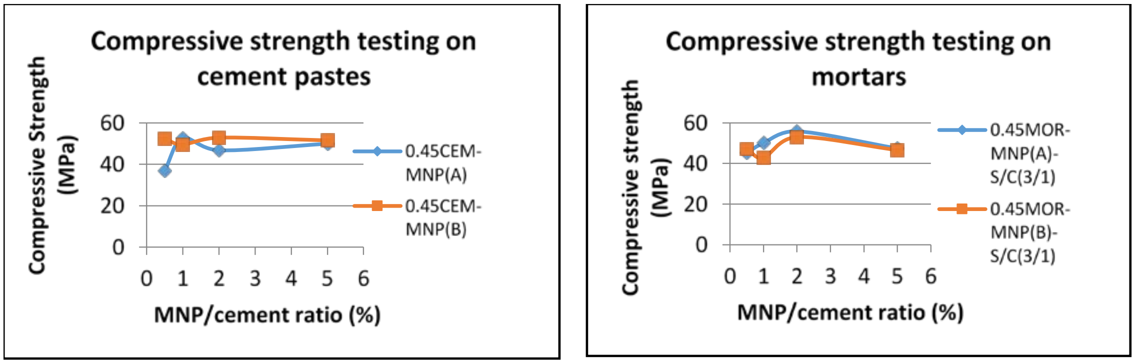

Figure 21. Compressive strength for pastes (left) and mortars (right) after integration of exhaust MNPs.

Mortars with both type-A and type-B MNPs had similar compressive strength, however samples with type-A MNPs showed slightly increased compressive strength values.

It is worth mentioning that MPN solution presented some unique characteristics regarding their homogeneity. Even though the MNP solutions had been shaken in an orbital shaker for 24 hours prior to mixing, the solutions could not maintain a high level of homogeneity for a long period after they were removed from the shaker. The higher the content of MNPs in the solution, the easier it was for the solutions to lose their homogeneity.

Regarding next steps, the investigation of the incorporation of the functionalised MNPs into concrete formulations will take place, as soon as the new functionalised MNPs are produced.

Table 9. WP5 Deliverables submitted

Deliverable Number	Deliverable Description	Date
D5.1	Process model and process multidisciplinary design optimization	26/11/2020
D5.2	Conceptual and Basic engineering	26/11/2020
D5.5	Preliminary report on the recyclability of used MNPs of bench scale studies	30/11/2020

Table 10. WP5 Milestones

Milestone Number	Milestone Description	Date

MS6	First engineering design for electroless line approved by GASER	11/02/2021

6. WP6 - Demonstration activities

6.1 Overview of activities in WP6

6.1.1 Task 6.1: Production of functionalized MNPs aggregates

Within this task, the capacity of the optimized pilot production plant to produce MNPs in a scale of batches from 1 to 10Kg was tested. CaptiveS in collaboration with PoliMi performed several productions runs for obtaining MNPs coated with anionic, cationic and non-ionic coating to be used for the treatment of wastewater with a pH $\geq$ 5.5. Size distribution, morphology and structure were checked on every batch produced. The results were compared to the one referring to the lab scale production. The MNPs obtained with the pilot plant were comparable to the lab scale ones in terms of size, morphology and structure, confirming that the scale-up process was done efficiently.

Runs to verify the scale-up process of the new bio-polymer coated MNPs suitable for the treatment of water at a pH $\leq$ are ongoing and will be completed once WP4 activities are fully implemented.

7. WP7 - Industrial implementation issues

7.1 Overview of activities in WP7

7.1.1 Task 7.1: Recyclability & Circular economy

The aim of this Task is to establish operational and financial models for the development and functioning of networks promoting the circularity of the PureNano technology. The models foresee guidelines for the extension of the lifecycle of the PureNano products through their reuse and/or recycling.

A methodological approach has been proposed in order to address recyclability and circular economy aspects using a step-by-step approach (Figure 22). The proposed approach will enable the identification of current practices employed for the end-of-life management of the plating baths as well as the review of alternative circularity models applicable to PureNano innovations that take into consideration the regulatory environment.

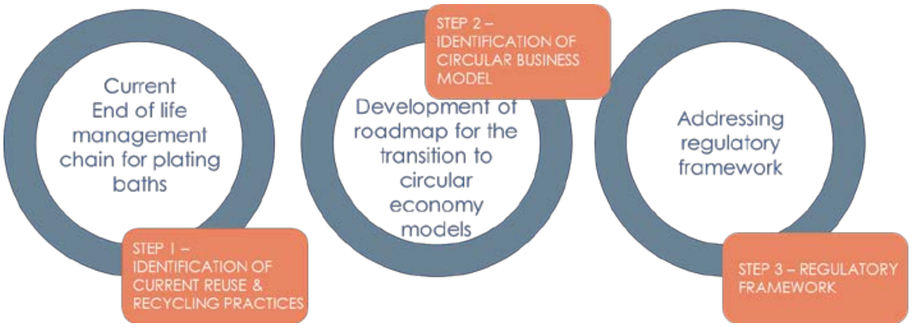

Figure 22. Methodological Approach.

Another important aspect that is considered in this task is the analysis of the challenges for the transition towards a circular system. These challenges are related not only to the technical process but also to the whole business strategy. The whole value chain has to be readapted taking into consideration a new and effective business model. The finishing industry is producing everyday hazardous waste that needs to be treated before disposal. These treatments produce a large amount of sludge that cannot be reused. To avoid the environmental pollution caused by this process, new treatment technologies such as the ones developed within PureNano, where waste becomes a resource for other processes, are proposed. Against this background, this task will provide an analysis of the elements that need to be changed in the new circular business model.

7.1.2 Task 7.2: Safe by design

Within this Task, the regulatory framework for Health, Safety and Environment was set out in detail, in order to reduce H&S risk since the design of the PureNano System.

An inventory of the REACH requirements for manufacturers and importers was presented to advise on compliance with the REACH obligations as well as a review on the hazards of the current technology with general recommendations for safe use and handling and a risk assessment for the processes. Hazards and events that can cause harm to health and safety of workers were identified using the preliminary hazard analysis (PHA) methodology. Several control measures, from a Safe-by-Design point of view and following the hierarchy of control, were suggested using available literature, namely standards, technical manuals, legislation, scientific articles, project results, and other relevant references.

Due to the pandemic, technical visits to the CaptiveS and Gaser pilot lines and the planned nanoparticle monitoring process were postponed. These activities must be completed later, once the circumstances allow safe traveling and fieldwork.

The HSE recommendations presented could be updated once the visits have occurred.

7.1.3 Task 7.3: Safety Lines & Nanosafety issues

This task aims to contribute to the improvement of the safety of all the pilot lines involved in the PureNano project based on the regulatory requirements (e.g. REACH) and standards.

The main activities carried out in the last twenty-four months include:

- The preliminary Health & Safety hazard analysis (PHA) for the 3 PLs CaptiveS, CreativeNano and Gaser. This analysis considered the information available at the time and was based on the standards ISO 31000:2018 "Risk management — Guidelines" and ISO/TR 13121:2011 "Nanotechnologies — Nanomaterial risk evaluation".
- In order to identify the risks, identification and description of chemical substances involved in the pilot lines, including nanomaterials, was undertaken through the use of PL questionnaires, MSDS and chemical substances databases (e.g., ECHA, PubChem, ILO).
- The information collected from the PLs was contrasted against different hazard lists, such as: Substances included in the candidate list of SVHC according to Regulation (EC) Nº 1907/2006 (REACH); substances classified as carcinogenic to human by IARC; list categories by ACGIH and MAK.
- Based on the available literature (standards, legislation, technical manuals, etc.), several control measures were suggested for the different chemical hazards and risks identified. Concerning nanomaterials, a review on their safe handling was performed and the hazards associated with the NPs used in the PLs were recognised. For the risks identified, several control measures were suggested using available literature, namely standards, technical manuals, legislation, scientific articles, project results, and other relevant references.
- An inventory of the REACH requirements was presented to advise on compliance with the REACH obligations, including nanomaterials issues.
- A control banding tool (StoffenManager Nano) was applied to CaptiveS in order to prioritize the health risks of the exposure to Fe3O4.

7.1.4 Task 7.4: Standardization activities

The main objective of this task is to facilitate the acceptance and utilization by the market of the developed materials and processes. To this end, an initial analysis of the standardization landscape has been performed, starting from needs of

other WPs about existing standards that can be related, as well as the related standardization committees and organizations involved.
Additionally, the current state of HSE standards development for nanotechnologies have been also examined.
Moreover, a first version of policy document aiming at providing an insight at major topics that are related to the nanotechnology and wastewater treatment and are thus pertinent to the PureNano project, has been drafted. The document provides information for the elaboration of new standard documents related to four major topics that are fundamental for the project and the acceptance of its results in the target market.

7.1.5 Task 7.5: Training activities

During the first period, the partners have discussed and decided on the training plan of the Project. Two types of training activities will be organized based on the different target audiences. Internal training activities aiming the project partners and external training activities aiming engineers and workforce intended to work on the developed technology and stakeholders from several sectors.
So far, one external and on internal training activity have been held by partners.
The first external activity, organized by ASFIMET in collaboration with CaptiveS, originally planned to take place during the MECSPE exhibition on the 30th of October 2020, was held as an online workshop on the 11th of November 2020 with the participation of 25 participants active in the metal finishing and industrial wastewater treatment sector. The aim of the activity was to present the PureNano technology and possible applications to external stakeholders.
The first internal training activity reported was decided to be implemented in the framework of a Stakeholder Engagement training and was organized by AXIA. The main objectives of the training activity were:

- Highlight the importance of stakeholder engagement in innovative projects, the benefits and the challenges of the process
- Give some guidelines for the stakeholder engagement process
- Identify and prioritize the main actors involved in the PureNano project

The activity involved a theoretical overview of the stakeholder engagement process and presentation of the tools to prepare an effective stakeholder engagement plan for the PureNano project. Moreover, an interactive part where partners identified the main actors of the PureNano projects, the way to engage them and to prioritize them, completed the activity.

7.2 Achievements and results of WP7

7.2.1 Task 7.1: Recyclability & Circular economy

The activities implemented during the last reporting period include the assessment of the state of the art end-of-life management identifying opportunities and challenges in the management of the material flows. Moreover, circular economy business models have been analyzed with the aim to identify the most appropriate for the purposes of the project.

A detailed analysis of the current state of the art related to the management chain for plating bath has been performed and will be further developed.

The key actors within the PureNano value chain have been identified and the main differences and improvements concerning the traditional processes highlighted. Within the value chain analysis three reusability/recyclability routes have been included:

- Electrolytic recovery of captured metals from the Zinc/Copper electroplating and integration for concrete formulation
- Electrolytic recovery of captured metals from the electrolytic nickel bath, and reuse of the metals.
- Removal of heavy metals from wastewater using MNPs which have been used to capture the orthophosphites accumulated in the electroless nickel baths.

For each recyclability route, key partners have been already identified and the challenges and the solutions from the technological, economical and managerial point of views will be analysed.

7.2.2 Task 7.2: Safe by design

Main achievements of this task include:

- List of the chemical substances (including nanomaterials) to be used by the PureNano technology, as well as the identification of the main hazards associated to them.
- Progress on the literature review related to the risk assessment of nanomaterials, under a safe-by-design approach; and on the available tools required to carry out this risk assessment.
- Establishment of the framework to advance the risk assessment of the PureNano technology, based on the HSE standardization landscape and applicable standards.
- Within a SafebyDesign concept a risk analysis was performed for the Captive Pilot Line.

7.2.3 Task 7.3: Safety Lines & Nanosafety issues

Main achievements of the task include:

- Preliminary list of the chemical substances (including nanomaterials) employed in Creative Nano pilot line, as well as the identification of the main hazards associated to them based on MSDS and chemical databases.
- Identification of the significant hazards and hazardous situations, as well as recommendations on control measures, including the validation of the aspirators' airflow that are installed in the Creative Nano tanks, based on "EN 17059:2018 Plating and anodizing lines - Safety requirements".
- General recommendations for safe use and handling and a risk assessment for the processes was performed.

7.2.4 Task 7.4: Standardization activities

Main achievements of Task 7.4 are:

- identification of several standards relevant to the PureNano project.
- assessment of the incorporation of the technology used in the project in the plating lines based on "EN 17059:2018 Plating and anodizing lines - Safety requirements".
- preparation of the first version of the policy document aiming at providing an insight at major topics that are related to the nanotechnology and wastewater treatment

7.2.5 Task 7.5: Training activities

Main achievements of Task 7.5 are:

- Definition of a training plan involving both internal and external activities for the project.
- Organization of the first external training activity entitled: "MagnetoSponges: innovative technology for industrial wastewater treatment"
- Organization of the first internal training activity entitled: "Stakeholder engagement for nanotechnology applications"

Table 11. WP7 Deliverables submitted

Deliverable Number	Deliverable Description	Date
D7.1	Report on the standardization landscape and applicable standards	16/01/2020
D7.2	Recommendation document on safety issues of pilot lines	26/11/2020
D7.3	Detailed training plan and material	30/11/2020

8. WP8 - LCA/LCC

8.1 Overview of activities in WP8

The aim of this WP is to assess the environmental and economic performance of the PureNano technology to support decision-making, as well as to raise awareness about possible adaptation of the technology to other sectors.

The progress of WP8 activities for this reporting period is presented below:

8.1.1 Task 8.1: Life Cycle Analysis

In line with ISO 14040:2006 and 14044:2006, a detailed LCA of the PureNano technology will be performed. Following the conventional phases of an LCA, the main activities carried out in the last twenty-four months include:

1. Definition of goal and scope of the study:
    a. Delimitation of system boundaries and functional unit.
    b. Literature review of similar technologies (magnetic nanoparticles - MNPs).
    c. Establishment of scenarios to compare new technology (PureNano) vs conventional treatment (e.g. underground deposit).
2. Life Cycle Inventory:
    a. Development and application of questionnaires with the purposes of 1) collect preliminary information on inputs (materials, energy, other resources) and outputs (products, by-products, energy, emissions and waste) of the PLs; and 2) identify the current waste and disposal treatment given to the spent bath.
    b. Analysis of information contained in several deliverables, including 2.1, 2.2, 3.1.
    c. Collection of some background data/based on existing LCIA databases.
    d. Construction of a chemical substances inventory (including nanomaterials), of those that will be employed in the PureNano technology.
    e. Construction of a preliminary processes and scenarios model, in SimaPro, and uploading of the available data into the model.
    f. Modeling of processes, inputs and outputs, for both materials and energy aspects, of MNPs production and functionalization.

3. Life Cycle Impact Assessment:
    a. Selection of environmental impact assessment method (ReCiPe) and impact categories, based on ILCD recommendations.
    b. Application of the environmental impact assessment to the MNPs production and functionalization processes.
4. Interpretation of the results:
    a. Analysis of the partial results obtained for MNPs production and functionalization processes.
    b. Perform sensitivity analysis for significant variables, identified at this stage of the project.

8.1.2 Task 8.2: Life Cycle Cost

This task focuses on the life cycle cost (LCC) of the processes and products involved in the PureNano technology. The aim is to approximately estimate the costs of the selected technical proposal to support decision-making processes for the scaling up.

The LCA model has been used as the basis for a life cycle costing analysis to quantify the cost benefit of the new technology. Additionally, to perform the LCC analysis, a process based cost model (PBCM) was created for the PureNano System, in order to account for the costs drivers, including material cost, energy cost, labour cost and equipment costs.

The model considers equations for both fixed and variable costs.

8.1.3 Task 8.3: Eco-efficiency assessment

This task aims to apply an eco-efficiency evaluation tool assessment (ecoPROSYS©ISO ISO 14045:2012), to improve the environmental and economic performance of the new developed products and processes. The eco-efficiency analysis implementation of ecoPROSYS© methodology will be accomplished once task 8.1 and 8.2 have achieved more progress, since it links the LCA and LCC results. At this time, progress has been made in reviewing the ecoefficiency methodology, accordingly with the ISO 14045:2012 guidelines (Environmental management — Eco-efficiency assessment of product systems — Principles, requirements and guidelines), used by ecoPROSYS© to assess its applicability in this project.

8.2 Achievements and results of WP8

8.2.1 Task 8.1: Life Cycle Analysis

Main achievements of this task, so far, include:

- Stablish the method for the development of life cycle assessment.

- Literature review of similar LCAs regarding spent bath treatment.
- Delimitation of the system boundaries and functional unit.
- Construction of a preliminary processes and scenarios model, in SimaPro, and uploading of the available data into the model.
- Construction of a chemical substances inventory (including nanomaterials), of those that will be employed in the PureNano technology.
- Modeling of processes, inputs and outputs, for both materials and energy aspects, of MNPs production and functionalization.
- Application of the environmental impact assessment to the MNPs production and functionalization processes.

8.2.2 Task 8.2: Life Cycle Cost

Main achievements of this task, so far, include:

- The LCA model has been used as the basis for a life cycle costing analysis.
- A process based cost model (PBCM) was created for the PureNano System, in order to account for the costs drivers, including material cost, energy cost, labour cost and equipment costs.

8.2.3 Task 8.3: Eco-efficiency assessment

Main achievements of this task, so far, include:

- Pre-analysis of the Key Performance Indicators (KPIs) of the LCA and LCC methodologies to be used in the eco-efficiency analysis (ISO 14045:2012) in order to assess and communicate in a suitable manner the eco-efficiency of the PureNano technologies under development.

Table 12. WP8 Deliverables submitted

Deliverable Number	Deliverable Description	Date
D8.1	Interim report on Life Cycle Assessments (LCA, LCC)	26/11/2020

9. WP9 - Dissemination & Exploitation

9.1 Overview of activities in WP9

9.1.1 Task 9.1: Exploitation activities

This task aims at the development of an exploitation and commercialization strategy including different aspects such as product identification, market analysis, preparation of product launch and strategic alliances. The exploitation strategy targets to plan market uptake using specific business case studies for each partner and Key Exploitable Result (KER) and to continuously monitor the market situation as well as to assess arising business opportunities.
Individual business plans for each SME that is part of the consortium are developed, identifying important aspects such as value proposition, business model CANVAS, SWOT, PESTLE and risk analysis.

9.1.2 Task 9.2: Dissemination & Communication activities

The dissemination and communication plan has been already defined in the beginning of the project and has been updated during the past months. It ensures project visibility and disposes of key performance indicators and monitoring tools that help measuring the impact of the actions taken. Dissemination material (newsletter, press release, video, roll-up, posters etc.) has been prepared and distributed through social media and the project website allowing a coordinated dissemination of the results and news.

9.1.3 Task 9.3: Knowledge management and IPR protection

The management and IPR protection of the knowledge and technology encompasses result ownership, access rights to background and results, and transfer of results enabling partners to exploit the results generated to their fullest potential.
The Data Management Plan has been updated after the first version created at month 6 of the project defining further, how the consortium collects, processes, publishes and stores data at project and work package level.
The main activities carried out so far include:

- Knowledge management. This activity includes the identification, compilation, representation, and distribution process of knowledge generated.
- IP Protection. A protection strategy will be developed in collaboration with each partner. A patent search will support this activity.
- PoliMi has taken responsibility for the collection, management, and sharing of the research data, as well as for the day-to-day quality assessment.

9.1.4 Task 9.4: Innovation management

A comprehensive exploitation plan is under development since the early stages of the project including all prerequisite actions that have been taken to reinforce the Exploitation Strategy with qualitative and quantitative measures. Innovation management works in parallel to the dissemination activities of project results with the aim to raise the awareness of stakeholders and the public.
The activities of this task so far include:

- A market analysis to further support SWOT and PESTLE analysis. The initial assessment of the above-mentioned means is included in D9.3 and will be used as guideline for the preparation and reinforcement of the Exploitation strategy that has been adopted so far.
- The organization of workshops and training activities to raise awareness about the project and train the partners on how to attract the stakeholders.
- Identification and update of the Key exploitable results for the development of the business plan.

9.2 Achievements and results of WP9

9.2.1 Task 9.1: Exploitation activities

Exploitation activities and strategy were planned at the beginning of the project and are based on effective updates of the KERs. KERs have been categorized into 3 different groups according to the type:

- Group A: Product Development
- Group B: method of the purification process
- Group C: Consulting

Regarding the KERs identification, new KERs have been added during the first period to make a better subdivision of the ownership of the results. A preliminary estimation of the KERs ownership has been also made and will be updated towards the end of the project. The outcome of this first analysis is a draft business plan for the exploitation of the results and a preliminary IPR analysis. In the business plan a preliminary SWOT, PESTLE, Market analysis and business model Canvas for each SMEs have been developed and will be further updated. All information acquired from the partners have been analyzed and are included in the Deliverable 9.3 ''MidPlan for the Exploitation and Dissemination of Results – PEDR''.

9.2.2 Task 9.2: Dissemination & Communication activities

Website:
The PureNano website (https://www.purenano-h2020.eu/) aims to increase public awareness of the project by providing visual and easy to comprehend information

about the project. The social media profiles of the project have been setup within the project webpage and the website is being continuously updated as far as the news-events and activities sections are concerned. The website can be used to download documents (public deliverables, publications) and other informative material (newsletter, press release, flyer, etc.). Moreover, a Newsletter subscription tab was added in order to allow visitors to receive the latest activities of the project.

Website statistics:
Audience: The PureNano H2020 website is a website of worldwide interest with visitors from 70 countries around the globe. The main bulk of visitors are from the European continent (nearly 53%), the American (nearly 16%) and Asian (nearly 27%). From the 830 unique visitors that visited the website nearly 12.5% are returning visitors that often check for news and updates in the website.

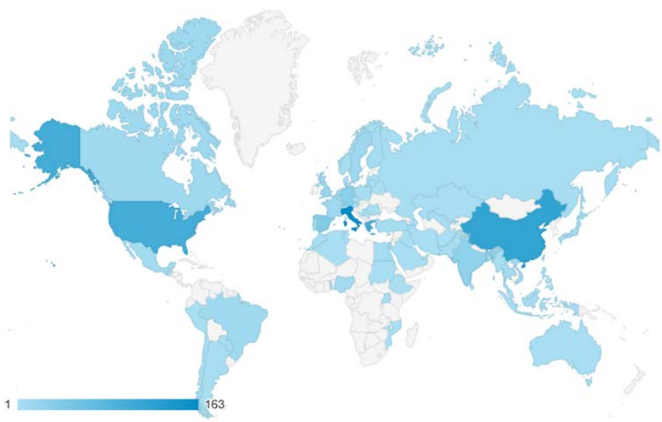

Figure 23. *Visitors around the globe.*

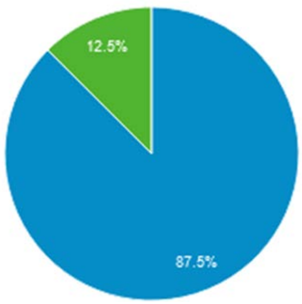

Figure 24. *New vs returning visitors.*

Social Media:
The project has profiles in three major Social Media (SM) channels (Facebook, Twitter, LinkedIn) that serve as a complementary dissemination and communication channel in addition to the project website. They include general project information with the aim to proactively promote the project and its results, and are constantly updated with news, events and dissemination information related to the project.

Social media statistics:
PureNano Facebook page has currently 163 followers. LinkedIn page has a total of 502 followers, and 27201 post impressions that represent the total number of times our posts were seen and is one of the indicators of our project presence. Finally, Twitter account has 35 followers.

Facebook: https://www.facebook.com/PureNanoProject/

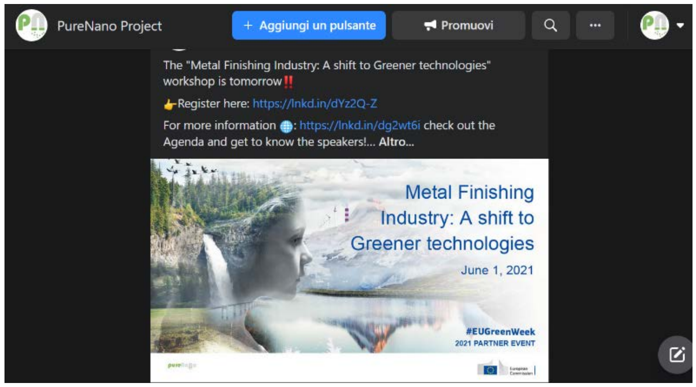

Figure 25. PureNano Facebook page.

LinkedIn: https://www.linkedin.com/company/purenano-project

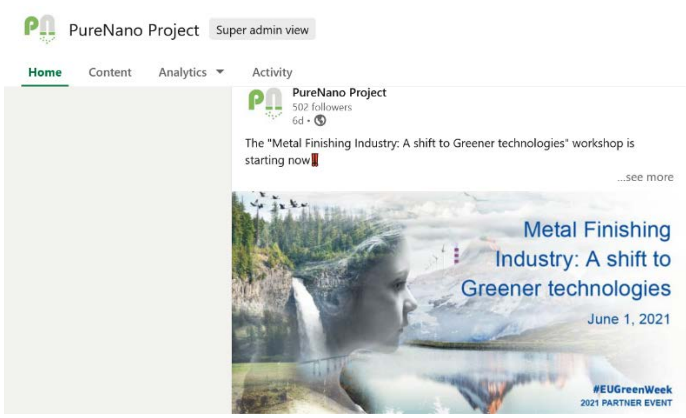

Figure 26. PureNano LinkedIn page.

Twitter: https://twitter.com/PureNanoProject

Figure 27. *PureNano Twitter account.*

Communication and Dissemination kit:

AXIA is responsible to monitor and prepare all the communication activities of the project. Accordingly, the following activities have been implemented:

- Design of the PureNano Corporate Identity
- Development of the projects´ dissemination & communication kit which includes templates for agendas & presentations and for word documents, a folder, a leaflet, a roll-up, and a barcode
- Press release, Newsletter and video
- Infographic for PureNano dissemination

Figure 28. *Dissemination material.*

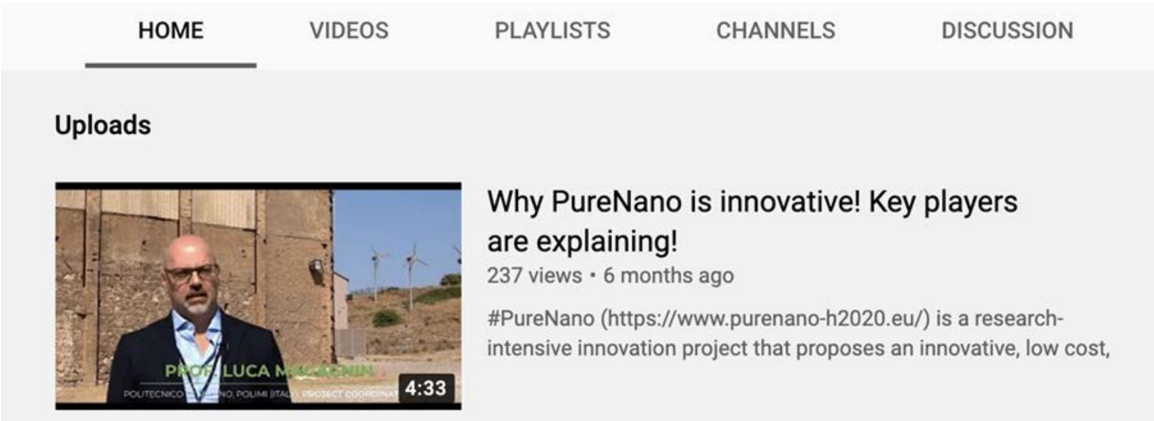

Figure 29. *PureNano video.*

Press Release: The aim of the press releases is to attract media attention and increase public awareness of the PureNano project and its outcomes and events. The first project press release was published in October 2019 to inform about the kick-off meeting of the project and its objectives.

Newsletters: The 1st issue of the PureNano newsletter was published in February 2020 and included an overview of project objectives, news, upcoming events related to the sector and the progress of the project up to that date.
The 2nd issue was published in February 2021 and included a description of PureNano partners and their involvement in the project; the progress made in each WPs, workshop and training activities and future events.

Figure 30. *PureNano 1st Newsletter issue.*

Figure 31. *PureNano Press release.*

Figure 32. *PureNano 2nd Newsletter*

Dissemination plan:

PureNano dissemination plan addresses different target groups (stakeholders, companies, investment groups, Academia, Research institutes, policy makers, European and regional authorities, general public and media) has been coordinated on a regular basis between partners.

In order to keep track of dissemination activities, two questionnaires circulate periodically to identify all past and potential upcoming events to be attended by each partner (Figure 33). Additionally, a third questionnaire has been prepared regarding the publications of each partner involved in PureNano.

In the first months of the project, the partners have been active, participating in several dissemination activities as planned in the dissemination plan. The last year has been affected by the COVID-19 pandemic and therefore the planned events have been most of the times cancelled or postponed, and only some of them were held online.

Figure 33. *PureNano Questionnaires on D&C activities, upcoming events, and publications.*

Table 13. D&C activities database.

Category	Title	Date	Purpose(s)	Estimated audience size
Attended events	European green deal by Crowdhelix	8 October 2020	Green Deal event	12000
	32.BI-MU - Metal cutting, metal forming and additive machines robots, digital manufacturing and automation, enabling technologies, subcontracting.	14-17 October 2020	Promote the Project	9000

	Digital Conference on Industrial Technologies IndTech2020	27-28 October	Discuss future development and challenges	
	Magnetosponges: la tecnologia innovativa per il trattamento delle acque reflue industriali	11 November 2020	External workshop	20
	Stackeholder engagement training	4 December 2020	Internal workshop	
	Innovative methods to remove hazardous substances and contaminants from secondary raw materials for the circular economy	29 January 2021	External workshop organised by Executive Agency for Small and Medium-sized Enterprises (EASME)	
	EuroNano Forum	5-6 May 2021	Conference	
Poster	Magnetosponges: la tecnologia innovativa per il trattamento delle acque reflue industriali	11 November 2020	Dissemination of the workshop	
PureNano Presentation	-	January 2021	Dissemination of PureNano	
2nd Newsletter	-	February 2021	Dissemination of PureNano	-
Poster	EuroNano Forum	5-6 May 2021	Dissemination of PureNano	
Organized events	Metal Finishing Industry: A shift to Greener technologies	1 June 2021	External workshop during the European Green Week	90

The stakeholder engagement training course has been held online on the 4th of December. The training was one of the six activities that have been planned in the framework of the PureNano project.

The main objectives of the training were:

- Highlight the importance of stakeholder engagement in innovative projects;
- Highlight the benefits and the challenges of the engagement process;
- Give some guidelines for the stakeholder engagement process
- Identify and prioritize the main actors involved in the PureNano project

After the theoretical presentation related to the steps to be performed to engage stakeholders in research projects, and an interactive section was organized using the Miro platform, where the project partners have been involved in two exercises. In the first exercise, they have been asked to identify the stakeholder's group to be involved in the exploitation of each exploitable result, the reason to involve them, why they would like to be involved, how to engage them and when to engage them. In the second exercise, the project partners had to prioritize the stakeholders on the base of the kind of collaboration they would like to start with them. The results of the two exercises are shown in Figure 34.

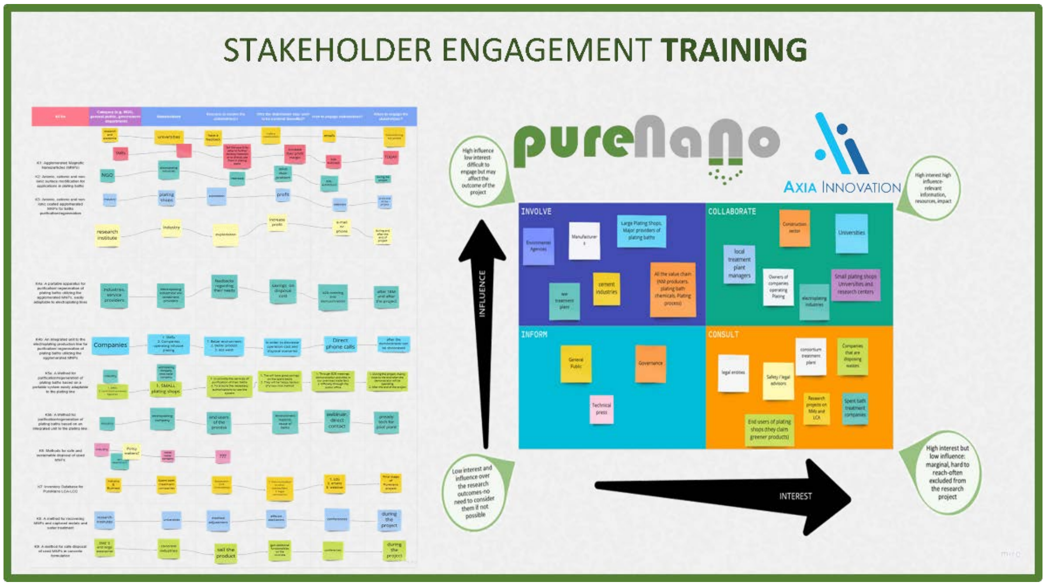

Figure 34. *Miro platform exercises*

The partners participated actively in the section, giving some interesting inputs for further discussion.

Another important event that has been organized is the partner event of the European Green Week. The workshop, titled "Metal Finishing Industry: A shift to Greener technologies", was held successfully online on the 1st of June with the participation of 94 attendees. The workshop attracted experts in the field of the finishing industry and important stakeholders from different companies participated to the event as speakers.

Figure 35. *“Metal finishing industry: A shift to greener technologies” workshop organized during the European Green Week.*

9.2.3 Task 9.3: Knowledge management and IPR protection

The agreement on the initial ownership levels between done through an initial questionnaire and AXIA has started activities for analyzing the market segments and the business environment towards the development of individual business plans for each partner. A preliminary draft of the KERs ownership and protection strategy is already available and included in the Deliverable 9.3 ''MidPlan for the Exploitation and Dissemination of Results – PEDR''. Further updates will be implemented during the following months. Moreover, the first version of the PureNano Data Management Plan has been elaborated and updated on Mo18 without reporting though significant changes from what collected in the beginning of the project.

9.2.4 Task 9.4: Innovation management

The monitoring and collection of market needs and customer requirements as well as the identification of mismatches between the project values and market/customer needs has been commenced by AXIA. An adequate dissemination strategy has also been developed in order to increase the awareness of the public through social media and focus on the communication channels (Task 9.2).
During the last 24 months, important steps have been already performed such as the KERs redefinition, the draft of the individual business plans and protection strategy and the organization of events and training. The project dissemination is also part of the innovation strategy implemented in PureNano and thanks to this activity, it is possible to promote the project and reach a large audience.

Table 14. WP9 Deliverables submitted

Deliverable Number	Deliverable Description	Date
D9.1	Project Web-portal, Blog and Social Media Groups	30/10/2019
D9.2	Data management Plan	20/01/2020
D9.3	MidPlan for the Exploitation and Dissemination of Results – PEDR	30/11/2020

Table 15. WP9 Milestones

Milestone Number	Milestone Description	Date
MS5	**Draft PEDR accepted by SMEs**	**30/11/2020**