EU-DOCS for SmUCS

CO-SUPERVISED SUBJECT PROPOSAL FOR A DOCTORAL CONTRACT

Title of the thesis project: "Green biocoat: anticorrosion coatings by biosourced molecules for renewable energies"	
La Rochelle University Research Unit: LaSIE (Laboratoire des Sciences de l'Ingénieur pour l'Environnement)	**Partner university:** Universidad Complutense de Madrid (UCM), Spain **Cotutelle research unit:** Dept. of Chemical and Materials Engineering
Name of the LRUniv supervisor: Fernando Pedraza Full professor (PR - HDR)	**Name of the co-supervisor:** Francisco Javier Pérez Trujillo University Professor
Non-academic partner: REP Energy Solutions (Spain) - 3rd quarter of the 3rd year of PhD	
Keywords *(6 max)*: green chemistry, marine biopolymers, coatings, high temperature corrosion, biomass and solar renewable plants.	

Scientific description of the research project

Context:

In view of responding to the very significant demand in energy supply while fighting against global warming, a robust and reliable use of renewable energies is mandatory. However, current wind and photovoltaic power do not ensure continuous supply and they largely depend on imports from mostly China, which compromises the European sovereignty [*A. Carfora, R. Vega Pansini, G. Scandurra: Energy dependence, renewable energy generation and import demand: Are EU countries resilient? Renewable Energy 195 (2022 1262-1274*]. In contrast, biomass and thermal solar plants are readily accessible in different countries of the European Union at very competitive prices, even when compared to fossile sources [*IRENA, COP28, COP29, GRA, MoEA and Government of Brazil (2024), Delivering on the UAE Consensus: Tracking progress toward tripling renewable energy capacity and doubling energy efficiency by 2030, International Renewable Energy Agency, COP28 Presidency, COP29 Presidency, Ministry of Energy of the Republic of Azerbaijan, and Government of Brazil, Abu Dhabi*]. Unfortunately, **burning biomass or heating solar salts are extremely corrosive to infrastructures, let alone when they are placed on coastal areas** whereby the external brine majorly contributes to additional degradation e.g., [*G. Mori et al. The influence of NaCl and $CaCl_2$ induced high temperature corrosion on the aqueous corrosion resistance of stainless steels, Materials and Corrosion 70 (2019) 1071-1086*]. From the environmental and societal perspectives, increasing the yield of such power plants while extending their lifetime is a real challenge and huge research programmes have been developed in the USA, Europe or China, which are the three main players worldwide in this field [*Energy Pathways to 2050, Executive summary, RTE (October 2021)*]. Whether for biomass or solar thermal, the infrastructures are generally made of steel, which is prone to corrosion as mentioned above. High grade steels or even Ni-based alloys have been proposed in the open literature but the thousands of kilometers (tons) of these alloys make of the overall cost of infrastructures not viable. **In this view, the application of protective coatings appears as the best choice, provided that they are applicable on large components (not just at lab scale), cost-efficient and environmentally friendly.**

In recent European projects (POEMA, 2012-2016, BELENUS, 2019-2024), the application of aluminium-diffused coatings using slurry technology was demonstrated to be quite successful on various types

of steels like the ones employed in biomass and solar thermal power plants, e.g. [*F. Pedraza et al: Behavior of slurry aluminized austenitic stainless steels under steam at 650 and 700 °C, Oxidation of Metals 87 (2017) 443–454*]. These slurries are based on aqueous suspensions to which an organic binder (polyvinyl alcohol, PVA) is added to make a viscous paste that suspend Al microparticles (from recycled Al). **Unfortunately, PVA is fabricated from petrol through various chemical reactions and is fully imported in the European Union, hence, limiting our sovereignty.** However, the international interest on these coatings is growing worldwide because of the ease of application (spray, dip, paint), customisation possibilities (Al mixed with other protective elements and different heat treatments) to result in a diffusion coating that does not detach from the substrate, as opposed to overlay (e.g., thermal spray) coatings, and that forms a protective oxide scale against various corrosive and oxidation environments.

Because of the above, the **MAIN GOAL** of "Green biocoat" is to **radically replace the petrol-outsourced PVA binder by marine biopolymers than can be extracted from marine resources**. However, the role of their composition in the ease of application of the new bio-slurry, the protection they may provide under high temperature corrosive environments and their cost and environmental efficiency are unknown given the originality of this research. Therefore, **five specific objectives** have been identified:

- **SO1**: Extraction, identification and screening of biopolymers issued from marine algae. The idea is to assess the optimal oxidic compositions, molecular masses and sulfation degree that can be added to the slurry.
- **SO2**: Understand the interaction phenomena between the constituents of the slurry resulting in appropriate rheological properties hence ensuring the ease of application.
- **SO3**: Study the mechanisms of formation of the coatings on two typical steels (P91/P92 and 347) upon the application of different heat treatments.
- **SO4**: Identify the mechanisms of protection developed by the green biocoatings in relevant biomass (mixed sulphates and saline) and solar thermal (molten nitrates) environments.
- **SO5**: conduct lifecycle analysis to assess the economic and environmental impact of the coatings and link with industry through secondments in industry (manufacturer of turbine and end user).

The **methodology of investigation** is very robust and based on the use of **interdisciplinary approaches** to meet the objectives. In addition to the conventional follow up of literature, the candidate will benefit of an interdisciplinary team including a biochemist (H. Groult, LIENSs @ LRUniv, a process engineer (Z. Maache-Rezzoug, LaSIE @ LRUniv), a chemist (F. Pedraza, LaSIE @ LRUniv), two materials engineers (G. Boissonnet, LaSIE @ LRUniv and FJ Perez Trujillo @ UCM) and an industrial engineer (G. Martin @ UCM). Advanced analytical techniques of the different disciplines will be made available, like e.g., inductively coupled plasma mass spectrometry, high-pressure size-exclusion chromatography with multi-angle light scattering to achieve SO1, rheometers and zetameters to meet SO2, thermogravimetric and calorimetric analyses to achieve SO3, electron microscopy/EDS mapping, Raman spectroscopy and EDX chemical analysis to achieve SO4 and the use of SimaPro software to conduct lifecycle analysis.

The activities and expected results are split in 6 work packages (WP) including deliverables (D), milestones (M), risks (R) and mitigation strategy (MS).

WP1: Training, dissemination and communication
This work package is key so as to train the PhD student to acquire vertical and transferable skills. The vertical training will be ensured by both La Rochelle and Complutense Universities. The framework of the horizontal training will be based on RESEARCH COMP of the European Commission allowing to the PhD becoming a citizen of tomorrow with a decision-taking profile. In addition, specific training on SMUCs (e.g., an on-boarding event, participation in an EU-CONEXUS Summer School (end of 1st year) and in a mobility to an EU-CONEXUS Research Conference (2nd or 3rd year)) will be included in training programme. Likewise, training at LRUniv on innovation (by CampusInnov), Science & society (by the Medialab) and project management (by the orientation and develop office) will also take place. It shall be noted that courses proposed by/through La Rochelle's doctoral school will be also offered to the PhD candidate, in particular ethics in research and drafting papers and communicating in English. Similarly, training on lifecycle assessment will be ensured during the secondment period at REP Technologies.

The academic and non-academic supervisors as well as the administrative and technical support

colleagues will gather for a full day upon the kick-off meeting to fully review the scientific, technical and personal challenges the PhD will tackle over the whole duration of the thesis. Another general meeting will take place 3 and 6 months after the start of the thesis to make sure that everything is on track. This includes the adequate integration in the first host institution. The same will be done in their second host institution to make sure that the change of environment does neither affect the student nor their work. In addition, the **regular meetings** will ensure the progress of the scientific and training activities and seek for the well-being of the PhD student. The progress meetings are planned every fortnight if physical at each location and monthly or upon the student's request if virtual between the 2 universities to ensure the PhD student has sufficient time to advance on their own path in their specific location. The meetings will be settled every fortnight between the industry and the academic supervisors during the secondment period and will be mostly online except at the start and at the end of the non-academic placement., with a new "kick-off". This will ensure a good integration and facilitate the understanding of the tasks to be conducted upon the secondment. The closing period will allow to comprehensively review the results obtained and their potential exploitation.

The **dissemination** of the major findings will be made through open access publications in highly ranked journals and conferences in the field. However, the findings will be also disseminated in high schools motivate scholars and avoid the brain drain from the scientific fields covered in *Green biocoatings*.

Communication will be designed to reach different target groups including political and economic stakeholders through e.g., events of the LUDI federation and meetings in the chamber of commerce and industry. Society at large will be also made aware through the Fête de la Science week, MT180 contest and "Festival du Film pas trop scientifique" (both in La Rochelle University and Museum of Natural History in La Rochelle).

- D1.1: Courses/events attended dispatched along the duration of the PhD.
- D1.2: Meetings with political, economic and society stakeholders dispatched along the duration.
- M1.1: vertical and horizontal training ensured (Month 36)

- R1.1: refuse of the political or economic stakeholders to meet (low)
- *MS1.1: contact Vice-President of research to link with relevant stakeholders.*

WP2: Extraction of marine outsourced biopolymers
The extraction and characterization of three pre-selected biopolymers are the main focus of WP2. The idea is to work with negatively charged, positively charged and neutral biomolecules/biopolymer in order to assess the linkage with water and the Al microparticles that compose the bio-slurry. Special attention will be also given to the influence of the osidic compositions, the molecular mass and degree of sulfation. The latter is a key parameter because sulphur contents above a critical threshold (> 0.5 ppm S) are known to lower the oxidation resistance of coatings. The precise amounts of each constituent in the mixtures of the biopolymers with water and with Al microparticles will be unveiled from the rheological study of the slurries and the TGA curves to observe their behaviour at high temperatures.

- D2.1: at least three differently charged biopolymers are shortlisted from rheology and thermal analyses to prepare the mixtures (Month 9)
- D2.2: the rheological properties of the new slurries are fully assessed (Month 12)

- M2.1: Adequate biopolymer that is compatible with the slurry constituents and with rheological properties as the ones made with PVA (Month 12)

- R2.1: excessive content of sulphur (moderate)
- R2.2: insufficient viscosity (low)

MS2.1: a reactive element (e.g. Ce from cerium nitrates in aqueous solution) car trap sulphur
MS2.2: increase the amount of biopolymer till the adequate viscosity is achieved.
MS2.3: selection of nano-sulphated marine biomolecules, eventually a mixture of them to reach similar performance than PVA.

WP3: Synthesis of green biocoatings
The mechanisms of formation shall be elucidated upon application of different amounts of slurry containing the optimal biopolymer and by customising the heat treatment to induce sufficient interdiffusion between the coating and the steel substrates. Features like the chemical composition, optical density and microstructure of the coatings shall allow to shortlist adequate coatings to fight against corrosion. This will be accomplished using various complementary analytical techniques that include chemical (e.g. EDS) structural (e.g. XRD and Raman spectroscopy) and thermal (TGA, DSC) analyses.

- D3.1: mechanisms of formation robustly elucidated (M18)

- M3.1: synthesis of optimised coatings completed (M27)
- M3.2: patent on new coatings filed (M30)

- R3.1: insufficient comprehension of the mechanisms governing the coating formation (low)
- R3.2: excessive number of critical parameters to ensure full production of coatings (low)
- R.3.3: the findings cannot be patented (low)

- *MS3.1: the group has very large experience. Yet, external advice (Dechema Institute, Spain; INTA Institute, Spain) could be sought to find support.*
- *MS3.2.: The focus would be put on the amount of slurry deposited and thermal treatment to limit the number of parameters (e.g., apply the same drying conditions, etc.)*
- *MS3.3: after a thorough literature review including patents search, no such initiative like the one proposed by Green biocoating has been found. Yet, through the "Aquitaine Science Transfer" services the manner how to breach other (unknown) patents will be found.*

WP4: Corrosion protection in relevant biomass and solar thermal environments
Set-up of the corrosion tests to simulate the biomass and the solar thermal environments. Short time tests (max. 1 week) will be conducted to understand the mechanisms of corrosion protection afforded by the green biocoatings. The most suitable coatings will be then shortlisted and tested at relatively longer times (3 months) with in-situ monitoring techniques (e.g., electrochemical impedance spectroscopy) and post-mortem. This will allow to make sure that robust coatings could be applied at semi-industrial scale. Control of comparison with initial PVA-based slurry will be systematically added.

- D4.1.: Set-up of the corrosion tests to simulate the biomass and the solar thermal environments (month 28).
- D.4.2: Potential best coatings shortlisted from short term tests (month 28)
- D4.2: Best coatings selected from 3-months corrosion tests (month 30)

- *M4.1: Best green biocoatings selected for secondment in REP.*

- R4.1: unsuccessful corrosion set-up (low).
- R4.2: the coatings are not sufficiently protective (moderate).

- *MS4.1.: the experience in La Rochelle and in Complutense lowers the risk. Yet, already built corrosion set-ups will be made available to the PhD candidate.*
- *MS4.2: the main element providing protection is Al from the slurry. If ever there was excessive sulphur, this would be limited by adding rare earths like in MS2.1 above. In the unlikely event this would still happen, addition of Al/Si instead of plain Al would enhance the corrosion resistance. Similarly, the use of non-sulphated marine biopolymer limits the risk of introducing deleterious sulphur.*

WP5: Linking science with industry and society
This work package concerns the secondment period in the non-academic sector (REP) to learn how to conduct the lifecycle analysis for future integration in industry or in other decision-taking body or prepare a start-up company.

- D.5.1: lifecycle analyses completed in REP Energy Solutions*.

- M5.1.: successful secondments with transferable skills gained by the PhD candidate.

- R5.1: unsuccessful integration of the PhD candidate in the non-academic secondment host (low)
- R.5.2: insufficiently developed industrial skills (low)

- MS5.1: the host has the experience in guiding PhD students. In the unlikely event this would happen, the secondment could take place in R-Tech (a company based in Germany with whom the proponents have close contacts).
- MS5.2: the industrial skills will be complemented by the horizontal training proposed by the service "Campus Innov" at La Rochelle University.

It shall be noted that all the experimental activities may lead to a significant number of tests. Therefore, design of experiments using the Taguchi method and Quality by Design (QbD) approaches will be applied to identify and shortlist the most critical tests. This ensures the adequate implementation of the activities during the whole PhD duration.

** REP Energy Solutions is located in Madrid and was created from Universidad Complutense de Madrid. This lowers the travel costs between the University Complutense of Madrid and the secondment location and facilitates the integration of the PhD in the geographical location, including accommodation and language (https://www.rep-energysolutions.com/).*

Scientific alignment with EU-DOCs for SmUCS objectives

Urban coastal sustainability is at the forefront of the proposal "Green biocoatings" in relation to the use of coastal resources to extend lifetime of coastal infrastructures to generate renewable energy in vulnerable cities like La Rochelle with a tremendous mass tourism. It perfectly aligns with the strategy of the LUDI Federation of Research (FRA-2000) recently created between La Rochelle University and the French National Research Council (CNRS).

The interdisciplinary team between La Rochelle University and Universidad Complutense de Madrid researchers will improve the overall skills of the PhD candidate allowing them to reach scientific and technical maturity on resilient solutions to face the challenge of developing resilient energy solutions on coastal cities significantly marked by mass tourism.

The secondment in industry and the various communication activities will impact the economy and society at large through the valorisation and farming of marine resources and carbon neutral energy, hence limiting ocean acidification.

Societal and economic challenges and contributions

Coastal cities like La Rochelle are facing major challenges including sea level rise, flooding and contamination often associated with "natural" phenomena. Whether there is much controversy on this topic, the GIEC has repeatedly warned about the limitation of emissions of greenhouse emissions from the combustion of fossil fuels. Paradoxically, coastal cities like La Rochelle are also facing a tremendous increase of mass tourism, which requires supply of "green" energy.

About 75% of the energy produced in France comes from nuclear power plants, which are considered low in CO_2. Yet, the current nuclear production is at the stake because the plants are old and require maintenance and mostly because of the overall energy demand. The only efficient way to limit such greenhouse emissions is to reduce dramatically the use of energy but no one wants to accept this mostly for economic and comfort reasons. Therefore, the development of resilient CO_2-neutral/free renewable power plants is the only way to face energy demands on request any time of the day or of the year.

Resilience necessarily implies durability to avoid corrosion and flushing of contaminants to the ocean and to the air. It also implies repairability and reuse of components to avoid the use of raw often critical materials. The very in fashion wind and photovoltaic resources are fair but they are mostly imported from China, are not recycled in most cases and require the use of very critical materials like rare earths and silicon. In contrast, biomass and solar thermal do not but they can also degrade during operation at high temperatures and the external walls are exposed to marine brine which is highly corrosive.

Therefore, the proposal "green biocoatings" will **majorly contribute to face the economic and societal challenges** as follows:

1) Through the use of marine extracted biopolymers, green coatings will be investigated and tested. If successful, the extracted biopolymers will have the potential to be used in other coatings or the same coatings will be potentially applied in other fields (e.g., transport sector).
2) The extended durability of the components will limit the potential contamination of the shoreline by the fluxing of the corrosion products.
3) The resilience of the renewable power plants will allow to switch on and off to face the demand of local population and of tourists in a CO2-neutral manner and free of pollutants.

Partnership context

An impressive interdisciplinary team has been gathered to guide the PhD candidate over the 3 years of duration of the thesis. They are all used to work in an international atmosphere and have current and past collaborations that demonstrate the stability of the team. The team is composed of biochemists, chemists, process, industrial and materials engineers all needed to provide a common response to face the coastal challenge addressed in green biocoatings.

Furthermore, one industrial partner will be joining the team. Baker and Hughes (Florence, Italy) are experts in the fabrication of steam turbines like the ones employed in the biomass and solar thermal power plants. The PhD candidate will learn how to apply coatings on real scale components to increase their employability in the private sector if foreseen by the candidate.