RESEARCH THEMES

CURRICULUM: CHEMICAL SCIENCES AND TECHNOLOGIES

1) Bioplastics: from novel formulations to end of life

This theme focuses on the study and development of formulations and strategies to improve the characteristics of bioplastics, materials that can play a fundamental role in the transition from a linear to a circular bioeconomy. Indeed, a detailed analysis of the application of bioplastics must take into account several issues, mainly related to the properties of these materials, which are very often inferior to those of traditional plastics. In this context, the proposed project aims to develop new bioplastics-based formulations, considering both scientific and application aspects. In particular, the design of the research will take into account several factors, such as the exploitation of preparation methods that are i) economic, ii) environmentally friendly, iii) easily scalable, iv) with low impact on the intrinsic properties of the material, especially in terms of degradability. Furthermore, with the aim of following the industrial trends, polymer matrices of wide interest, such as polylactic acid, polycaprolactone and polyglycolic acid, will be considered.

The strategies proposed will concern in particular the combination of bioplastics with suitable "bio" fillers/nanofillers and the development of polymer blends. Regarding the former aspect, the novelty compared to the current literature is that the inorganic component will be combined with the surface of the bioplastic-based object. Potentially, this strategy will only change some properties of the matrix, such as gas permeability, without changing the characteristics of the polymer bulk. In the development of polymer blends, particular attention will be paid to methods of forming blends by in situ polymerization, using unconventional methods, such as the frontal polymerization and the reactive extrusion. For both the strategies described, the end life of the materials developed will be studied in detail, in terms of degradation and recycling.

Another aspect that will enrich the research program and the activity of the enrolled PhD student will be the active collaboration with the company where the student will spend 6 months. Indeed, AEP Polymers S.r.l. is an innovative company focused on applied R&D in the field of industrial polymers and formulations from non-edible biomasses, with applications in composites, polyurethanes, coatings and adhesives. The company's expertise is therefore complementary to that of the research group and the collaboration will add value to the project.

Supervisor: Orietta Monticelli

2) Development of non-conventional and innovative photocatalytic technologies for the degradation of emerging pollutants and a green management of water resources

From an environmental and economical point of view, the identification and optimization of new procedures for an effective degradation of emerging contaminants and their by-products will provide useful information for a better management of water resources. This can improve the quality of the water itself, also on a large scale, reducing its toxic side-effects on humans as well as on ecosystems health. This will increase its availability, in particular for non-human purposes, because many "types" of wastewaters will be retrieved and purified, bringing them back to acceptable purity levels. Indirectly, expected results will have repercussions on the zoo-technical and sanitary branches which usually involve the use of pharmaceuticals.

The current project will focus on the development of a new technology for the treatment of water polluted by emerging contaminants. Basic research on new photocatalytic devices has been already carried out within the proposing laboratory; the aim of this project is the scale-up of a pilot plant (maximum volume of 10 L) for evaluating and assessing the optimal working parameters. In addition, obtaining a technology for the treatment of specific emerging pollutants (i.e. antibiotics and drugs) will be among the main aims of the project; indeed, the possibility to remove and degrade these kinds of contaminants will offer the opportunity to make cleaner drinking water in increasing quantities available.

Titanium dioxide "TiO_2" nanoparticles, supported on persistent luminescence materials "PeLM" (which allow the extension of TiO_2 photocatalytic efficiency in turbid waters or in absence of light) and on magnetic materials derived from industrial wastes "MaM" (which allows the easy recovery and reuse of TiO_2, thus reducing the costs) represent the employed materials, whose efficiency has already been tested on a lab scale. Another aspect that will enrich the research program and the activity of the enrolled PhD student will be the active collaboration with the multi-utility company IREN S.p.A., where the student will spend a period of 6 months to one year.

Supervisors: Maurizio Ferretti – Federico Locardi

3) Sustainable Synthesis of APIs (Active Pharmaceutical Ingredients)

The search for efficient and sustainable organic syntheses is a highly topical subject. Bioindustria L.I.M., Fresonara (AL) is an Italian company, leader at an international level in the synthesis of APIs. Several synthetic processes have been carried out for long times in the production site of Fresonara. However, the scarcity of raw materials and energy sources means that there is an urgent need to find new, greener synthetic routes to such substances. In this project we aim at finding alternative routes to the traditional ones, employing photochemical processes, reactions under continuous flow and metal/organo catalysis.

The new routes will be first designed on a laboratory scale and then implemented on industrial scale. In addition, the existing routes to APIs will be improved by the use of greener solvents and the optimization of the reaction conditions by DOI (Design of Experiments) studies. Parameters such as PMI (Process Mass Intensity) or SPy (Specific Productivity) will be used to evaluate the reduced impact of the new methodologies, with the final aim of reducing the impact of industrial production on climate change and promoting sustainable development. From an educational point of view, the PhD student involved in the project will be formed at the principles of Green Chemistry and environmental sustainability, thus also enhancing the human capital.

Supervisor: Andrea Basso

CURRICULUM: MATERIALS SCIENCE AND TECHNOLOGY

4) Eco-batteries based on Alkali metal ions

Modern alkali metal ion batteries nowadays make use of Li and are moving toward the usage of other metals like Na. The commercial cathodes for high performance (i.e., high energy density) batteries are based on mixed Ni and Co oxides and such elements have known issues as raw materials and as recycling processes. The anodes are usually made out of graphite with a limited storing capacity which is potentially improved by the usage of Si. However, the main issue to solve by using Si is the excessive expansion during the charge due to the intercalation of Li with dramatic consequences on the battery stability during cycles.

The PhD project focuses on the investigation and application of alternative cathodes and anodes able to solve the above-mentioned issues. The halides will be taken into account as cathode materials in agreement with recent researches where they are successfully used with aqueous electrolytes. A solid-state electrolyte might be used to solve the safety issues by using aqueous electrolyte. The anode will be manufactured starting from graphite obtained by the treatment of waste from the processing of agricultural products naturally rich in Si (i.e. corn and rice) to obtain nano-crystalline Si embedded in the carbon matrix. Recent papers have shown the greatest stability of this solution compared with others under investigation. Moreover, natural plants make use of atmospheric CO_2 to grow the fibers and once transformed into graphite it corresponds to a permanent sequestration of CO_2 in the form of C. The usage as a base material for anodes enhances the importance of such a contribution for the reduction of CO_2 concentration into the atmosphere. According to the nature of the electrodes used such batteries can be labeled as ECO friendly contributing to the fight against the greenhouse gases. The enrolled PhD student will spend a period of up to one year in the company Phase Motion Control S.p.A., Genova.

Supervisors: Paolo Piccardo – Roberto Spotorno

5) HERMES - Colorimetric pHotonic crystal sEnsoRs for Mitigation of volatilE organic compound pollution in industrial environmentS – Curriculum: Materials Science and Technology

HERMES is a PhD project aiming to create a new professional figure with expertise in Environmental and Green Sciences, Polymer Chemistry and Photonics applied to mitigation of environmental impacts of industrial activities and in soft skills involving scientific writing, communication, and Science popularization to increase awareness of the public opinion on environmental themes.

HERMES specifically pursues one of the 12 Green Chemistry principles, targeting real-time sensors for toxic, carcinogenic and greenhouse Volatile Organic Compounds (VOCs) in industrial and urban realities to prevent pollution and allow prompt mitigation actions. The sensors consist of polymer photonic crystals whose optical response (i.e. color) is modified upon analyte intercalation. The spectral variation, having characteristic dynamics, will provide a specific fingerprint for any analyte and their mixtures and their concentrations. The sensors will be a new paradigm to reduce environmental impact of industries and potentially polluting activities allowing sustainable development and reducing the impact of human activity on the environment.

The project will be run in collaboration with an industrial partner, Plastipoliver s.r.l. (Group ReLife S.P.A.), that is continuously strengthening its role in the challenging green transition. After a basics training, the student will test virgin, recycled, and bio-derived polymers sensitive to VOCs at the industrial sites. Different structures will be then designed and tested in the company premises to assess VOC levels and evaluate proper mitigation/prevention actions. The project will allow sensors with high technology readiness level that will be suitable for testing and for monitoring of VOC in different environments including both industrial and urban ones.

Supervisors: Davide Comoretto – Paola Lova

6) Magnetorheological electrolytes based on ionic liquids: towards green micro fabrication processes – Curriculum: Materials Science and Technology

Magnetorheological fluids are composites capable of modulating their apparent viscosity upon modulation of an external magnetic field. The concept of magnetorheological electrolyte (MRE) extends such a property to an electroactive fluid, i.e. a medium that is capable of conducting electricity via ionic mass transport. The novel and unique properties of MREs would prove useful in various technological applications ranging from microfabrication to robotic space exploration. Microfabrication, especially, is currently an energy and material intensive industrial process. Suitably formulated MREs have the potential to greenify

microfabrication substantially because they would enable selective material deposition or removal in specific regions of a substrate instead of on the entire substrate surface. Formulating a stable fluid possessing such multifunctional properties constitutes a scientific and technological challenge because it requires crafting nanoparticles with tunable magnetic properties, shape, and surface functionalization. Further, the interaction between the magneto-responsive and electroactive portions of the MRE has to be carefully investigated. Among the possible candidate carrier fluids for an MRE, ionic liquids offer several advantages: chemical inertness against corrosion processes, low vapour pressures, and wide electrochemical windows. This project aims to identify a pool of promising magneto-responsive/electroactive couples for application in microfabrication. The PhD candidate will develop a finite element analysis platform accounting for relevant variables from simulations and experiments, in view of constructing a full multiscale model of the MRE pool.

The selected PhD student will spend a period of up to 8 months in the company Gemmate Technologies S.r.l., Buttigliera Alta (TO).

Supervisors: Diego Colombara – Davide Peddis

CURRICULUM: PHARMACEUTICAL, FOOD AND COSMETIC SCIENCES

7) Formulation of a new nutraceutical ingredient using green technologies. Curriculum: Pharmaceutical, Food and Cosmetic Sciences

An innovative food ingredient will be formulated starting from waste or by-products, usually sold at low cost or discarded, deriving from collateral flows of agricultural and fishing industries. Aqueous extracts rich in ellagitannins (ETs) will be extracted by green technologies from several fruits (i.e. berries) and nuts (i.e. chestnuts) exocarps and sub sequentially purified.

Ultrasounds assisted extractions (UAE) either in continuous or in pulsed mode will be performed only using GRAS (Generally Recognized As Safe) solvents. The process variables (i.e., temperature, time, …) will be optimized by means of Design of Experiment (DoE) in terms of yield in bioactive compounds and energy saving. The extracts will be chromatographically characterized and titrated in ellagic acid (EA), since ETs release ellagic acid (EA) upon hydrolysis and under the physiological conditions of the gastrointestinal tract.

Since, these aqueous extracts lack long-term stability, they will need to be formulated and stabilized over the time. Spray-drying, widely used in the food industry to convert a liquid state into a powder product due to its efficiency and low cost, will be chosen as stabilization technique. The spray-drying technology, in respect to the freeze-drying, allows to drastically reduce the process costs and the environmental impact in terms of energy consumption. This technology will allow the most promising phenolic extract to be physically wrapped in a protective "coating material", represented in this proposal by compounds extracted themselves from fishery wastes. The extraction, the purification and the stabilization of the "coating material" will be performed in collaboration with two industries working in fishery waste recovering. The nutraceutical properties of this new ingredient will be tested in collaboration with Prof. Elena Grasselli (DISTAV-UNIGE). An LCA (life cycle assessment) will be performed to assess the economic and environmental impact of this new ingredient.

The selected PhD student will spend a period of 6 months in the company Themis S.p.A., Legnano (MI).

Supervisors: Raffaella Boggia – Federica Turrini