





#### Purposes

The PhD-student day has two main goals:

- Enable PhD students to present their research work to the IEM members.
- Make master students aspire to a PhD and discover all the research thematics approached at the IEM.

This day give to the PhD students the opportunity to add value to their project, to share their skills, especially their different laboratory techniques, and to lead their project to a constructive discussion about their work evolution. The master students will be able, for their part, to discover the work type's diversity and to refine their professional project

#### Organization

The event takes place in the IEM's hall and conference room. All the institute members are invited, since the success of this day strongly depend on their presence and their involvement in the diverse discussions.

The day has been divided into four sessions. While the latter, students will present their project and show their work advancement through oral presentations. During the breaks multiple poster sessions will be held in which you are invited to discuss with the students regarding their work.

Besides, students from the theatre group of the University of Montpellier (TAUST association) will present a play named "Thought from a seminar" that has been written for this special occasion. Morevoer, the day will be complemented by two conferences holded by PhD graduated from the IEM. Currently working either in the public and private parties, *Dr. Chrystelle Salameh* and *Dr. Georges Moussa* will present their professional career and share their feedback on their experiences. Finally, the day will end on the award of the three best performances (i.e. oral presentation, poster, and flash communication).

#### Acknowledgements

YoChiN association acknowledges the direction of IEM for the technical and financial organization of this day. YoChiN also acknowledges financial supports from "la Banque Populaire du Sud" that has allowed to award the best presentations. Finally, we thank all adherents of the association for allowing us to organize such gathering occasions and hope to meet you very soon for our next events...

Have a nice day!

YoChiN

9h00 Welcoming-coffee & poster session preparation

9h15 Opening speech from the Director Philippe Miele and presentation of YoChiN

Session 1: Chairs Habib & Octavio

### 09h30

#### **David Lopez Ferber**

Molecular level processing of ceramics: From preceramic polymers with tailored spinnability to ceramic fibers

9h45

## Poster

## **Maxime Balestrat**

From design to application of TiC(N)/SiC(N) nanocomposites derived from preceramic polymers

## Aijing Lu

Synthesis and self-aseembly of amphiphilic block copolymers from bio-based hydroxypropylmethylcellulose and Poly(L-lactide)

## Maya Abdallah

Controlling the stiffness and porosity of Polyacrylamide hydrogel matrices and evaluating their effect on podocyte-behavior

## Ana Luisa Parra Guardado

Enzymatic depletion of antibiotics in wastewaters: Effect of redox mediators in the bio-catalytic system

## 10h00

#### **Flash Communication**

### Sher Ahmad

Coupling enzymatic and monolithic supports for waste water treatment: Experimental and modeling study

#### Qazi Sohaib

 $\label{eq:control} \begin{array}{c} \mbox{Modelling and simulation of CO}_2 \mbox{ capture process in hollow fiber membrane} \\ \mbox{ contactors coupled with ionic liquids} \end{array}$ 

#### Zoulkifli Amadou Yacouba

Zero-discharge advanced treatment for a safe and sustainable urban wastewater reuse

#### 10h15

#### **Lucie Ries**

Two-dimensional materials as building blocks for membrane separation

## 10h 30 Coffee break & poster session

Session 2: Chairs Lucie & Damien

## 10h 45

#### **Thomas Babut**

Self-assembling of amphiphilic peptides and polymer for the elaboration of new membranes

## 11h Poster

#### Fabrice Ndiapa Wandji

Elaboration and characterization of microfiltration membranes impregnated with silver nanoparticles: application to the treatment of drinking water

#### Joel Kinfack

Development by PECVD of phosphonic type proton conductive membranes for hydrogen production by photo-electrolysis of water

### Danae Gonzalez

Inverse pickering emulsion stabilized by exfoliated heganonal boron nitride (h-BN)

11h15

#### Flash communication

#### **Marianne Benoit**

Conception of polymers actuator to elaborate reconfigurable membranes in situ

#### **Mingyuan Fang**

Innovative membranes based on covalent organics frameworks

## **Gbenro Folaranmi**

High performance printable membranes from cellulose based bio-plastics

## 11h30 Pièce de Théâtre

Taust Asso: Thoughts from a seminar

12h-12h15 Lunch break & poster session

### Session 3: Chairs Marianne & Clément

#### 14h00

#### **Emilie Marhuenda**

Glioma stem cells mechanoreception in a new 3D matrix

### 14h15

#### **Flash Communication**

#### **Gauthier Bousquet**

Superhydrophilic/Superoleophilic polymeric membranes elaboration for oily wastewaters treatment

#### **Ahmed Jarboui**

Design of innovative materials for better control of transfers through a contact lens

### Marine Harguindeguy

New bio-based immobilization supports for enzymatic removal of micro-pollutants in fluidized-bed reator

## 14h30

### **Octavio Graniel**

ZnO deposited by ALD on Si nanowires for optical biosensing applications

## 14h45 Flash communication

### **Carlos Castilla**

Reduction of carbon dioxide using boranes compounds

## Julien Jouannaux

Development of porous structures and dense membranes based on mixed ionicelecronic conducting ceramics for thermochemical production of solar fuels

### Maria Di Vincenzo

Development of reverse osmosis membranes incorporating artificial water channel (AWC) systems

### 15h00 Feedback: Ex-PhD students of IEM

## Chrystelle Salameh (IEM) & Georges Moussa (ACCELINN)

15h30 Coffee break & poster session

Session 4: Chairs Carlos & Matthieu

### 15h45

#### Habib Belaid

New generation of scaffolds allowing multiple drug delivery for the treatment of bone metastasis in breast cancers

16h

#### **Flash Communication**

## Cyril Oberlin

Indirect addictive manufacturing of ceramic cores

#### Rui YU

Synthesis and applications of Chitosan-based Hydrogel

## 16h15

### Zaineb Bouaziz

Dual role of layered double hydroxide nanocomposites on antibacterial activity and degradation of tetracycline and oxytetracyline

16h30 Restitution of 2017 PhD investigation survey

C. Innocent & G. Lesage

16h45 Jury's deliberation & awards ceremony

17h Closing speech & Aperitif

## David Lopez Ferber – 2<sup>nd</sup> year

Thesis director: Damien Quemener, Denis Bouyer and Samuel Bernard

# Molecular Molecular level processing of ceramics: From preceramic polymers with tailored spinnability to ceramic fibers

Summary: Ceramic fibers are of great interest as reinforcing agents for ceramic matrix composites (CMCs). Research and development over last decades have mainly focused on using silicon carbide (SiC)-based fibers as reinforcing agents because of their high mechanical properties. There are three generations of SiC-based fibers; the properties of the third-generation fibers approaching those of pure crystalline SiC. This was in particular related to the addition of boron in the Si-C-O precursor fibers; boron acting as a sintering aid of SiC during the decomposition of the oxycarbide phase. These works nicely illustrated the contribution of the organosilicon precursor chemistry to fiber design. These fibers are still being produced by NGS Advanced Fibers Co., Ltd, Ube Industries, Ltd and COI ceramics, Inc. Alternative compositions based on the silicon-carbon nitrogen (Si-C-N) system allows significantly reducing the cost of polymer-derived non-oxide ceramic fibers while comparable mechanical performances could be expected. Such fibers are derived from polysilazanes as precursors. Additionally, the introduction of boron in polysilazanes offers an excellent stability to the derived amorphous Si-C-N network at high temperature. These properties make Si-B-C-N fibers a prime candidate for applications as reinforcing agents.

In this presentation, we will discuss our recent results concerning the elaboration and characterization of Si- B-C-N fibers. We will focus our work on the chemistry behind the synthesis of boron-modified polysilazanes. A detailed characterization of melt-spinnable polymers is provided. Then, polymers are melt- spun into green fibers before curing under ammonia then pyrolysis under nitrogen at 1000°C. The high temperature behavior and mechanical properties of fibers are investigated. As a proof of concept, we will present the design of hollow fibers that opens application of these materials as support for membranes.

Maxime Balestrat – 2<sup>nd</sup> year

Thesis director: Marc Cretin, Samuel Bernard

# From design to application of TiC(N)/SiC(N) nanocomposites derived from preceramic polymers

There is a trend toward more flexibility and an increased interest in "smart" and "adaptive" materials with the objective to meet most industrial specifications. Carbides and carbonitrides can be considered as such strategic materials. They attract increasing interest due to their properties targeted for future materials and technologies especially because they bear intrinsic multifunctionality through the synthesis of multi-element compounds. Inherent difficulties to the traditional techniques for manufacturing such multi-element materials can be overcome by the development of synthetic paths where chemistry of materials and ceramic science are combined rationally to process multi-scale complex solid state architectures. The Polymer-Derived Ceramics (PDCs) route offers new preparation opportunities in ceramic sciences. The molecular origin of preceramic polymers and the possibility to shape then pyrolyze them into advanced materials play a major role in the preparation of ceramics endowed with properties that reach far beyond those of existing materials. Here, the aim of this work is to prepare and characterize TiC(N)/SiC(N) nanocomposites to offer functionalities to SiC. The chemistry behind the synthesis of these polymers as well as their processability to prepare dense pieces will be presented and discussed. The characterization of the materials will be done at each step of their elaboration process.

Aijing Lu – 2<sup>nd</sup> year

Thesis director: Suming Li

# Synthesis and self-assembly of amphiphilic block copolymers from biobased hydroxypropylmethylcellulose and poly(L-lactide)

Micelles self-assembled from amphiphilic block copolymers attracted great interest for controlled delivery of hydrophobic drugs and DNA.<sup>1</sup> Bio-based hydroxypropyl methyl cellulose (HPMC) and poly(L-lactide) (PLA) are widely used in the biomedical and pharmaceutical fields due to their biodegradability and biocompatibility<sup>2,3</sup>. In this work, amphiphilic block copolymers composed of PLA as hydrophobic block and HPMC as hydrophilic block were synthesized and characterized, and their self-assembly properties were studied to evaluate their potential as drug carrier.

Synthesis of HPMC-PLA diblock copolymers: Amino terminated PLA (PLA-NH<sub>2</sub>) with DP of 10, 20, 30 and 40 was synthesized by ring opening polymerization of L-lactide using 3-(Boc-amino)-1-propanol as initiator and Sn(Oct)<sub>2</sub> as catalyst, followed by deprotection with trifluoroacetic acid. HPMC with Mw of 8000 was obtained by acid depolymerization. HPMC-PLA was then synthesized by reductive amination of PLA-NH<sub>2</sub> and aldehyde terminated HPMC, using sodium triacetoxyborohydride as reducing agent. The copolymers were characterised by <sup>1</sup>NMR, DOSY-NMR, FT-IR, GPC, *etc.* 

Self-assembly of HPMC-PLA diblock copolymers: Copolymer micelles were prepared by dissolution in water. The size of micelles was determined by using Anton Paar Litesizer, and the morphology by TEM. The critical micelle concentration (CMC) of copolymers was determined with F-7000FL spectrophotometer, using pyrene as fluorescence probe.

The signals g and f belong to the methyl and methine protons of PLA block, and signals m and n belong to methyl and methylene of HPMC. Both components are present in DMSO, but the signals belonging to PLA are not detected in  $D_2O$ . This is due to the fact that the copolymer self-assembled to form micelles, and only the signals of the hydrophilic shell are detected.

The diameter of micelles was determined by using DLS. It increases from 171.6 nm for HPMC8k-PLA<sub>10</sub> to 212.2 nm for HPMC8k-PLA<sub>40</sub>. The PDI is narrow, ranging from 0.15 to 0.26. TEM shows that micelles are spherical in shape, and low CMC values are obtained.

HPMC-PLA block copolymers with various PLA block lengths were synthesized by reductive amination of PLA-NH<sub>2</sub> and HPMC. The copolymers self-assembled in water to yield spherical micelles with low CMC. Thus bio-based and amphiphilic HPMC-PLA copolymers could be promising as carrier of hydrophobic drugs.

References

- 1. Nicolas J. et al. Chem. Soc. Rev., 42:1147-1235, 2013
- 2. Siepmann J. et al. Advanced Drug Delivery Reviews.48: 139–157, 2001
- 3. Castro-Aguirre E. et al. Advanced Drug Delivery Reviews. 107:333–366 , 2016

## Maya Abdallah– 2<sup>nd</sup> year

Thesis director: Sebastien Balme, Mikhael bechelany

# Controlling the stiffness and porosity of Polyacrylamide hydrogel matrices and evaluating their effect on podocyte-behavior

Chronic kidney disease (CKD) is characterized by reduced kidney function that progresses to endstage renal disease (ESRD). Podocytes are highly specialized glomerular epithelial cells which form with the glomerular basement membrane (GBM) and capillary endothelium the glomerular filtration barrier (GFB). Extracellular matrix (ECM) acts as a scaffold support and provides both mechanical and biophysical signals in order to control podocytes molecular behavior, essential for normal kidney filtration. Many materials have been used as ECM like Polyethylene Glycol (PEG) and Gelatin. The modulus of elasticity E or stiffness is an essential characteristic of the ECM that controls the cell function. Among these materials, hydrolyzed polyacrylamide (PAAm) hydrogel is a non-toxic cross-linked polymer, which is characterized by its high water content, nonbiodegradability and biocompatibility. The hydrogel properties provide a resemblance to in vivo setting for tissues opening great opportunities for biomedical applications. Therefore, hydrolyzed PAAm hydrogel is investigated for its potential use as a new construct to engineer a functional in vitro glomerular-like filtration barrier and to regulate podocyte cell functions by controlling the physical properties (stiffness, swelling and porosity) of PAAm membrane acting as an ECM.

In the present work, several PAAm hydrogels layers were prepared by changing the crosslinker concentration. The macromolecular microstructure and stiffness are evaluated by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques respectively. The physicochemical properties of PAAm hydrogels were tailored over a wide range of crosslinker amount (0.5 to 30<sup>III</sup>). We showed that by controlling the crosslinker concentration, the swelling degree, the mechanical properties and the polymeric network porosity can also be controlled. Swelling test indicated that an increase in crosslinker concentration contributed to a significant decrease in the swelling ratio, and this variation is due to network rigidity that diminishes the network chain movement. In addition, PAAm Hydrogel with the highest amount of crosslinker (30<sup>III</sup>) is a very connected network with pore size of 29 <sup>III</sup> m and represents a high rigidity with a young modulus of 46 KPa. We are currently in the process of optimizing podocytes culture on PAAm membranes with the aim of understanding the molecular mechanisms by which podocytes respond and react to the mechanical properties of the substrate

## Ana Luisa Parra Guardado – 3<sup>rd</sup> year

Thesis director: Jose Sanchez-Marcano

# Enzymatic depletion of antibiotics in wastewaters: Effect of redox mediators in the bio-catalytic system

In recent years bio-catalytic processes have attracted attention as an interesting option for the degradation of persistent pollutants as they are capable to catalyze specific reactions at mild conditions and low environmental impact. Oxidative enzymes, specifically laccases, have been studied as a promising green alternative to eliminate certain recalcitrant pollutants including antibiotics from water. In the present work a novel laccase isolated in Northeast Mexico from the white rot fungus *Pycnoporus sanguineus* CS43 and commercial laccases from *Trametes versicolor* and *Myceliophthora thermophila* were used to evaluate the degradation of the antibiotics amoxicillin (AMX), sulfamethoxazole (SMX) and ciprofloxacin (CIP) in different bio-catalytic systems.

Firstly, free enzyme systems were tested and the optimum reaction conditions were evaluated. The three laccases were able to degrade AMX, the highest degradation yield (72%) was obtained by *P. sanguineus* CS43 after 72h of treatment at optimum conditions. Afterwards, free enzymes systems were tested again but now the effect of the redox mediators, syringaldehyde, p-coumaric acid and ABTS, was evaluated. Degradation yields varied between mediator and laccase type, *M. thermophila* and *T. versicolor* laccases were the most reactive enzymes showing high affinity towards syringaldehyde. Mediator syringaldehyde was the most efficient leading to high degradation yields for all antibiotics (50-100%) in short periods of time, especially towards SMX that was complete degraded after 10 min of reaction by all enzymes. The effectiveness of syringaldehyde was followed by ABTS and p-coumaric acid which presented the slowest reaction rates

The oxidative ability of laccases to transform antibiotics has been demonstrated. The present study represents the first approach for the configuration of an enzymatic membrane reactor using enzymes that can be successfully coupled to conventional wastewater treatment plants as demonstrated in previous work developed by our research group.

## Sher Ahmad – 1<sup>st</sup> year

Thesis director: Jose Sanchez-Marcano, Marie-Pierre Belleville

# Coupling enzymatic and monolithic supports for waste water treatment: Experimental and modeling study

Every year 100,000 tons of Pharmaceutical Products (PPs) are produced due to high consumption rate. PPs are discharged to environment through waste water. Due to recalcitrant nature and long life, PPs remain in water for long time and absorbed on solid surfaces. PPs are difficult to remove through conventional techniques like activated sludge system. Research studies are underway to find the economical and efficient techniques for removal of PPs from waste water. Different techniques used to remove PPs are inefficient as well as uneconomical to be implemented on large scale. Enzymes immobilized on different organic and inorganic surfaces have been used as a catalyst for removal of PPs. Membranes are used as a support for enzyme grafting however low degradation rates were observed due to low porosity, limited surface area, low hydrodynamics and fouling issue. In contrast, monolithic supports provide large surface area with high hydrodynamics. Due to the macro-meso porous structure, monolith offers high surface area and high permeability. Mass transfer in macro porous channels takes place through convection results in high mass transfer, meanwhile large surface area provide high immobilization yield. Current this research study is focused on monolithic supports to study the degradation rates of PPs in synthetic waste water. Experimental study will be performed to determine the reactivity of catalyst with most commonly used PPs and will set the parameters to be used in CFD simulation. Due to limitation of data and to interpret the factors affecting the hydrodynamics, CFD modeling will be performed using COMSOL MULTIPHYSICS. Model will be validate using experimental data, effects of parameters such as concentration of PPs, enzyme concentration, flow velocity will be studied using validated model. Optimum conditions will be set for further experimental studies on monolithic supports in future.

## Qazi Sohaib– 1<sup>st</sup> year

Thesis director: Stephanie Druon-Bocquet, Jose Sanchez-Marcano

# Modelling and simulation of CO<sub>2</sub> capture process in hollow fiber membrane contactors coupled with ionic liquids

Carbon dioxide is a major contributor to climate change and global warming. Therefore,  $CO_2$  capture is of great importance concerning global climate change[1]. There are three basic  $CO_2$  capture methods, post combustion, pre combustion and oxy-fuel combustion. Various technologies have been used previously to capture  $CO_2$ . Among these technologies, Hollow Fiber Membrane Contactors (HFMCs) are more advantageous over other technologies due to large interfacial area, no flooding, foaming and entrainment, easy scale up and independent flow rates[2]. The concept of using ionic liquids for  $CO_2$  absorption is gaining more attention due to its high solubility for  $CO_2$ , negligible volatility, tailorable structures and thermal stability[3]. This work is aimed to model and simulate  $CO_2$  capture. The  $CO_2$  absorption behavior will be investigated based on various operating conditions and process parameters. Various models will be developed and compared with experimental data. The model developed for mass and momentum transport of  $CO_2$ , coupled with other equations, will be simulated using COMSOL Multiphysics<sup>®</sup>, MATLAB and Excel. **References** 

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- [2] A. Gabelman and S. Hwang, "Hollow fiber membrane contactors," vol. 159, 1999.
- [3] Z. Dai, R. D. Noble, D. L. Gin, X. Zhang, and L. Deng, "Combination of ionic liquids with membrane technology: A new approach for CO2separation," J. Memb. Sci., vol. 497, pp. 1–20, 2016.

## Zoulkifli Amadou Yacouba- 1<sup>st</sup> year

Thesis director: Stephane Brosillon, Julie Mendret and Geoffroy Lesage

# Zero-discharge advanced treatment for a safe and sustainable urban wastewater reuse

Nowadays, water scarcity and quality are big challenges facing humanity in many places around the world. To solve this problem, municipal wastewater (WW) is thus considered to be an alternative water source for various applications after proper treatment. Nonetheless, urban WWs are increasingly contaminated with organic micropollutants. In addition, human and veterinary antibiotics have been found widespread in different environmental compartments due to their persistence and low degradability. As a consequence, the presence of antibiotic resistance genes (ARGs) is increasing in the environment. These toxic compounds have become a major issue for the Water Utilities (REACH 2006, WFD 2000 and 2012) and legislations in European Union in the coming years will be tightened with regard to OMPS in municipal WW and to their discharge. These evolutions are driving the WW treatment to come up with advanced technologies.

In this view, membrane processes are widely used but they are only a separation step, they must be coupled with techniques for the efficient destruction of pollutants and then provide new hybrid processes as a posttreatment step. With this aim in mind, ozonation ( $O_3$ ) and peroxone processes ( $O_3 + H_2O_2$ ) are also investigated, as they generate highly active species, hydroxyl radicals. Coupling of membrane processes and Advanced Oxydation Processes (AOP) could thus be a promising treatment for WW reuse.

The main scientific objectives of the PhD are to monitor the fate of six priority and representative substances in a new treatment process coupling membrane bioreactor (MBR), nanofiltration (NF) using organic and innovative inorganic material and ozonation ( $O_3$ ) for a safe and affordable WW reuse, to propose the best design of such combined process and to verify the processes efficiency using a smart combination of analytical techniques, toxicity assessments within an holistic evaluation.

Lucie Ries – 2<sup>nd</sup> year

Thesis director: Philippe Miele, Damien Voiry

#### Two-dimensional materials as building blocks for membrane separation

Membrane separation technology plays an important role in various fields including water treatment, gas separation for the recovery and purification in many industrial processes, and food processing. There has been a renewed focus on multilayered membranes fabricated using exfoliated-restacked 2D materials, since their atomic thickness could theoretically lead to enhanced separation performance<sup>1</sup>.

Exfoliated nanosheets of transition metal dichalcogenides (TMDs) constitute an attractive platform as 2D-material based membranes. Well above other TMDs, recent works were carried on molybnenum disulfide  $(MOS_2)^2$ . Its lamellar structure similar to that of graphene shows rather improved stability. In addition, chemical modifications of the surface of the nanosheets have opened up new separation properties in both fields of molecular<sup>3</sup> and gas sieving. Yet the influence of these modifications on the separation performance remains unclear.

We have studied the performance of lamellar  $MoS_2$  membranes towards the separation of various chemical species. In order to assess the role of surface chemistry, we developed strategies to covalently functionalize  $MoS_2$  nanosheets<sup>4</sup>. Here we will present our recent investigations on the performance of lamellar membranes based on chemically exfoliated  $MoS_2$  and the role of its covalent functionalization towards the sieving of molecules. Our results open novel directions for fine tuning the sieving behavior of membranes based on 2D materials.

- <sup>1</sup> C. N.Yeh J. X. Huang, Nat. Chem., 2015
- <sup>2</sup> M. Deng, H.G. Park, Nano Lett., **2017**, 17 (4), pp 2342–2348
- <sup>3</sup> L. Sun, X. Peng, ACS Nano, **2014**, 8 (6), pp 6304-6311
- <sup>4</sup> D. Voiry, M. Chhowalla, Nature Chemistry, 2015, 7, pp 45–49

## Thomas Babut – 3<sup>rd</sup> year

Thesis director: Marc Rolland, Damien Quemener

# Self-assembling of amphiphilic peptides and polymer for the elaboration of new membranes

The project is articulated arround the self-assembling properties of peptide and more especially the amphiphiles properties. The form of the micelle is dictated by the formula of the peptide. In our case the form is a cylinder with the hydrophilic part of the petide in the external part. This posotion allows us to associate the micelle with an anionic polymer. Together they form a really strong interaction which can be quantified in rheology or observed in AFM. At the end, many problems could happen for the cohesion of the material because it is not formed in one block but many assembled blocks. It is important to notice that a tiny changing in the formation process lead to big cohesion issues. Different methods of deposition have been used in order to find the best compromize in term of thickness, stiffness and robustness. The final test which is filtration has been run only after finding the best deposition and formation process for the material.

The final goal of this self-assembling is the formation by the peptide's fibrous structure of a porous material with which we can control the pore size by changing the peptide formula or the different proportion of the mixture.

## Fabrice Ndiapa Wandji – 3<sup>rd</sup> year

Thesis director: Marc Cretin, Sophie Cerneaux

# Elaboration and characterization of microfiltration membranes impregnated with silver nanoparticles: application to the treatment of drinking water

The present work aims the valorization of Cameroonian clay from the Yagoua region to produce macroporous ceramic filters for water treatment. Several analyzes were carried out to characterize the clay powder used for the formulation of the ceramic supports. These include the elementary chemical composition, the specific surface area by nitrogen adsorption - desorption method (BET), and the particle size analysis. These characterizations were supplemented by measurements of Xray diffraction (XRD), vibrational spectroscopy (IR), thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The elaboration of flat membrane supports involved the formulation of a plastic ceramic paste consisting in a combination of clay powder, water and an organic material, rice husk as a pore former. Several parameters were considered in the formulation of the supports namely, the clay - rice husk ratio in various mixtures (90-10; 80-20; 70-30; 60-40), the drying time of the paste (24h) and the final sintering temperature (900°C, 1000°C, 1100°C and 1200°C). The porous volume, mean pore diameter, surface morphology, mechanical strength, chemical resistance and weight loss after firing ceramic filters were measured. The sintered supports at 1100 °C with a clay-rice husk ratio of 70-30 had a porosity of 43.7% and an average pore diameter of  $6.2\mu m$ . The mechanical strength obtained for this chosen formulation was 10.4 MPa. The flat ceramic supports processed by rollpressing and fired at different sintering temperatures (5 cm in diameter and 3 mm in thickness) presented no defect on the surface and were resistant in both acidic and basic media. The ceramic filters obtained are of great interest in the preparation of different microfiltration membranes for water purification.

#### Arnaud Joël Kinfack – 3<sup>rd</sup> year

Thesis director: Stephanie Roualdes, Vincent Rouessac

## Development by PECVD of phosphonic type proton conductive membranes for hydrogen production by photo-electrolysis of water

Les piles à combustible à membrane électrolyte polymère (PEMFC) constituent actuellement le type de piles le plus prisé. Leurs applications sont multiples autant dans le domaine automobile que dans les domaines stationnaire et portable. Ces systèmes fonctionnent grâce à de l'hydrogène et de l'oxygène. L'hydrogène pur peut être obtenu à partir d'électrolyseurs à membranes échangeuses de protons [1]. Les membranes électrolytes les plus utilisées pour le transport protonique dans les électrolyseurs et les PEMFC sont les membranes commerciales perfluorosulfoniques (Nafion®). Ces membranes présentent de nombreux avantages mais également quelques inconvénients comme notamment la dépendance à l'eau du mécanisme de transport des protons qui engendre une baisse de conductivité protonique à des températures supérieures à 80 °C. Afin de rendre les PEMFC et les électrolyseurs réellement compétitifs, le développement de membranes moins sensibles à l'eau s'avère donc déterminant. De par leur caractère amphotère, les polymères à base de fonctions acide phosphonique sont considérés comme des candidats potentiels pour une application membranaire dans les électrolyseurs et les PEMFC ; ils peuvent également constituer le cœur d'un photo-électrolyseur pour la production d'hydrogène, qui est l'application visée dans cette étude.

La membrane électrolyte développée dans ces travaux (qui font suite à la thèse de Joëlle Bassil [2]) est une membrane polymère de type acide phosphonique préparée par PECVD (Plasma Enhanced Chemical Vapor Deposition) à partir d'un précurseur unique, le diméthyl allylphosphonate. Les procédés plasma, dont en particulier la PECVD, sont généralement compétitifs pour l'obtention de couches minces de grande intégrité et compacité. Le système envisagé (Figure 1) est basé sur une géométrie de type multicouches micro-architecturée avec des couches minces obtenues par procédés plasma [2-3]. La membrane PECVD est prise en sandwich entre deux électrodes, une anode de TiO2 et une cathode de platine. Ces travaux ont pour but d'optimiser les propriétés structurales et de transport de la membrane afin d'assurer de bonnes performances à l'assemblage multicouches plasma dont l'intérêt pour la production/séparation d'hydrogène (H2) parvoie solaire doit être démontré.

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J. Bassil, S. Roualdes, V. Flaud, J. Durand, J. Memb. Sci. 2014, 461, 1.

[3] M. Zhou, S. Roualdes, J. Zhao, V. Autes, A. Ayral, Thin Solid Films 2015, 589, 770.

#### Danae Gonzalez Ortiz – 3<sup>rd</sup> year

Thesis director: Céline Pochat-Bohatier, Julien Cambedouzou, Mikhael Bechelany and Philippe Miele

# Inverse pickering emulsion stabilized by exfoliated heganonal boron nitride (h-BN)

Pickering emulsions or solid-stabilized emulsions were defined at the beginning of the 20<sup>th</sup> century in pioneering works of Ramsden and Pickering. They are described as colloidal suspensions stabilized by solid nanoparticles instead of organic surfactants, which localize at the interface between two phases. In the last years, many researchers have paid attention to the ability of two-dimensional (2D) materials to promote the formation of special classes of Pickering emulsions. We focus our attention in exfoliated boron nitride due to its high surface area and its planar structures. BN monolayer has demonstrated outstanding properties such as biocompatibility, high temperature stability and corrosion resistance, enhanced oxidation resistance, a large band gap and thermal conductivity.

In this study, we reported for the first time a simple method to prepare inverse Pickering emulsions using non-modified exfoliated hexagonal boron nitride (h-BN) as stabilizer agent and its use in the preparation of new porous materials using them as soft templating. Ethyl benzoate was ascribed as the oil phase, because this aromatic organic solvent is almost completely insoluble in water and has been already successfully used for preparing Pickering emulsion with graphene oxide. The stability and type of h-BN Pickering emulsions formulated with different BN concentrations and by varying oil/water (o/w) ratios are studied and discussed. Besides, the BN nanosheets are characterized by AFM, water contact angle (WCA) and SAXS and the characteristics of emulsions are discussed using a multiscale approach. First the emulsion structure is analyzed microscopically through optical and epifluorescence microscopy, and macroscopically by the study of the rheological behaviors. The average droplet size decreases with h-BN concentration whereas the emulsions achieve good stability at high BN concentrations and high o/w ratios. In all formulations, the emulsions are water-in-oil (W/O) type due mainly to the hydrophobicity of h-BN. The Pickering emulsion formulated with 2 wt% of BN is the most interesting due to its high longterm stability and its high viscosity. This research paves the way for the fabrication of boron nitride-based functional materials with novel nanostructures and microstructures using Pickering emulsions as soft template.

### Marianne Benoit – 1<sup>st</sup> year

Thesis director: Claire Antonelli, Damien Quemener

# Conception of polymers actuator to elaborate reconfigurable membranes in situ

The objective is to prepare membranes able to adapt their intrinsic characteristics in operando thanks to the integration of polymeric actuators. Polymeric actuators are materials that change, in a reversible way, their shape and volume in response to an environmental modification **[1-3]**. The external stimuli of theses responsive polymers materials may be the temperature, mechanical or electrical stress, magnetic field, light (UV) and chemical exposure **[2,3]** (pH, solvent, moisture). The change in volume and/or in shape can be observed at nanometric scale as well as macroscopic level. The purpose of this PhD is thus to integrate polymeric actuators to the structure of a filtration membrane allowing its partial or total reconfiguration on request. As an example, a polymer actuator will be localize inside the membrane pores to control their number, size and shape (see figure). It will be also possible to localize actuators at the membrane surface to modify its roughness and thus enable changes in permeability (surface chemistry, contact chemistry) but also to facilitate unclogging operations. Finally, actuators will be integrated in the bulk membrane to study more significant structural configurations with the aim to elaborate stimulables nanomembranes.

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### Mingyuan Fang – 1<sup>st</sup> year

Thesis director: Damien Quemener, Mona Semsarilar

#### Innovative membranes based on covalent organics frameworks

Better and more efficient membranes are needed to face imminent and future scientific, technological and societal challenges. Covalent Organic Frameworks (COFs) are novel porous organic materials, inspired by Metal-Organic Frameworks (MOFs) which feature only covalent bonds and do not contain heavy metals. COFs have lower density than MOFs and retain a very well-ordered highly porous structure. This emerging class of materials is very interesting from a fundamental aspect and for their potential applications (gas storage, catalysis, nanomedicine). However, the use of current COF materials is limited by their small pore size and high crystallinity.

The focus of this project is to develop a novel class of COFs for membrane application that features well-ordered, tuneable and functional pores and better processability compared to existing organic and inorganic membranes. To face the limited pore size and high crystallinity, the addition of soft polymer chains on the building blocks of COFs could open up new avenues for design and synthesis COF materials.

This project will develop a strategy to design and synthesise novel COF building blocks with embedded polymerisation sites, and assemble new tunable COFs onto large surface areas. The pore dimensions of these COFs, prepared from robust methods (boroxine formation), will be adjustable using RAFT (Reversible Addition Fragmentation chain Transfer) polymerisation. Growing polymers within the walls of the COF pores will allow the controlled modification of their shape and size, and the addition of desirable functionalities. Thin films made from this novel COFs will be assessed as separation membranes. This interdisciplinary project will provide enabling technology for advanced porous materials with potential applications as high performance membranes, capture and release devices and catalysis.

#### Gbenro Floranmi – 1<sup>st</sup> year

Thesis director: Damien Quemener, Mona Semsarilar

## High performance printable membranes from cellulose based bioplastics

Water is the essence of life. Safe drinking water and sanitation are indispensable to sustain life and health, and fundamental to the dignity of all. Shortage of clean water is a global problem. A probably underestimated 884 million people do not have access to improved sources of drinking water, while more than 2.5 billion lack access to improved sanitation facilities. Membranes are favored over other technologies for water treatment such as disinfection, distillation, or media filtration; they require less energy, little chemical additives, or thermal inputs. Pressure driven membranes processes remain the most widely used membrane technology for water treatment.

Majority of these membranes are made of polymers sourced from petroleum and are nonbiodegradable with lack of selectivity and fouling challenges. The key to solve these problems is to design novel materials allowing the fabrication of membranes with enhanced separation capability, consuming less energy, from renewable material with reduced environmental impact and via costefficient, industrially acceptable methods.

# The challenge is thus to make membranes that are highly selective, as well as atom and energy efficient.

To address these problems and challenges, this project aims to make membranes from cellulose based bio-plastic material which have the following properties:

- Reduced environmental impact (greener material with enhanced biodegradability)
- Lower energy consumption
- Improved separation and selectivity
- Adjustable properties conveyed via the surface property of the individual building blocks such as antifouling, chelation, etc.
- More atom efficient (cheaper and greener)
- Industrially viable fabrication method

This project aims to synthesize printable membranes for water filtration from cellulose-synthetic polymers hybrid materials. These hybrid materials will be obtained by covalently binding synthetic polymers obtained by RAFT polymerization to cellulosic backbones.

## Emilie Marhuenda – 3<sup>rd</sup> year

Thesis director: David Cornu

#### Glioma stem cells mechanoreception in a new 3D matrix

Current standard of care against glioblastoma (GBM) including surgery, chemotherapy and radiotherapy have limited efficiency on the overall patient survival expectancy. Invasive tumor cells, called glioblastoma stem cells (GSC), disseminate within the normal brain parenchyma, escaping surgical resection, resisting localized radiation and chemo-therapies, and are responsible for the fatal outcome. Clinical observations demonstrate that GSC preferential migration areas are fibrous in nature (corpus callosum, blood vessels, brain parenchyma or subarachnoid space).

If the role of chemotaxis and the integration of chemical signals in migratory behaviors have been described, little is known about the perception of physical stimuli to induce an invasive phenotype.

Cancer stem cells (CSC) have been reported to be sensitive to the mechanical properties of the surrounding tissue/microenvironment (pressure, confinement, fiber diameter and tissue rigidity) and to use the microenvironment stiffness to enhance invasion. GSC can thus perceive their physical microenvironment and translate it into mechanical membrane deformation by mechanotransduction.

In this context, we developed a 3D artificial fibrillary tissue on the first hand which can allow *in vitro* recapitulation of the migration behavior observed *in vivo*. We designed 3D electrospun fibers to study the influence of the morphological and mechanical properties of the support on CSCs migration. This 3D matrix is highly plastic as key physical parameters were modulated including stiffness and the alignment of the fibers.

On the second hand, we placed glioblastoma stem cells neurospheres on the developed 3D artificial tissue. This support will allow us to describe the correlation between physical parameters and different migration behavior, as well as changes in the RNA and EMT protein expression.

## Gauthier Bousquet – 1<sup>st</sup> year

Thesis director: Denis Bouyer

## Superhydrophilic/Superoleophilic polymeric membranes elaboration for oily wastewaters treatment

This research project aims at adressing serious environmental concerns on water and soil pollution by oily wastes. These wastes are constantly generated by numerous industries, which do not propose any up-to-date efficient process to treat them, owing to extra-cost generated from potential treatment or recovery process. Thus, the project will focus on the formation of novel membranes whose surface structure and surface chemistry will allow achieving efficient and scalable recovery of oily wastes.

The main objective is to develop a new generation of polymeric membranes for the filtration of oilin-water. To achieve this goal, superhydrophilic membranes will be developed to separate oil-inwater emulsions. They will bear non adhesive properties will permit the break-up of oil-in-water emulsions.

The project is divided in several parts: First, the preparation of novel copolymers in order to create superhydrophilic/superoleophobic matrices. Indeed, it's primordial here to focus on the membrane elaboration and characterization to get insights into membrane formation mechanisms to control membranes structure.

Another main task of the project is the application of membranes in emulsion separation, using several kinds of emulsions and oily industrial wastes. Thus the understanding on emulsion behavior and properties will be crucial to come-up with an efficient, cost-effective treatment of oily wastes.

In facts, separation of oil-in-water or is not the number one focus in research related to membrane filtration. Yet, it is undeniable that solutions have to be found to recover oily wastes, considering environmental issues but also societal and economic issues arising from direct discharge in the environment. The innovative nature of the project lie on several aspects, regarding polymer chemistry, membrane formation, analysis and control of interface properties, and use of energy-efficient separation process to recover oily wastes.

## Ahmed Jarboui – 1<sup>st</sup> year

Thesis director: Denis Bouyer

# Design of innovative materials for better control of transfers through a contact lens

Ophtimalia specializes in the design and development of medical electronic devices for outpatients follow-up, for the prevention and treatment of eye diseases (glaucoma). Ophtimalia aims in particular to design a medical device for continuous measurement of changes in intraocular pressure (IOP). The PhD project will aim for the search of new technological solutions using effective and innovative materials. The project will integrate coupled (i) experimental and (ii) modelling approaches.

In the present device, the contact lens used is made by assembling different membranes, also integrating a sensor. During in-vivo testing, the measured corneal swelling due to oxygen deprivation is considered high due to low oxygen permeability of the lens material, as well due to consideration related to the current design.

The objective of the thesis work is therefore threefold:

- Design and test alternative materials to replace one or more membranes,

- Study, through an experimental approach, the phenomena of transfers through the materials identified and implemented (scale of the laboratory pilot)

- Model the phenomena of coupled transfers (matter / heat).

In parallel with the search for innovative materials, a laboratory prototype will be sized to study their permeability to water vapour and oxygen under controlled conditions of temperature and relative humidity. The third part of the thesis will consist in modelling the phenomena of coupled transfers. The model will simulate all the involved phenomena, for better material selection and their morphology.

## Marine Harguindeguy – 1<sup>st</sup> year

Thesis director: Marie-Pierre Belleville, Céline Pochat-Bohatier

## New bio-based immobilization supports for enzymatic removal of micropollutants in fluidized-bed reator

The presence of pharmaceutical pollutants and endocrine disruptors in urban and industrial effluents is becoming an actual problem for environment and public-health. Their presence may come from different sources, such as human drugs and pharmaceutical production which cause contamination in domestic and industrial wastewater, and veterinary drugs which result in soil contamination [1]. Their removal is very difficult because the compounds are generally refractory to classical wastewater treatments and are present at very low concentration (<  $\mu$ g/L). The enzymatic treatment of such effluents can be an interesting alternative to classical wastewater treatments, in particular when enzymes are immobilized in beads in order to be reused and increase their stability [2,3]. In this thesis, new immobilization bio-based supports will be designed for laccase immobilization. Firstly, a repeatable process of elaboration of supports needs to be found. Gelatin has been chosen as a support as it is biodegradable, the elaboration process is simple and cheap, and it will also reduce the environmental impact of the project. Then, immobilization of laccase on the beads will be studied using glutaraldehyde as a cross linking agent. Finally, a fluidized-bed reactor will be designed and optimized to study the degradation of a model micro pollutant from wastewater, in which the fluidized bed will be composed of the beads supporting the enzymes.

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## Octavio Graniel – 2<sup>nd</sup> year

Thesis director: Mikhael Bechelany, Sebastien Balme and Philippe Miele

# ZnO deposited by ALD on Si nanowires for optical biosensing applications

ZnO is one of the most used transducer materials due to its optical properties and biocompatibility. Silicon nanowires (Si NWs) have attracted much attention for applications in photovoltaics, lithium-ion batteries, electronics and biosensors due to their mechanical, electrical and optical properties.

The high aspect ratio of SiNWs and the optical properties of ZnO are exploited to build the substrate of an optical biosensor. In this work Si NWs were obtained by combining metal assisted chemical etching (MACE) and nanosphere lithography (NSL). The resulting structures were later covered with a 50 nm thick ZnO layer and characterized by SEM and photoluminescence. As a first approach, the photoluminescence response to H2O2 was investigated.

## Carlos Castilla – 1<sup>st</sup> year

Thesis director: Umit B.Demirci

#### Reduction of carbon dioxide using boranes compounds

Global warming due to rising levels of greenhouse effect gases such as atmospheric  $CO_2$  is one of the major challenges nowadays. The concentration of  $CO_2$  is currently increasing by more than 1.9 ppm per year, so decreasing its emissions is thus a key issue. With respect to transformation of  $CO_2$ , there are 16 valorization recovery methods. They can be classified as 3 main routes: no transformation, biological transformation and chemical transformation, being the last one the one of interest for the project. The most investigated method of chemical transformation is hydrogenation of  $CO_2$ . Depending on the conditions and the nature of hydrogenation of  $CO_2$ , this leads to different products.

The aim of the project is to explore, optimize and develop a new hydrogenation strategy using a couple of reactive hydrides as hydrogen and heat carriers, due to the high reactivity of these compounds. One component of the couple of reactive hydrides is a boron and nitrogen-based compound. The approach is based on the following criteria: I) No solvent is used, allowing to simplify the process; II) No catalyst is used, avoiding problems related to catalyst deactivation; III) Required H<sub>2</sub> is *in situ* generated by the reaction. Next to the exothermic reaction of the couple of hydrides, CO<sub>2</sub> is hydrogenated by the *in situ* H<sub>2</sub> generated and the reaction being activated by the temperature increase. Various by-products are expected to form. Depending on their nature, the cycle is closed differently. Assuming the formation of chemicals like methanol and formic acid, they are extracted and separated to be used as feedstocks. Assuming the formation of salt-like compound, it will be recovered and fully characterized. Thus, the objectives are to alleviating global climate changes and developing a simple process that could be integrated to existing industrial processes (synthesis of borohydrides from borates).

## Julien Jouhannaux – 1<sup>st</sup> year

Thesis director: Anne Julbe, Martin Drobek and André Ayral

## Development of porous structures and dense membranes based on mixed ionic-elecronic conducting ceramics for thermochemical production of solar fuels

European and global regulations concerning greenhouse gases continue to evolve in an increasingly restrictive way. Hence, the application of alternative energy sources which could possibly substitute the fossil fuels and thus reduce  $CO_2$  emissions is a relevant alternative for decreasing both the dependence on fossil resources and global warming. In this context, solar thermochemical looping is a particularly promising option because it directly uses a high temperature heat source to produce the fuel (H<sub>2</sub> and CO).

The proposed approach involves materials based on metal oxides able to produce  $H_2/CO$  and  $O_2$  separately in two distinct steps: (1) reduction of the oxide generating  $O_2$ ; (2) reaction of the reduced oxide with  $H_2O/CO_2$  forming  $H_2/CO$ . The concentrated solar energy is used as a heat source at high temperatures (1000-1400 °C).

Two types of oxygen-ions conducting oxides will be considered: perovskites (ABO<sub>3</sub>) and metal doped ceria ( $M_xCe_{1-x}O_2$ ). The work will mainly focus on the fabrication, characterization and optimization of both porous reactive structures and dense membranes based on these materials.

The methods for tailoring the shape and architecture of the membrane materials (e.g., self-supported membranes with porosity gradient, supported thin layer, etc.) and their characterization (ion conductivity, oxygen transport kinetics, thermal stability at high temperature, mechanical strength, etc.) will be studied. Finally, the thermochemical performance during  $H_2O$  or  $CO_2$  splitting will be assessed. A detailed study of the materials physico-chemical properties will be carried out at the IEM (Institut Européen des Membranes- Montpellier) with a special attention devoted to dilatometric studies in an environmental chamber simulating the operating process conditions.

The samples developed in the form of porous materials or dense membranes will be optimized for their integration in dedicated solar reactors that will be designed and tested at the PROMES lab (PROcédés, Matériaux et Energie Solaire- Odeillo).

### Maria Di Vincenzo– 1<sup>st</sup> year

Thesis director: Mirai barboiu, Yves-Marie Legrand and Stéphanie Roualdès Development of reverse osmosis membranes incorporating artificial water channel (AWC) systems

The market of high rejection membranes for seawater desalination is currently dominated by thinfilm composite (TFC) membranes comprising an active layer of polyamide (PA) made by interfacial polymerization (IP). In particular, IP reaction of m-phenylenediamine with trimesoyl chloride gives rise to fully aromatic films, used predominantly for high pressure membrane applications. However, traditional PA membranes suffer from inherent flaws, which reduce their performance during operation. Weaknesses of these membranes include surface roughness and the presence of a significant residue amount of terminal unreacted carboxyl groups. These characteristics have been related to fouling, and in this context further research is needed in order to lead to the robust and high performance membrane design. The Institut Européen des Membranes (IEM) has the experience for upscaling the molecular/supramolecular ion channel systems to microscopic membrane materials [1-3]. Producing defect-free Artificial Water Channels (AWCs) membranes with large area remains the most critical challenge. One clear advantage is that the AWCs may be more readily incorporated than Aquaporins-AQPs into the planar membrane structures. In other words, one might expect the use of AWCs to lead to the formation of highly permeable layers with excellent salt rejection. This work presents a possible route for membrane surface functionalization with AWCs systems, whose self-assembled channels can enhance water passage through the membrane. An IP approach is presented, in which the classical interfacial condensation between a polyamine monomer and a monomer comprising acyl halides is modified in order to form a three-dimensionally cross-linked polyamide layer with the AWCs embedded. The membranes fabricated with this procedure are fully characterized and their permeability and selectivity performances are evaluated by filtration of solutions containing NaCl, MgCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub> and  $MgSO_4$  in reverse osmosis conditions. The proposed strategy using novel TFC-AWCs biomimetic membranes represents a possible route for desalination.

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## Habib Belaid – 2<sup>nd</sup> year

Thesis director: David Cornu, Mikhael Bechelany, Vincent Cavailles and Catherine Teyssier

# New generation of scaffolds allowing multiple drug delivery for the treatment of bone metastasis in breast cancers

Breast cancer is the most common invasive cancer in women, and the second main cause of cancer death in women. In metastatic breast cancer, cancer cells spread to the bones through the blood and lymphatic system causing considerable pain and high patient morbidity.

The treatment of bone is a challenge due to the difficulty that has the bone to repair itself. Thus, patients are often treated by implanting a passive artificial junction. The principle of this method is based on the promotion of cell growth on a bio-inspired 3D material "scaffold". In this approach, the morphology, the chemical composition and the physicochemical properties of the "scaffold" play a key role. Indeed the materials must exhibit morphology and properties mimicking the multi-scale structure of the extracellular matrix of the bone to allow the adhesion and the cell proliferation. Finally, for the treatment of patients with bone metastasis, it would be interesting that the "scaffold" could allow the controlled and local release of anticancer drugs.

The aim of this thesis is the development and characterization of novel biomimetic biodegradable implants allowing both bone regeneration and breast cancer cell eradication. Our goal is to develop new original processes for the development of "scaffolds" based on 3D printing or/and Injectable scaffolds. The major advantage of such structures lies in the perfect biocompatibility with the mechanical properties similar to those of tissues.

The scaffolds will contain molecules stimulating bone formation (bisphosphonates) and inhibiting the proliferation of estrogen- dependent breast cancer cells (Raloxifen).

The Project is divided into 3 main parts: Design of drugs/biopolymer scaffolds, understanding the drug release kinetics, study the in vitro toxicity and the kinetics of cancer cell death for the scaffolds and understanding the in vivo biocompatibility and efficacy of the scaffolds on bone regeneration and cancer cell death.

## Cyril Oberlin – 1<sup>st</sup> year

Thesis director: Phillipe Miele, Céline Pochat-Bohatier and Mirna Bechelany

## Indirect addictive manufacturing of ceramic cores

This thesis is part of the development of new processes to realize new cooling systems of complex shapes by simplifying or even eliminating the assembly of cores and the problems related to demoldability. The combination of additive manufacturing with the injection process will allow the development of this type of cooling systems while satisfying the objectives of reduction of time and manufacturing costs.

A first approach is to use sacrificial resin molds made by 3D printing in place of the metal molds and to substitute the high pressure injection process with a low pressure process. A second approach is to overmould an insert disposed in an injection mold and obtained by 3D printing with a fluid ceramic paste and then removing the insert to obtain a complex core.

# Rui Yu – 1<sup>st</sup> year

Thesis director: Suming Li

## Synthesis and applications of Chitosan-based Hydrogel

In present study, bone ash-reinforced chitosan-based hydrogels were obtained by encapsulation of bone ash into the hydrogel structure which was fabricated by photopolymerization of chitosangrafted-glycidyl methacrylate (CTS-g-GMA) and poly(ethylene glycol)diacrylate (PEGDA) under the UV light. Hydrogels were characterized by ATR-FTIR, SEM and XRD analyses. Mechanical performance of the hydrogels was determined by universal mechanical tester. Cytotoxicity tests for hydrogels were conducted to determine cellular compatibility. Swelling tests were carried out to investigate the water uptake capacity of hydrogels. Drug delivery was selected as the model drug. The release of drug was provided at different PH and controlled manner. All results visualized that the obtained pH-sensitive chitosan-based hydrogel with enhanced mechanical properties could be a potential candidate as a drug carrier for treatment of diseases in the future applications.

## Zaineb Bouaziz – 3<sup>rd</sup> year

Thesis director: Sebastien Balme

# Dual role of layered double hydroxide nanocomposites on antibacterial activity and degradation of tetracycline and oxytetracyline

The intercalation of antibiotics in the layered double hydroxide layers was usually considered for water decontamination but rarely for delivery. Here, tetracycline (TCH) and oxytetracycline (OXY) were immobilized on Zn<sub>2</sub>Al-Cl LDH following two methods: co-precipitation and anion exchange. Depend on the method of immobilization the interfacial concentration of antibiotic varies from 0.04 to 0.5. The antibiotic are not intercalated in he interlayer space which allows their release in 10 Hours. The antibacterial activity against both E. coli and S. epidermidis revealed that the loaded antibiotics are still active but less efficient compared to the free ones. After exposition to UV irradiation or to high temperature storage (30, 60 and 120°C), their activity decreases significantly due to the degradation, especially when antibiotic is loaded by co-precipitation. This is promising route to reduce antibiotic contamination in waters.



# **Acknowledgements**













