Qu’est-ce que le dispositif ExposUM Doctoral Nexus ?

Les Doctoral Nexus proposés par l’Institut ExposUM sont des réseaux de 3 à 4 doctorantes et doctorants, issus de disciplines différentes et affiliés à au minimum deux unités de recherche différentes.

Par rapport à une thèse classique, participer à un Doctoral Nexus favorisera la capacité à travailler en équipe et à concevoir des projets de manière transdisciplinaire tout en approfondissant son propre champ d’expertise.

Un programme pédagogique spécifique sera proposé et les doctorant(e)s concerné(e)s auront également l’opportunité d’organiser un séminaire au sein du réseau Nexus.

Les thèses sont financées d’emblée pour 4 années, comprenant le salaire du doctorant ou de la doctorante ainsi qu’une enveloppe d’environnement.

Sujet de thèse

Coupling nanofiltration and highly effective and stable membranes for electro-oxidation of persistent pollutants in water

Context

The widespread infiltration of PFAS into our drinking water systems poses a significant challenge, spurring the need for advanced water treatment solutions. Membrane filtration, in particular nanofiltration, is able removing PFAS from water but generates concentrates that need to be handled [1]. Electrochemical-based advanced oxidation processes (AOPs) play a pivotal role in addressing this issue, offering the unique capability to break down a variety of recalcitrant organic substances. These processes generate reactive species directly within the water, thereby reducing reliance on external chemical agents and enabling the integration with renewable energy sources for operation. They hold great promise for effectively purifying drinking water from PFAS. Current research aims to overcome the existing drawbacks related to the creation of harmful by-products and limited efficiency due to the low concentrations typically found in drinking water [2]. Additionally, advancements are being pursued to enhance the cost-effectiveness and durability of electrocatalysts essential for the scalability of such treatment methods in potable water applications

Objective and methods

The global objective of this thesis is to study the coupling of nanofiltration and electrochemical-based advanced oxidation to remove PFAS (PFOA and PFOS) and produce safe drinking water. The novelty of the project is based on the development of porous 3D Perovskite oxides membrane ($CaCu_3Ti_4O_{12}$ (CCTO)) as novel electrocatalysts that aim at providing a suitable trade-off between reactivity and stability. The 3D structure will allow for implementation of continuous flow-through reactors for improving mass transport conditions owing to fast radial diffusion within pores combined with convection-enhanced mass transport during filtration.

Our objective is organized around four tasks.

Task 1. Characterization of the efficiency of PFAS removing using nanofiltration membranes

In this task, we aim to assess the efficacy of NX nanofiltration membranes in the filtration of water contaminated with PFAS. The originality of these membranes relies in the hollow fiber configuration which is still rare for nanofiltration [3]. The NX nanofiltration membranes, characterized by their fine pore size and high selectivity, present a promising solution. The experimental setup involves exposing the membranes to a controlled concentration of PFAS-laden water and monitoring their performance in terms of removal efficiency, flux rates, and durability. The goal is to investigate the membrane's ability to selectively reject PFAS molecules while maintaining optimal water permeability. The concentrate solution will be analyses by PhD 2 and tested by Dr. Cavailles's group and PhD 3.The concentrate will then be treated by electro-chemical oxidation in task 3.

Task 2. Design of porous calcium copper titanate membrane electrodes

In this task, we will investigate the synthesis of perovskite porous based electrodes. Perovskite oxides (specially $CaCu_3Ti_4O_{12}$ (CCTO)) are particularly popular in electrocatalysis due to their low-cost and simple synthesis techniques with excellent stoichiometric control, repeatability, and homogeneity. They also offer a high capacity to accommodate a wide variety of substituting and doping elements to regulate their properties. We will first synthesize this perovskite and study the doping with different elements (Silver, Cobalt etc.) in order to enhance the electrocalytic properties. The preparation of porous membrane (macro/meso) will be realized using a templating approach (PMMA, Polycarbonate spheres etc.) in order to obtain material with controlled porosity. The obtained membranes will be characterized by various approaches including SEM, TEM, EDX, XPS, XRD, Raman and FTIR.

Task 3. Batch reactivity for removing persistent pollutants

In this task, PFAS concentration will be in the range 5-20 ppm to avoid analytical issues. First, we will identify the reaction mechanisms using radical quenchers and probe molecules (e.g. terephthalic acid for •OH). Then, we will evaluate the kinetics and the pathway for the degradation and mineralization of selected pollutants, the evolution of by-products (degradation by-products; ClO_3- and ClO_4-) and the competition with scavengers. In addition, we will quantify the reactivity of perovskite powders for activation of externally added H_2O_2 and/or $S_2O_8^{2-}/HSO_5^-$; the reactivity of the suspension of catalysts in a batch electrochemical reactor used for in situ production of H_2O_2 (from reduction of dissolved O_2 at carbon-based materials) and/or $S_2O_8^{2-}/HSO_5^-$ (from sulfate oxidation at TiO_{2-x} or boron-doped anodes); and the reactivity of catalysts immobilized on electrode surface in a batch electrochemical reactor. Finally, we will quantify the influence of electrode polarization and water matrix on the lifetime of catalysts: using an approach based on accelerated lifetime tests.

Task 4. Flow-through validation over catalysts using nanofiltration concentrates

First, we will optimize the porosity of CCTO membrane and we will study mechanical stability (shock and attrition tests). Then, we will determine the optimal configuration of the flow-through reactor with model pollutants. We will validate the flow-through configuration for treatment of model water. Finally, we will apply and optimize the treatment of nanofiltration concentrates as performed in previous study in IEM [4]. The treated solution will be analyzed by PhD 2 and tested by Dr. Cavailles's group and PhD 3.

Expected results

The completion of this research project will definitely lead to a treatment scheme dedicated to the eradication of PFAS for drinking water production. This project will allow to obtain the first prove of concept for electrochemical water purification using perovskite based membrane. It could lead ultimately to a substantial industrial valorization through several industrial partners that have close collaboration with our laboratory.

Feasibility

The feasibility of this project is based both on the expertise of the host laboratory and the wide national and international collaborations already in place. In addition, this project benefits from the technical and scientific support of a scientist and a technician. All the facilities necessary for the implementation of the project are already available within the IEM.

Candidate profile:

The candidate (M/F) should hold a Master's or Engineering degree in Materials Science, Chemistry, Process Engineering, Physical Chemistry, or a related field. The candidate should have strong foundational skills and an inclination for experimental work in the laboratory. Excellent writing and communication skills, particularly in English, are required, along with the ability to work independently. Previous experience in membranes would be advantageous.

1 Tow EW, Ersan MS, Kum S, Lee T, Speth TF, Owen C, et al. Managing and treating per- and polyfluoroalkyl substances (PFAS) in membrane concentrates. *AWWA Water Sci*. 2021;**3**(5):1–23.

2 Mirabediny M, Sun J, Yu TT, Åkermark B, Das B, Kumar N. Effective PFAS degradation by electrochemical oxidation methods-recent progress and requirement. *Chemosphere*. 2023;**321**:138109.

3 Wendy A. Jonkers, Emile R. Cornelissen, Wiebe M. de Vos, Hollow fiber nanofiltration: From lab-scale research to full-scale applications, Journal of Membrane Science, Volume 669, 2023,121234,4

4 Azaïs A, Mendret J, Petit E, Brosillon S. Influence of volumetric reduction factor during ozonation of nanofiltration concentrates for wastewater reuse. *Chemosphere*. 2016;**165**:497–506.

Modalités de candidature

La candidature doit être composée des éléments suivants :

- Un CV
- Une lettre de motivation
- De la copie du diplôme permettant l'inscription

- Des éléments spécifiques demandés par l'école doctorale GAIA (https://gaia.umontpellier.fr/)

Si vous souhaitez postuler sur ce sujet, adressez au plus vite un mail à mikhael.bechelany@umontpellier.fr (co-directeur de thèse) et julie.mendret@umontpellier.fr (co-directrice de thèse et porteuse du projet Doctoral Nexus PYPHAS) et et exposum-aap@umontpellier.fr afin de les informer de votre intérêt.

Avant le dimanche 21 avril, 20h CET

The University of Montpellier

KEY FIGURES

52372 students

74 research facilities

TOP 200 in the Shanghai ranking

657 National and institutional diplomas

17 faculties, schools and institutes

9 doctoral schools

3rd worldwide in ecology

5132 employees including **2818** teachers, researchers and research assistants

6500 scientific publications in 2021

RESEARCH CENTERS

From space exploration and robotics to ecological engineering and chronic diseases, UM researchers are inventing tomorrow's solutions for mankind and the environment.
Dynamic research, conducted in close collaboration with research organizations and benefiting from high-level technological platforms to meet the needs of 21st century society.
The UM is committed to promoting its cutting-edge research by forging close links with local industry, particularly in the biomedical and new technologies sectors.
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SCIENTIFIC APPEAL

Open to the world, the University of Montpellier contributes to the structuring of the European higher education area, and strengthens its international positioning and attractiveness, in close collaboration with its partners in the I-SITE Program of Excellence, through programs adapted to the major scientific challenges it faces.
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