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

Understanding of mechanisms and pathways of PFAS degradation by electro-oxidation in drinking water

Context

The overall objective of the research project is focused on Per- and Polyfluoroalkyl Substances (PFAS). These environmental molecules are widely used and practically nonbiodegradable. Consequently, they are detected ubiquitously in the environment and received increasing attention as global environmental contaminants. In biology, a recent study suggests that PFAS may activate the PXR nuclear receptor, which senses the presence of foreign toxic substances and in response up regulates the expression of proteins involved in the detoxification and clearance of these substances from the body. Interestingly, PXR is also a regulator of the growth and apoptosis of colon tumors.
Numerous studies have demonstrated the degradation of perfluoroalkyl substances (PFAS) in water by advanced oxidation or reduction processes. Nevertheless, there is a lack of comprehensive and comparative overview of the various degradation pathways and mechanisms [1]. In water treatment, toxic degradation byproducts form a substantial obstacle for industrial applications of electrochemical technologies. Concerning PFAS degradation by electro-oxidation, if the total applied energy density is not sufficient and/or if the electroactive material is not well adapted, PFAS are merely degraded to shorter-chain compounds potentially toxic. Additionally, in water containing chloride or bromide at relevant concentrations, the formation of perchlorate, bromate, and toxic organic halides is a concern. It is therefore important to evaluate the toxicity of the electrochemically treated water and to determine mechanisms and pathways of PFAS degradation.

Objective and methods

The global objective is to gain better understanding of the degradation pathways and mechanisms of PFAS degradation by electro-oxidation processes. The methodology of the project is to (i) evaluate the treatment effectiveness using electrochemical methods (ii) identify degradation pathways and characterize byproducts of PFAS model molecules (iii) assess the toxic potency of the water before and after treatment using bioassays using bioluminescent bacterizes commonly developed at IEMM (iv) hence propose a selection of the most relevant water samples at different time treatment to Dr. Cavailles's team (INSERM Montpellier) to characterize the effects of PFAS and oxidation byproducts as PXR activating- environmental disruptors on colorectal tumorigenesis, on the tumor immune microenvironment and the response to chemotherapies in relation with PhD project 3 of the NEXUS project named PYPHAS.

Our objectives for this PhD are then organized around three tasks.

Task 1. Analytical development

Liquid chromatography hyphenated to tandem mass spectrometry (LC/MS/MS) represents the state-of-the-art analytical technology to monitor organic compounds in complex matrices with high sensitivity and specificity. The total concentration of PFAS in drinking water should not exceed 0.50 µg/L in Europe, and the individual concentration of 20 of them should be less than 0.1 µg/L. Thus, an optimized LC/MS/MS workflow associated with an efficient sample treatment, such as a pre-concentration step by solid phase extraction (SPE), will be developed to reach the targeted PFAS quantification limits. Regarding the identification of unknown degradation products issued from electro-oxidation, further investigation will be conducted by high resolution mass spectrometry (HR-MS) for exact mass measurement combined with iterative fragmentation steps (MSn) to ensure unambiguous structural elucidation. Pr Christine Enjalbal (IBMM-UMR5247) expert in mass spectrometry will oversee this analytical task. Guillaume Cazals and Eddy Petit, both engineers at the Pôle Chimie analytical facilities (PAC Chimie Balard, newly created UAR 2041) master all available technologies required to identify and quantify PFAS and byproducts by mass spectrometry.

Task 2. Identification of chemical pathways

Heterogeneous AOPs use catalysts to activate oxidating agents (e.g., H_2O_2, O_3, persulfate), which contribute to the generation of powerful reactive oxidant species (ROS) such as hydroxyl radicals (•OH) and sulfate radicals (SO_4^-•). The defluorination (breaking C−F bonds) and the elimination of head groups (e.g., carboxylate and sulfonate groups) depend on the dominant ROS engaged on the process. The objective of this task is to identify the transformation pathways during oxidation reactions so as to provide insights into PFAS degradation mechanisms, which are fundamental for the design of heterogeneous AOPs. IEM's group has a long time experience on the development of electrochemical techniques for water remediation focused on emergent micropollutants and pharmaceuticals [2,3]. More recently, the team focused its attention on the degradation of perfluorooctanoic acid (PFOA) by anodic oxidation with the concomitant identification of shorter polyfluoroalkyl substances (from C7 to C3) [4].

Task 3. Evaluation of toxicity via bioassays

The generic Aliivibrio fischeri bioluminescence assay will be carried out to give information on the general toxic potency of the water. Herein, exposure of the marine bioluminescent bacterium A. fischeri to toxic components in the extracts results in a decrease in bioluminescence compared to a blank caused by the inhibition of the bacterial metabolism. The main objective will be to make a correlation between degradation pathway and toxicity of PFAS and byproducts according to process and time treatment. This type of bioassay has been used previously to evaluate the effectiveness of water treatment with advanced oxidation in our group [5]. In parallel, the most relevant treated water samples *(i.e.* non-toxic and/or presenting a toxicity due to the presence of a specific compound or byproduct identified through bioluminescence assay) will be tested by Dr. Cavailles's group and PhD 3 (INSERM Montpellier).

Excepted results

This study lays the groundwork for future research to analyze and elucidate the transformation products and pathways of PFAS in various treatment systems. The completion of this research project will give knowledge on the possible breakthrough and low removal efficiencies which is important since short chain PFAS are known to be formed during degradation of long chain PFAS. Designing and evaluating new removal technologies that will eliminate a wide range of PFAS, particularly the short chain molecules, is a crucial direction for future research to help mitigate the PFAS crisis.

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 scientists and a technical staff. All the facilities necessary for the implementation of the project are already available within the university and IEM.

[1] Chemical Engineering Journal 450 (2022) 138352
[2] Electrochimica Acta 188 (2016) 378-384.
[3] Chemical Engineering Journal 419 (2021) 129467
[4] ChaÏma Gomri, Advanced Water Remediation: Adsorption and Electrooxidation Techniques for Effective PFAS Treatment, Thèse Université de Montpellier, 15 déc. 2023
[5] Chemosphere 172 (2017) 1-9

Modalités de candidature

La candidature doit être composée des éléments suivants réunis en un seul fichier PDF:

- un CV,
- une lettre de motivation,
- les relevés de notes de Master disponibles jusqu'à la date de clôture des candidatures et des années d'études antérieures,
- de façon facultative, un avis ou une lettre de recommandation (2 au maximum)
- D'autres éléments spécifiques demandés éventuellement par l'école doctorale SCB (https://edscb.umontpellier.fr/)

Si vous souhaitez postuler sur ce sujet, adressez au plus vite un mail à christine.enjalbal@umontpellier.fr (co-directrice de thèse) et marc.cretin@umontpellier.fr (co-directeur de thèse) ainsi qu'à 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.
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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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