Innovative tandem system of porous carbon sorption and photocatalytic degradation of TiO$_2$ nanomembranes for micro-nano-plastics and PFAS removal

PI: Anming Hu, Department of Mechanical, Aerospace and Biomedical Engineering (MABE)

Co-PI: Qiang He, Department of Civil and Environmental Engineering (CEE)

Objectives and rationale The overall goal of this proposal is to seek an innovative tandem flow-cell system integrating surface sorption by porous active carbon and the photocatalytic degradation of TiO$_2$ nanomembranes to effectively remove micro-nano-plastic (MNPs) and per- and polyfluoroalkyl substances (PFAS). To realize such a goal, following objectives have been identified: (1) Design and construction of a tandem flow-cell system integrating porous carbon sorption and photonic catalytic degradation; (2) optimizing of surface adsorption, filtration, and photonic catalytic degradation of typical MNPs and PFAS.

MNPs and PFAS are two typical anthropogenic and environmentally persistent pollutants. It is predicted that the world production of plastic will increase to 12 billion tons in 2050. Currently only 9% of plastics are recycled worldwide and the rest are treated as municipal solid waste. After fragmentation and decay, these plastics break down to microplastics (less than 5 mm) or nano plastics (less than 1 micro) entering aquatic ecosystem and posing serious environmental pollution and health risks [1]. It has been proven that these MNPs cannot be effectively removed through conventional municipal wastewater treatment plants (MWTP) [2-3]. MNPs have been unfortunately found in the whole food chain. It is estimated that the total mass of MNPs taken through food and water is equal to a plastic credit card per person per week. MNPs have been detected in human blood, tissues, and even neuron systems. Cytotoxicity of MNP has been evident and the chronic effect through long-term accumulation is under study.

PFAS is a big class of fluorinated aliphatic substances (more than 4,700 different compounds), which may cause serious health issues including tumor induction, endocrine disruption, immune toxicity and neurotoxicity. In April 2024, US Environmental Protection Agency (EPA) had issued regulations to prevent PFAS usage and establish the standards in drinking water: 6 PFAS at a level of 4-10 ng/L (ppt) includes perfluoro octanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) at a few pg/L. It is important to note that the MWTP cannot effectively degrade PFAS instead, it acts as a sink, discharges higher PFAS in effluent than that in influent [4]. Meanwhile, identifying robust microbes for biodegradation of these forever flroriated chemicals is still challenging in a conventional biodegrade method [5]. Therefore, the innovative degradation of PFAS is highly demanded. It is very critical to point out that PFAS can be strongly absorbed by MNPs and thereby MNPs work as carriers of PFAS [6]. This proposal thus presents a “one stone two birds” strategy which can degrade two persistent pollutants.

It is well known that there is no single removal technology to target multi-objectives. Surface sorption is reported as an economic and effective method to capture MNPs and PFAS [7,8]. However, MNP sorption is site-selected, and the adsorbent surface should be properly functionalized [7, 9]. Besides, the adsorption of short-chain PFAS is less effective [9]. Photocatalytic degradation can fully degrade PFAS by mineralization [10]. However, due to sluggish photo-induced chemical reaction, photocatalytic degradation is more suitable for

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organic pollutant removal at a low concentration. Our previous TiO$_2$ membranes are proven to effectively degrade various pharmaceutical and personal care products (PPCPs) and persistent chemicals for drinking water treatment [11-14]. Up to now, there is no report to integrate a flowthrough sorption and photocatalytic degradation for both MNP and PFAS removal.

Technical approach and research plan

(1) Design and construction of a tandem flow-cell system integrating porous carbon sorption and photonic catalytic degradation

In this task, we will design and build a flow-cell system enabling filtration through sorption and photocatalytic degradation using a TiO$_2$ nanowire membrane. The main idea is shown in Fig. 1. At first the contaminated water with typical MNPs and PFAS will pass through the porous pyrolytic wooden filter. We have tested over 10 wood materials and found softwood, such as birch wood or bass wood can generate nice microchannels by its nature structures. With KOH activation, we can generate nanopores. The micro-nano porosity is better than normal activated carbon by balancing the flowing rate and surface sorption while providing mechanical strengthen for filtration. To further improve the selection sorption of MNPs and PFAS the pyrolytic wooden structure will be further functionalized with polyphenol [7] and/or poly(ethylenimine) [15]. The middle part is a photocatalytic degradation reactor with TiO$_2$ nanowire membrane. A low-pressure UV lamp is inserted in the center to excite TiO$_2$ nanowires to generate highly oxidized radicals to de-fluoride PFAS and nanoplastics. The nanowire membrane will be mechanically supported by a stainless-steel mesh. The last part is to prevent any nanowire releasing from the middle reactor using porous wooden filtration. We will optimize filtration and degradation through micro-nanostructures control and surface functionalization of both pyrolytic wooden and nanomembranes.

(2) Optimizing of surface adsorption, filtration and photonic catalytic degradation of typical MNPs and PFAS

In this task, the performance of tandem reactors will be examined using typical MNPs and PFAS with the established EPA standards and analytic protocols (USEPA method 537.1) [7,10,15]. Typical MNPs include polystyrene (PS), polymethyl methacrylate (PMMA), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polyethylene (PE). Microparticles with different sizes to mimic MNPs. Selected PFAS are long-chain PFOS and PFOA and short-chain PFPeA (perfluoropentanoic acid) and PFHxA (per-fluorohexanoic acid). The concentration of MNP and PFAS, degradation intermediates will be determined by high performance liquid chromatography and tandem mass spectroscopy (HPLC-MS/MS). The total organic carbon (TOC) will be analyzed by a TOC analyzer with a non-dispersive IR sensor or gas phase chromatography and mass spectroscopy and used to quantify the mineralization efficiency, and the defluorination efficiency. The treated water will be sampling by solid state extraction. The concentration, temperature, pH value and flow rate will be measured to characterize the filtration, sorption and photocatalytic degradation [12-14].

Collaboration plan The design, fabrication and resting of tandem reactor will be conducted in Dr. Hu’s lab at MABE. The MNP/PFAS analysis will be carried on in Dr. He’s lab in CEE. Two
groups will collaborate on the data analysis, optimizing reactor performance, jointly preparing publication and developing proposals for external funds.

**Proposal development plan**

One proposal (>-$400K) targeting the PFAS removal and defluorination mechanism will be developed for EPA using prototype tandem reactor proposed in this project. The proposal will also include additive manufacturing of reactors, which is under investigated in Hu’s lab.

The 2\textsuperscript{nd} proposal (~-$300K) targeting MNP removal and photocatalytic degradation will be developed either for the consortium of Plastics led by National Renewable energy Laboratory or to the industrial innovative fund on sustainable environment (Eastman Chemical Company or Tennessee Valley Authority of electricity TVA).

**Dissemination plan**

Two publications are planned to submit to academic journals on water treatment. The first paper will focus on the synergistic effects of adsorption of MNP and PFOS and photocatalytic degradation. The adsorption vs porosity, sorption kinetics, degradation as a function of concentration of each micropollutants, the whole turbidity, pH, temperature will be studied. The second paper will elucidate the degradation mechanism with intermediate species identification.

**Timeline for all deliverables.**

July -Sept, 2024: student hiring, training, literature review, chemicals ordering, system design. By the end of September, the first hired student (MABE) will present the design of tandem system and research plans for degradation mechanisms

Oct. -Dec, 2024: carbonization of selected woods and characterization. TiO\textsubscript{2} nanomembrane fabrication, tandem system fabrication, exhibit the successful operation of tandem reactors.

Jan. -March, 2025: hire of the 2\textsuperscript{nd} student (CEE), adsorption characterization, photocatalytic degradation examination, system evaluation, first publication preparation

April-June, 2025, degradation mechanism study, 2\textsuperscript{nd} publication preparation, draft and submission of one proposal for external funding, planning the 2\textsuperscript{nd} proposal

**References:**

[8] Lei et al. Env. Poll. 321 (2023) 121138