Title	Multi-Component Nanostructured Active Platforms as Functional Toolkits for PFAS Remediation (NANOFUN)

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Project description (2 page max):

Nowadays the environmental economy is characterized by a dynamic multiscale nature and many different features which simultaneously account for different crucial aspects which span from technological, environmental, social and economic ones. To this regard, a suitable waste-management becomes an essential requirement which necessarily passes through the use of efficient approaches and methods to recognise resource and recovery opportunities. At present, the complete recycling and reuse of waste can be prevented by the presence of certain chemicals, which represent technical barriers to an appropriate resource recovery. These compounds may be hazardous molecules deriving from human activities, which constitute one of the principal hindrances to circular economy. Unfortunately, the majority of (waste)water processes currently available lack from both low energy consumption technologies and high efficiency. Consequently, key issues are advances in sustainable technologies enabling access to clean water in order to effectively underpin the global demand of social/industrial development in a carbon-neutral fashion. In this context, the recovery of nutrients (such as biomolecules, metals, organic and inorganic compounds, antibiotic resistant genes, by-product of disinfection…) represents a rational water use of vital importance for the wastewater management. The NANOFUN proposal will assess fabrication strategies to multi-component nanomaterials based on hybrid synthetic approaches [based on the coupling between Chemical Vapor Deposition (CVD), Radio Frequency (RF)-Sputtering and liquid-phase approaches, such as drop-casting and electrophoretic processes], through a flexible multi-step material design that will ensure the obtainment of active systems endowed with optimal functional performances and high operational stability toward the degradation of highly toxic and persistent perfluoroalkyl substances (PFASs) such as perfluorooctanoic acid (PFOA) and GenXchemicals. In particular, two different material types will be taken into account: 1) g-C_3N_4 specifically functionalized with MO_x nanoparticles (M = Mn, Fe, Fe-Co, Cu), will ensure the obtainment of high-surface-area electroactive scaffolds that can benefit from cooperative (catalytic, electronic, structural) effects deriving from the intimate contact of each component. These systems can be efficiently deposited on carbon-

based substrates (carbon cloth, carbon papers); 2) tailored functionalization of wood-based biochar with metallic nanoparticles will facilitate the degradation of C-F bonds. Wood-based biochars will be produced at 200, 300, 400, 500, and 600 °C (the time will be optimized) in a closed container under oxygen-limited conditions. The biochars will be subsequently milled to pass a 200 μm sieve and then treated in HCl (1 mol/L) to remove the mineral constituents and increase the surface area. All the prepared systems will be subjected to complementary analytical techniques: a) X-ray Photo-electron/X-ray Excited Auger-Electron Spectroscopies (XPS/XE-AES) as well as energy dispersive X-ray spectroscopy (EDXS) and Raman spectroscopy, to study the system chemical composition, the element oxidation states and their distribution as a function of the used preparation conditions and possible ex-situ treatments; b) UV-Vis-NIR spectroscopies, for the analysis of absorption properties of the supported nanomaterials; c) Field-Emission Scanning Electron Microscopy (FE-SEM), to analyse the system surface morphology and nano-organization; d) X-ray Diffraction (XRD), to investigate material microstructural characteristics; e) Transmission Electron Microscopy (TEM), electron diffraction (ED) and local EDXS chemical mapping, to analyse the system growth mode, local nano-structure and interfacial quality. The properties of the biochar such as the functional groups on the surface of biochars will be measured using a Fourier transform infrared spectroscopy (FTIR). The specific surface areas of the biochars will be measured by a Brunauer-Emmett-Teller. The zeta potentials of the biochars and other elemental composition, cation exchange capacity, pH, and redox potentials which are important chemical properties in controlling the interactions between biochar and contaminants will be measured. The in-situ distribution of nFe^0 in pore-network structures of biochar will be carried out by appropriate wet chemical strategies and also validated by means of absorption-edge synchrotron X-ray computed microtomography (SXCMT).
Subsequently, efforts will be devoted on the degradation of highly toxic and persistent perfluoroalkyl substances (PFASs) such as perfluorooctanoic acid (PFOA) and GenXchemicals. In fact, a complete detoxification of PFAS from the environment (i.e., soil and water) is a very important concern for health protection and homeland security [1]. Tests will be carried out using Advanced Oxidation Processes (AOPs), which allow the production of very reactive oxidizing species, capable of degrading recalcitrant pollutants.[2] Among these, techniques based on the Fenton effect have attracted much attention due to their theoretical and practical advantages, capable of generating active radical species in solution (such as: HO•, HO_2•) through the catalytic decomposition of hydrogen peroxide by the Fe^{2+}/Fe^{3+} couple. Particular attention will be also devoted to the analysis of catalyst stability upon prolonged utilization, as well as to the understanding of the degradation mechanism by means of MS spectrometry and liquid chromatography (LC) investigations in order to optimize functional activity. We will adopt the existing methods developed at the host institute for measuring PFOA [3]. We will modify the existing and validated methods toward incorporating GenX-chemicals (carboxylate anion of HFPO-DA and its ammonium salt, and E1) in the samples using LC-TripleTOF/MS. Batch experiments will be conducted in simulated groundwater and natural surface water by introducing the biochar composites into the artificially GenX-chemicals and PFOA contaminated water (0.1 μg/L, the limit as recommended by the EU drinking water directive) and the reductive defluorination of the chemicals will be monitored. The defluorination in the samples after treatment will be determined by measuring the amount of the chemicals (target analysis), their breakdown products (suspect-screening analysis) using LC-TripleTOF/MS. The concentration of F also will be measured as products of degradation. The pH of the mixture will be monitored. Determining the reductive defluorination mechanism of the GenX-chemicals and PFOA will be determined.

[1] M. Mirabediny, J. Sun, T. T. Yu, B. Akermark, B. Das, Chemosphere, 2023, 321, 138109.

[2] Y. Deng, R. Zhao, Current Pollution Reports 2015, 1, 167-176.

[3] F. Heydebreck, J. Tang, Z. Xie, R. Ebinghaus, Environ. Sci. Technol. 2015, 49, 8386-8395.