



**H.F.R.I.**  
Hellenic Foundation for  
Research & Innovation

**Zr<sup>4+</sup> MOFs with Exceptional Capability for Removal of  
Toxic Ions from Aqueous Media – IEMOFs**  
**1st Call for H.F.R.I. Research Projects to Support Faculty  
Members & Researchers and Procure High-Value  
Research Equipment**

**Title of the research project:**  $Zr^{4+}$  MOFs with Exceptional Capability for Removal of Toxic Ions from Aqueous Media

**Principal Investigator:** Emmanouil Manos

**Reader-friendly title:** IEMOFs

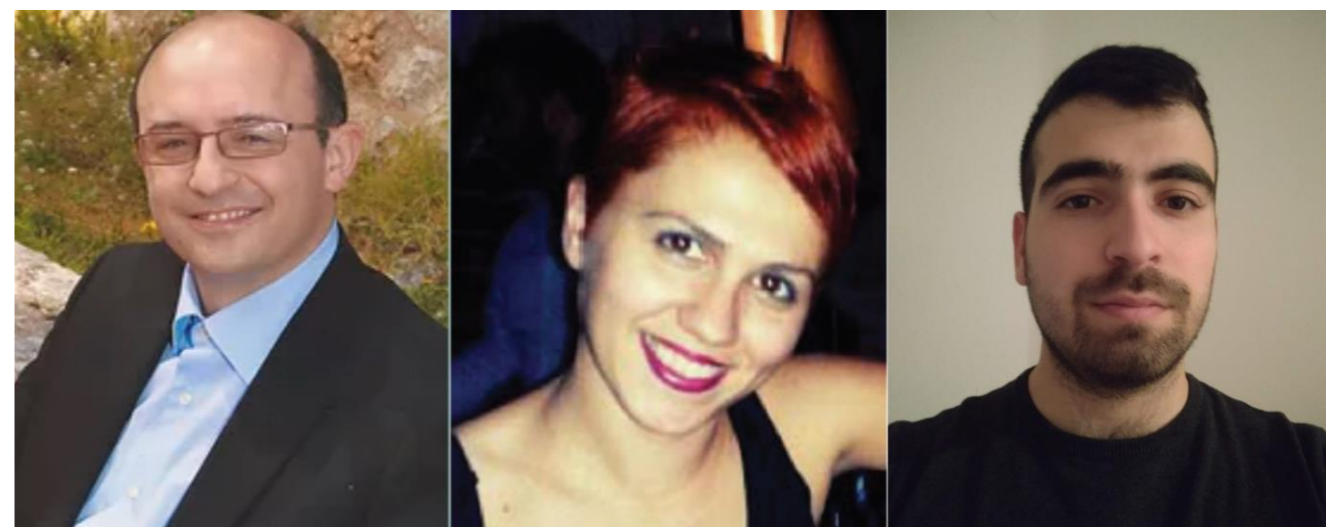
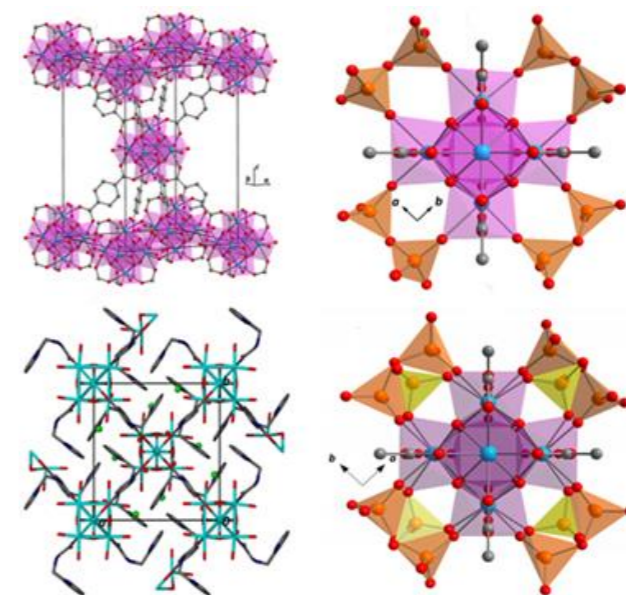
**Scientific Area:** Natural Sciences

**Institution and Country:** University of Ioannina, Greece

**Host Institution:** University of Ioannina

**Collaborating Institution(s):** University of Patras

**Project webpage :**  
<https://evageloudimitris19.wixsite.com/mysite?fbclid=IwAR3qS3wuy9976YRen7wFv-5hNrLdWiyFfsCKv5Rb2iz-8zLoqffDHyihXPY>



**Budget:** 200.000

**Duration:** 36 months

## Research Project Synopsis

Poisonous heavy metal ions (e.g.  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ) as well as carcinogenic (e.g.  $\text{CrO}_4^{2-}$ ) and deleterious (e.g.  $\text{HAsO}_4^{2-}$ ) anions represent major pollutants in industrial effluents and possess a serious threat for humans and other species. In the last two decades, metal-organic frameworks (MOFs), gained a great deal of interest in materials science due to their excellent properties, such as high surface area, multi-functionality, and chemical/thermal stability. MOFs with ion-exchange properties (Ion-Exchange MOFs, IEMOFs) seem to be very promising for viable applications toward wastewater treatment. Combining a highly ordered porous structure and a large variety of binding groups, IEMOFs may be considered as the next generation materials for ion-exchange applications. Thus, IEMOFs can be designed to carry out extremely fast sorption with unprecedentedly high selectivity toward the targeted ionic species. Among metal organic ion exchangers,  $\text{Zr}^{4+}$  IEMOFs with organic ligands are considered as the most promising ones, combining a number of important features, including a) robustness, b) high porosity, c) capability to incorporate various functional groups, and d) ease of synthesis. In the present research project, we explore the use of a series of organic ligands with appropriate functional groups for the isolation of a series of microporous  $\text{Zr}^{4+}$  IEMOFs. The capability of new IEMOFs for sorption of harmful cations or anions is investigated. Moreover, the IEMOFs are used as the basis to prepare composite materials with organic polymers. The composites do not show tendency to form fine suspension in water and thus, they exhibit capability to remain fixed in ion exchange columns. The materials are extensively studied for their ion sorption properties with batch methods, as well with ion-exchange columns. These ion-exchange columns consist mainly of silica sand with dispersed a relatively small quantity of IEMOF–organic polymer composite. Studies are conducted not only with synthetic wastewater but also with real waste.

## Project originality

The treatment of various types of aqueous wastes such as industrial effluents is of major concern for the countries all over the world. Sorption and ion exchange are relatively inexpensive and highly effective methods for elimination of various types of ions from water. However, common and abundant cation exchangers (such as clays and zeolites) and sorbents (such as activated carbon) suffer from low selectivity and capacity for toxic heavy metal ions. Organic resins, containing functional groups suitable for sorption of specific cations or anions, are the most widely-used sorbents in various remediation processes and in the purification of drinking water, however, have several demerits regarding limited chemical, radiolytic and thermal stability. Other materials that have been tested for various ion exchange processes include functionalized mesoporous silica, transition metal oxides, layered double hydroxides (LDHs) and metal sulfide ion-exchangers (MSIEs), showing in some cases very promising results. Nevertheless, issues like stability in extreme conditions existing in certain types of wastewater (e.g. nuclear waste), cost/reusability of the sorbents, selectivity for the targeted toxic ion in the presence of tremendous salt concentrations etc., need to be considered prior the employment of the sorbents in practical remediation applications.

From the above, it is clear that the “perfect” sorbents that can withstand the harsh conditions of various types of wastes and be highly selective for the targeted toxic ions as well as be affordable are still elusive. Although there have been several proof-of-principle studies showing that IEMOFs can be efficient sorbents, only a few systematic investigations of their ion exchange properties have been performed. Furthermore, the examples of IEMOFs fabricated in such a form to allow their use in ion-exchange columns, required for practical applications, are scarce. The present project has as main goals the isolation of new materials with unprecedented ion-exchange/sorption capacities and the development of new ion-exchange column technologies for water treatment applications. In addition, a challenge of the proposed work will be the isolation of materials with a dual cation/anion sorption capability, which will be a breakthrough achievement in the research on sorbent materials.

## Expected results & Research Project Impact

Several scientific, social and economic benefits at a local and international level will arise from the implementation of this project. Research in MOF chemistry is of significant importance not merely for the increase of basic scientific knowledge but also because this class of materials have important technological applications. One of these applications includes the sorption and removal of toxic ions from aqueous media. Pollution from heavy metals and other inorganic pollutants in the aquatic environment is now recognized as a major environmental concern in many countries. Especially in the countries located in the Mediterranean region, where the water resources are limited, there is a continuous need to develop inexpensive and efficient methods for the remediation and re-use of wastewater. Furthermore, considering the extent of research that has been carried out on sorbents for toxic ions and the huge market for these materials, the development of IEMOFs and their composites may open new horizons in the rapidly developing industry of sorbents.

## The importance of this funding

**Funding is the prerequisite for the successful completion of research projects and the production of high-quality scientific results. In terms of human resources, a significant number of young researchers are employed, given them the opportunity, whether experienced or not, to enhance their scientific skills, improve their knowledge on cutting edge research areas and propel their academic career. A significant part of the fund regards to the participation of the research team in conferences and scientific meetings. Thus, the research progress is presented to a broad audience and at the same time scientific ideas related to the research object are exchanged. Funding is also intended for the purchase of essential consumables and laboratory equipment for the smooth completion of the experimental design. Overall, funding is the driving force not only for the participants of the project but also for the scientific community in general, due to the multiple benefits that accompany the funding of the project.**



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