

# Self-assembling peptide-based magnetogels for the removal of heavy metals from water

Farid Hajareh Haghighi<sup>1</sup>, Roya Binaymotlagh<sup>1</sup>, Laura Chronopoulou<sup>1,2</sup>, Sara Cerra<sup>1</sup>, Andrea Giacomo Marrani<sup>1</sup>, Francesco Amato<sup>1</sup>, Cleofe Palocci<sup>1,2</sup> and Ilaria Fratoddi<sup>1</sup>

<sup>1</sup>Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy

<sup>2</sup>Research Center for Applied Sciences to the Safeguard of Environment and Cultural Heritage (CIABC), Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy

Corresponding authors: [farid.hajarehaghighi@uniroma1.it](mailto:farid.hajarehaghighi@uniroma1.it)

## 1. Abstract

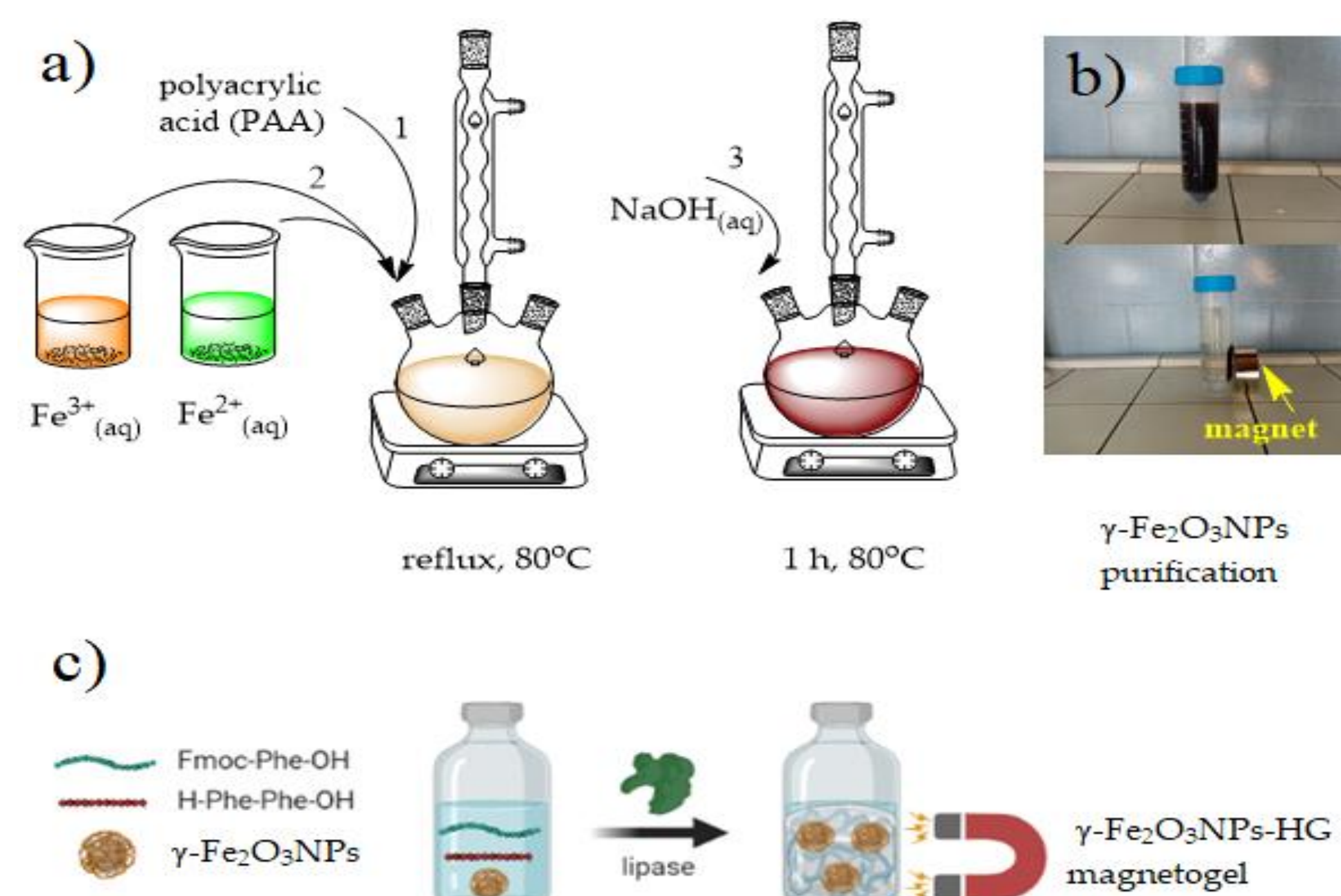
In this study, a novel **peptide-based magnetogel** obtained by the encapsulation of  **$\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-polyacrylic acid nanoparticles** ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs) into a hydrogel matrix was used for enhancing the ability of the hydrogel to remove **Cr(III), Co(II), and Ni(II) pollutants** from water.

Fmoc-Phe and diphenylalanine (Phe<sub>2</sub>) were used as starting reagents for the hydrogelator (Fmoc-Phe<sub>3</sub>) synthesis via an enzymatic method [1,2]. The PAA-coated magnetic nanoparticles were synthesized in a separate step, using the coprecipitation method [3,4], and encapsulated into the peptide-based hydrogel. The resulting organic/inorganic hybrid system ( **$\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs-peptide**) was characterized with different techniques, including FT-IR, Raman, UV-Vis, DLS,  $\zeta$ -potential, XPS, FESEM-EDS, swelling ability, and rheology.

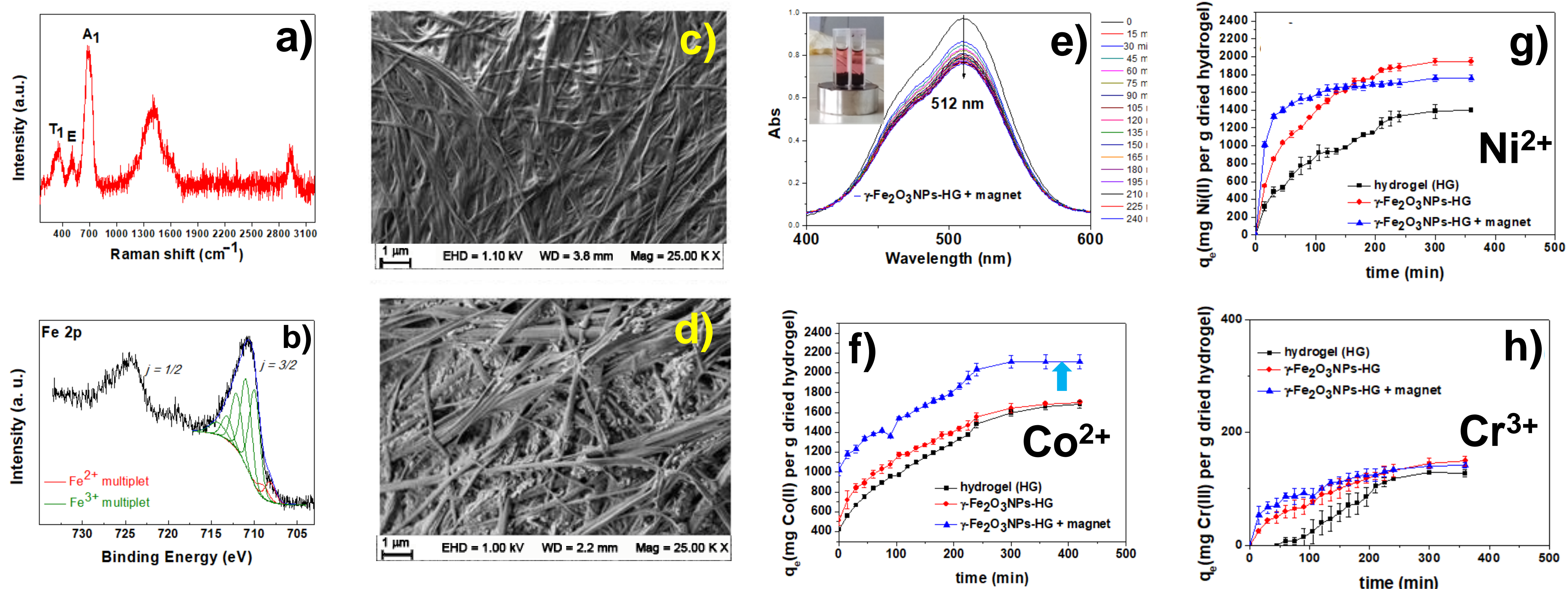
Four different systems were studied for the removal of heavy metal ions from aqueous solutions, including: 1)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs stabilized with PAA, ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs), 2) Fmoc-Phe<sub>3</sub> hydrogel (HG), 3)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs embedded in peptide hydrogel ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG), and 4)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG in the presence of an external magnetic field. To quantify the removal efficiency (RE (%)) of these four model systems, UV-Vis technique was employed as a fast, cheap and versatile method.

The results demonstrated that both Fmoc-Phe<sub>3</sub> hydrogel, and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs peptide magnetogel can efficiently remove all the tested pollutants from water. Interestingly, due to the presence of magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs inside the hydrogel, the **removal efficiency can be enhanced by applying an external magnetic field** [5].

## 2. Synthesis of nano hybrid



## 3. Characterizations



**a)** Raman spectrum of PAA-coated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs; **b)** XPS Fe2p spectrum of PAA-coated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs; **c)** FESEM of peptide hydrogel alone; **d)** FESEM of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG magnetogel; **e)** UV-Vis study of Co(II) adsorption by  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG upon magnetic field application versus time; **f)** Co(II) adsorption capacity of HG,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG + magnet versus time; **g)** Ni(II) adsorption capacity of the HG,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG + magnet versus time; **h)** Cr(III) adsorption capacity of the HG,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG + magnet versus time.

## 4. Discussion and conclusion

The goal of this work was to direct attention to emerging and novel research involving magnetogel nano hybrid materials that might be relevant in future applications for **the treatment of wastewater**, as well as in other fields.

Generally, composite hydrogels are promising adsorbents with tunable features, and we demonstrated that the addition of effective functional groups in nano hybrid materials through chemical conjugation is a promising strategy to further improve the adsorption abilities of hydrogels. In fact, the results achieved pointed out that the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs provides magnetic properties to the resulting nano hybrids, which can be applied for magnetic-based removal applications of contaminants, such as heavy metal ions, from aqueous phases. The results of the removal studies demonstrate that the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs in combination with the application of an external magnetic field increases the adsorption efficiency of the hydrogel matrix for all the metal ions tested in this study; in particular, the  **$\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG + magnet** was effective to absorb up to **2100 ± 70 mg/g for Co(II)**, **1760 ± 40 mg/g for Ni(II)**, and **142 ± 5 mg/g for Cr(III)**.

The kinetic models showed the chemisorption of these cations onto the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>NPs@HG (with and without the magnetic field). Regarding the native HG, Co(II) and Ni(II) showed chemisorption, but for the Cr(III), the results were fitted with a physical adsorption mechanism. This work showed that the peptide-based magnetogels can be introduced as promising adsorbing materials for wastewater treatment to remove heavy metals from aqueous solutions. In the future, this study could be expanded to test the recovering ability of the three adsorbing systems for the recycling of metal ions, and extensive efforts should be directed to scale up the applications and test the developed materials in practical scenarios.

The proposed magnetogel represents a **smart multifunctional nanosystem with improved absorption efficiency** and synergic effect upon applying an external magnetic field.

## 5. References

- [1] Binaymotlagh, R. et al., Peptide-based hydrogels: New materials for biosensing and biomedical applications. *Materials* **2022**, 15, 5871.
- [2] Chronopoulou, L. et al., Preparation of hydrogel composites using a sustainable approach for in situ silver nanoparticles formation. *Materials* **2023**, 16, 2134.
- [3] Veloso, S.R.S. et al., Magnetogels: Prospects and main challenges in biomedical applications. *Pharmaceutics* **2018**, 10, 145.
- [4] Hajareh Haghighi, F. et al., Surface modification of TiO<sub>2</sub> nanoparticles with organic molecules and their biological applications. *J. Mater. Chem. B* **2023**, 11, 2334–2366.
- [5] Hajareh Haghighi, F. et al., Self-assembling peptide-based magnetogels for the removal of heavy metals from water. *Gels* **2023**, 9, 621.