

# Mitigating Emerging Contaminants: Lettuce Root-Based Magnetic Nanocomposites for residual antihypertensive removal in water

Eduarda Zago<sup>1</sup>, Thiago S. Castão<sup>1</sup>, Jonatas L. Ramos<sup>1,2</sup>, Elma N.V.M. Carrilho<sup>1,2,3\*</sup>

<sup>1</sup>Laboratory of Polymeric Materials and Biosorbents, Federal University of São Carlos, Araras, SP, 13600-970, Brazil.

<sup>2</sup>Material Science Graduate Program, Federal University of São Carlos, Sorocaba, SP, 18052-780, Brazil.

<sup>3</sup>Department of Natural Sciences, Mathematics, and Education, Federal University of São Carlos, Araras, SP, 13600-970, Brazil.

Keywords: adsorption, emerging contaminant, bionanocomposite, magnetite nanoparticles.

\*Presenting author email: elma.martins@ufscar.br

## Introduction

Water contamination by atenolol (ATL), a beta-blocker widely detected in global effluents, represents a critical environmental challenge due to its persistence and capacity to induce physiological and behavioral alterations in aquatic species, such as increased stress, anxiety, and changes in defense reactions against predators (Godoy et al., 2015; Khasawneh & Palaniandy, 2021). Given the inefficiency of conventional treatment plants in removing emerging contaminants, biosorption based on the use of agricultural residues, such as lettuce root (LR), stands out as a sustainable alternative due to the abundance of oxygenated functional groups, such as hydroxyls and carboxyls, which possess high affinity for organic molecules (Soares et al., 2023). The operational efficiency of this material is optimized by the synthesis of magnetic bionanocomposites (LR-NP), which utilize magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles to enable rapid separation of the adsorbent via an external magnetic field, overcoming the technical limitations of post-treatment filtration and centrifugation (Qu et al., 2022). Thus, this study aimed to develop, characterize, and systematically evaluate the adsorptive potential of LR and LR-NP materials in the remediation of ATL in aqueous media, aiming to promote low-cost and high-efficacy technologies for the preservation of water resources.

## Methods

**Synthesis of LR-NP:** The magnetic bionanocomposite was synthesized by chemical coprecipitation. FeCl<sub>2</sub> and FeCl<sub>3</sub> solutions were mixed, and NH<sub>4</sub>OH was added dropwise to form magnetite nanoparticles (NP). Powdered lettuce root (LR) was then added to the suspension under constant agitation at 80 °C for 30 min. The resulting LR-NP was magnetically separated, washed, and dried at 50°C.

**pH assessment:** To evaluate the effect of pH, 10 mg of LR or LR-NP were added to 10 mL of 10 mg/L atenolol (ATL) solution. The pH range (6 to 10) was adjusted with 0.1 mol/L HCl or NaOH. After 15 min of orbital agitation (185 rpm), the adsorbents were separated (centrifugation for LR; magnetic field for LR-NP) and the remaining ATL was quantified by UV-Vis at 224 nm.

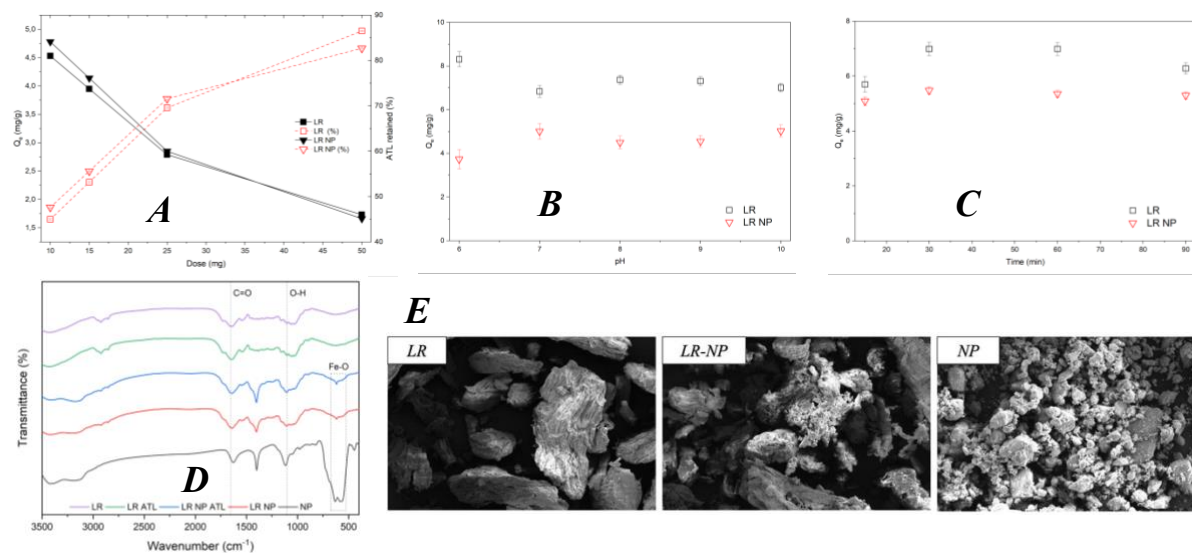
**Kinetic studies:** Adsorption kinetics were studied using 1.0 g/L dosage at pH 7 for 15, 30, and 60 min. The supernatants were collected and analyzed via UV-Vis. Data were fitted to pseudo-first order and pseudo-second order models to determine the rate-controlling mechanism.

**Experimental Sorption Capacity (SC<sub>exp</sub>):** Equilibrium tests were performed with ATL concentrations from 10 to 175 mg/L at pH 7 for 60 min (1.0 g/L dosage). Adsorbents were separated by centrifugation (LR) or a 7,000 Gauss neodymium magnet (LR-NP).

## Results and discussion

FTIR spectroscopic mapping revealed the presence of oxygenated functionalities, such as hydroxyl and carboxyl groups, which are fundamental constituents of the lettuce root lignocellulosic matrix and act as anchoring sites for the drug. Upon synthesis of the bionanocomposite (LR-NP), a variation in the amplitude of specific bands was observed, signaling the interaction between the organic support and the magnetite nanoparticles. The effectiveness of the magnetization was further corroborated by Fe-O vibration signals and X-ray diffraction (XRD) patterns. SEM micrographs exhibited a rough and heterogeneous morphology, with metallic clusters dispersed on the biomass surface, while EDS elemental analysis ratified the incorporation of iron into the final structure.

Regarding the operational parameters, the influence of pH was monitored between 6 and 10. The best adsorptive performance occurred at pH 7, favoring the attraction mechanism between the material's surface and the atenolol (ATL) molecules. Kinetic monitoring indicated that the system reaches thermodynamic equilibrium within 30 minutes. Furthermore, the pseudo-second-order model provided the best fit to the experimental data, indicating that the adsorption process is predominantly governed by chemisorption.



**Figure 1.** Adsorption studies of ATL using LR and LR-NP: (A) effect of adsorbent dose (10–50 mg), (B) effect of solution pH (6–10), and (C) effect of contact time (5–90 min) employing 10 mg/L ATL solution ( $n = 3$ ); (D) FTIR spectra of LR, LR-NP, and NP before and after ATL adsorption, and (E) SEM micrographs of LR, LR-NP, and NP surfaces at 1000 $\times$  magnification.

The maximum adsorption capacity ( $SC_{exp}$ ) found for the *in natura* biomass (LR) and the nanomodified material (LR-NP) was  $83.06 \pm 3.69$  and  $61.78 \pm 2.95$  mg/g, respectively. The slight reduction in  $SC_{exp}$  observed for LR-NP is commonly attributed to the partial occupation of the material's binding sites; however, this drawback is offset by the advantage of the easier adsorbent separation from the medium.

Furthermore, experiments conducted with real water samples demonstrated the robustness of both materials, although the presence of natural constituents may lead to moderate competition for active sites. Overall, these findings highlight lettuce roots, particularly in their magnetic form, as an efficient, low-cost, and sustainable alternative for the removal of pharmaceutical contaminants from water.

### Conclusion

The results demonstrate that lettuce root-based materials, particularly the magnetic bionanocomposite (LR-NP), represent a sustainable and efficient strategy for atenolol removal from aqueous matrices. The high adsorption capacity, rapid equilibrium, and good performance at neutral pH highlight their applicability in water treatment. Although magnetic modification slightly reduced adsorption capacity, it enabled fast and clean separation, improving operational feasibility. Overall, the valorization of agricultural residues into functional adsorbents supports waste minimization, circular economy principles, and the development of low-cost technologies to mitigate pharmaceutical contamination in aquatic environments.

### Acknowledgments

Authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Grant#144531/2024-0), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Grant#88887940746/2024-00), and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Grant#2022/08358-0), for the financial support provided.

### References

- Godoy AA, Kummrow F, Pamplin PAZ. Occurrence, ecotoxicological effects and risk assessment of antihypertensive pharmaceutical residues in the aquatic environment-a review. *Chemosphere*, 138, 281-291, 2015.
- Khasawneh O, Palaniandy P. Occurrence and removal of pharmaceuticals in wastewater treatment plants. *Process Saf Environ Prot*, 150, 532-556, 2021.
- Soares BC, Abilio TE, José JC, Labuto G, Carrilho ENVM. Removal of Cr(VI) from water by *in natura* and magnetic nanomodified hydroponic lettuce roots. *Environ Sci Pollut Res*, 30(4), 8822–8834, 2023.
- Qu Y, Qin L, Liu X, Yang Y. Magnetic Fe<sub>3</sub>O<sub>4</sub>/ZIF-8 composite as an effective and recyclable adsorbent for phenol adsorption from wastewater. *Separation Purif Technol*, 294, 121169, 2022.