DOI: http://doi.org/10.21698/simi.2026.ab44

FROM NATURAL POLYMERS TO MAGNETIC FUNCTIONAL MATERIALS: SUSTAINABLE SOLUTIONS FOR WATER AND WASTEWATER TREATMENT

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Keywords: *adsorption, agro-waste, circularity, magnetic bio-composites, natural polymers*

Introduction

The development of more resource-efficient water-treatment technologies increasingly requires a shift from conventional materials towards sorbents derived from renewable and secondary biomass resources. Beyond pollutant removal, the material itself becomes an important component of the sustainability profile of the treatment process, particularly in terms of resource origin, processing requirements, separation, and potential reuse. This has stimulated growing interest in bio-based sorbents whose chemical functionality can be combined with appropriate structural and recovery properties.

Naturally occurring polysaccharides provide versatile platforms for this purpose due to their abundance, renewable origin, and chemically functional backbones. Chitosan (CS), a polycation obtained by deacetylation of chitin, and sodium carboxymethyl cellulose (CMC), a cellulose-derived polyanion bearing carboxyl groups, offer complementary surface chemistries for pollutant interactions. However, their application as sorbents requires the transformation of soluble or poorly stable polymeric matrices into architectures that combine sufficient structural integrity with accessible binding sites and efficient separation from the aqueous phase. Crosslinking and incorporation of magnetic spinel ferrites provide a route to tailor these properties while introducing magnetic recovery as an additional material function.

A fundamentally different strategy is to use agricultural residues directly rather than converting biomass into a purified polymeric material. Walnut and pistachio shells, for example, contain lignocellulosic components and surface functionalities that can be exploited for pollutant uptake following relatively simple processing. In this case, the circularity potential derives primarily from direct biomass valorization and reduced material transformation, rather than from engineered recovery.

In this context, this work compares two complementary routes for the development of bio-based sorbents for the removal of organic pollutants from contaminated waters: (i) engineering chitosan- and cellulose-derived matrices into magnetic particles and macrospheres with tailored adsorption and recovery characteristics, and (ii) direct valorization of walnut and pistachio shell residues as non-magnetic lignocellulosic biosorbents. The comparison highlights how material origin, structural engineering, and recovery strategy can be combined differently to support more resource-efficient approaches to water treatment.

Materials and methods

Three magnetic polysaccharide-based systems were investigated: (i) chitosan microparticles covalently crosslinked with epichlorohydrin (CS-ECH) and containing cobalt-based spinel ferrite; (ii) porous chitosan macrospheres ionically crosslinked with sodium tripolyphosphate (CS-TPP) and containing nickel-based spinel ferrite; and (iii) CMC macrospheres obtained by Fe^{3+}-mediated ionic crosslinking and containing manganese-based spinel ferrite.

In parallel, walnut and pistachio shells were mechanically processed into granular biosorbents and, where appropriate, mildly surface-modified. The materials were characterized by FTIR, XRD, SEM/EDX, VSM, and surface-area analysis. Adsorption performance was evaluated using representative organic dyes, while magnetic recovery was assessed for the magnetic systems. Molecular modelling was additionally used to investigate selected pollutant–sorbent interactions.

Results and conclusions

The magnetic bio-composite systems exhibited high adsorption capacities towards anionic and/or cationic dyes, depending on the polymer chemistry and crosslinking strategy. The covalently crosslinked CS-ECH particles showed high adsorption performance towards anionic dyes, whereas the ionically crosslinked CS-TPP macrospheres exhibited adsorption activity towards both anionic and cationic dyes. The CMC-based macrospheres, owing to their polyanionic character, were particularly suitable for cationic dyes. All magnetic systems could be readily recovered from aqueous media, with the macrosphere architectures providing particularly convenient magnetic solid–liquid separation and potential for reuse.

The **agro-waste sorbents** followed a different circularity strategy. Walnut and pistachio shells retained their native lignocellulosic structure and were used after mechanical processing and mild surface modification. Their main sustainability advantage therefore derives from the direct valorization of secondary biomass and reduced material-processing requirements, rather than from magnetic recovery.

Overall, the study demonstrates that circularity in water treatment can be pursued through different material-design strategies: *recovery-oriented engineering of natural-based polymers* or *direct valorization of agricultural waste*. By combining different approaches to material design, pollutant affinity, processing, and recovery, these strategies provide complementary solutions for the development of bio-based sorbents for water and wastewater treatment.

Acknowledgement

The authors gratefully acknowledge the financial support provided by the Ministry of Research, Innovation and Digitization through CNCS-UEFISCDI, project PN-IV-P2-2.1-TE-2023-1830, within PNCDI III, and by the European Union through the Horizon Europe Research and Innovation Programme, under the Talent Pass Project, Grant Agreement No. 101217448 – HORIZON-WIDERA-2024-TALENTS-03.