Adsorption of Sulfamethoxazole Using a Magnetic Molecularly Imprinted Polymer (MMIP)

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Introduction

The presence of antibiotics in wastewater has become a major environmental issue due to their persistence, low biodegradability, and contribution to the development of antimicrobial resistance. Among these compounds, sulfamethoxazole (SMX), a member of the sulfonamide group, is frequently detected in domestic, hospital, and industrial effluents, as conventional water treatment systems are inefficient at removing it. The continuous presence of this drug in aquatic environments poses risks to ecosystems and public health by promoting the spread of bacterial resistance genes.

Various technologies have been investigated for the removal of emerging contaminants, including advanced oxidation processes, filtration membranes, bioremediation, and adsorption. Among these alternatives, molecularly imprinted polymers (MIPs) are attractive because their template-derived cavities can provide enhanced affinity toward target molecules. However, recovering these materials after the adsorption process remains an operational limitation. Incorporating magnetic nanoparticles enables the production of magnetic molecularly imprinted polymers (MMIPs), thereby combining enhanced affinity for the template molecule with rapid magnetic separation and convenient adsorbent recovery.

In this study, a core–shell MMIP was developed for the adsorption of sulfamethoxazole from aqueous solutions. The material's performance was evaluated using various physicochemical characterization techniques and subsequently tested in adsorption studies.

Materials & Methods

Magnetite (Fe_3O_4) nanoparticles were synthesized via the polyol method and subsequently coated with silica using the sol-gel process with tetraethyl orthosilicate (TEOS). The particles were then functionalized with 3-methacryloxypropyltrimethoxysilane (MPS), enabling the anchoring of the polymer layer. Polymerization was carried out using acrylic acid (AA) as the functional monomer, ethylene glycol dimethacrylate (EGDMA) as the cross-linking agent, 4,4′-azobis(4-cyanovaleric acid) (ACVA) as the radical initiator, and sulfamethoxazole as the template molecule, yielding the magnetic molecularly imprinted polymer (MMIP). A magnetic non-imprinted polymer (MNIP) was prepared under the same conditions but without the template molecule.

The resulting materials were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area analysis (BET), vibrating sample magnetometry (VSM), and UV-Vis spectroscopy. Subsequently, adsorption assays were conducted to evaluate the effects of pH, contact time, adsorbent mass, and initial analyte concentration.

Results and Discussion

Fourier-transform infrared spectroscopy confirmed the successful silica coating and surface functionalization of the magnetite nanoparticles. The spectra showed characteristic bands associated with Fe–O bonds, Si–O–Si groups, and organic moieties introduced by 3-methacryloxypropyltrimethoxysilane. X-ray diffraction patterns indicated that the crystalline structure of magnetite was preserved throughout the coating, functionalization, and polymerization stages.

Scanning electron microscopy revealed approximately spherical particles with a relatively uniform morphology. Brunauer–Emmett–Teller analysis showed that the magnetic molecularly imprinted polymer (MMIP) had a higher specific surface area than the magnetic non-imprinted polymer (MNIP), with values of 174.73 and 122.49 $m^2\ g^{-1}$, respectively. This greater surface area (Table 1) may improve the accessibility of the binding sites formed during the molecular imprinting process. Vibrating sample magnetometry confirmed the superparamagnetic behavior of the synthesized material, enabling its rapid recovery from aqueous media using an external magnetic field.

Table 1

Textural properties of the Fe_3O_4-based intermediates, MMIP, and MNIP obtained from N_2 adsorption–desorption analysis.

Sample	BET specific surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Mesopore surface area (m^2 g^{-1})	Micropore surface area (m^2 g^{-1})
Fe_3O_4 - NPs	35.96	0.000257	35	0.96
Fe_3O_4@SiO_2	17.15	0.000711	15.61	1.54
Fe_3O_4@SiO_2 - MPS	8.38	0.000957	7.95	0.43
MMIP	174.73	0.006996	160.19	14.54
MNIP	122.49	0.007687	107.19	15.30

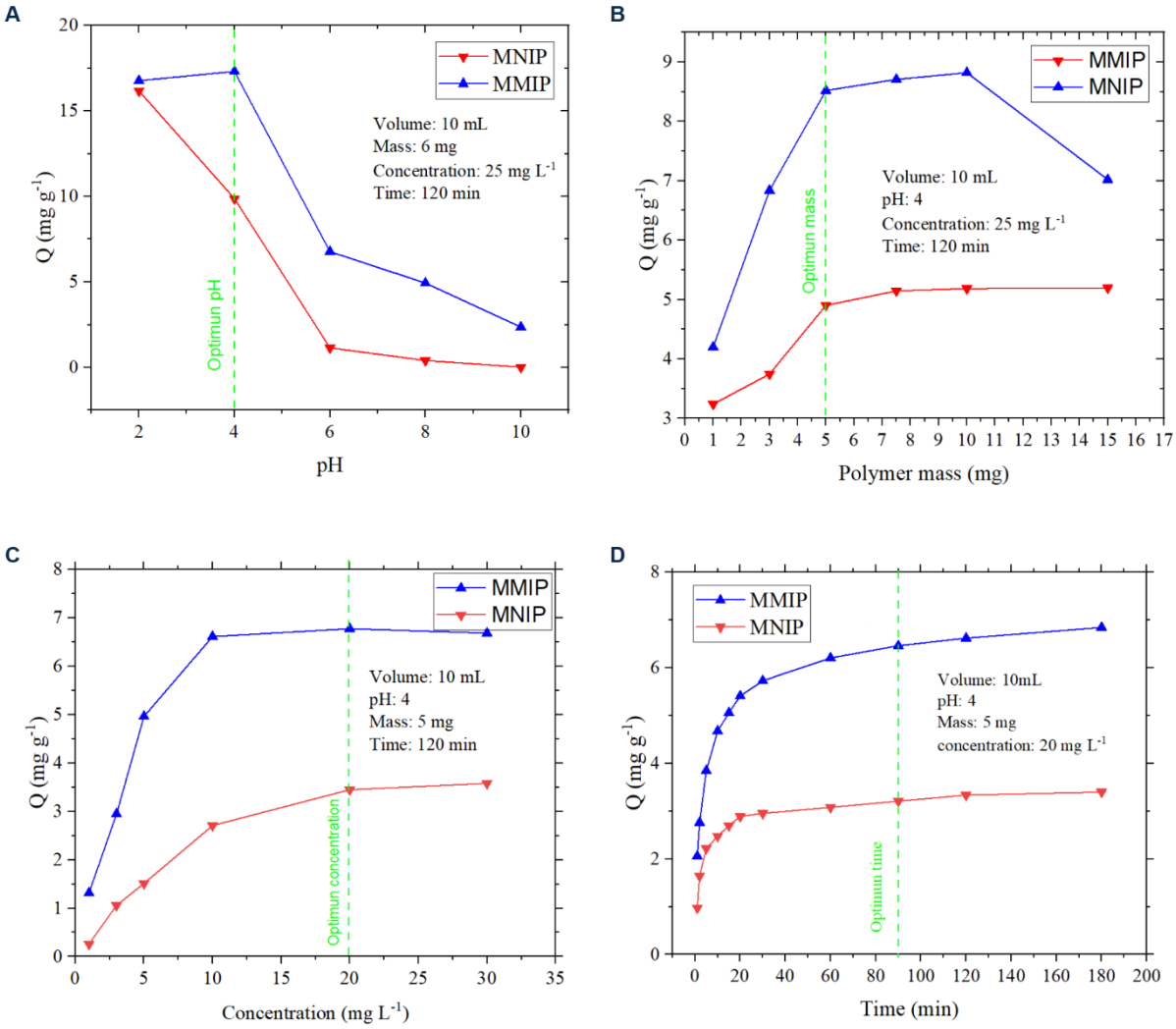
Sulfamethoxazole (SMX) adsorption was strongly influenced by solution pH, with the highest adsorption capacity observed at pH 4. The decrease in adsorption at higher pH values was attributed to changes in the ionization states of SMX and the functional groups within the polymer matrix.

An adsorbent mass of 5 mg was selected as the practical optimum because it provided a high adsorption capacity and maintained a pronounced difference between the MMIP and MNIP responses. Increasing the adsorbent mass to approximately 10 mg resulted in only a marginal improvement in the MMIP adsorption capacity and did not increase the difference between the imprinted and non-imprinted materials, despite doubling the amount of adsorbent used.

The adsorption capacity increased with the initial SMX concentration and approached a plateau at 20 mg L^{-1}. Under the selected conditions of pH 4, an adsorbent mass of 5 mg, and an initial SMX concentration of 20 mg L^{-1}, adsorption equilibrium was considered to be reached after approximately 90 min. Beyond this time, only a slight increase in adsorption capacity was observed. The MMIP reached an experimental equilibrium adsorption capacity of 6.46 mg g^{-1}, whereas the MNIP reached 3.45 mg g^{-1}. Thus, the MMIP exhibited an adsorption capacity approximately 1.87 times that of the MNIP, supporting a pronounced molecular imprinting effect.

Figure 1

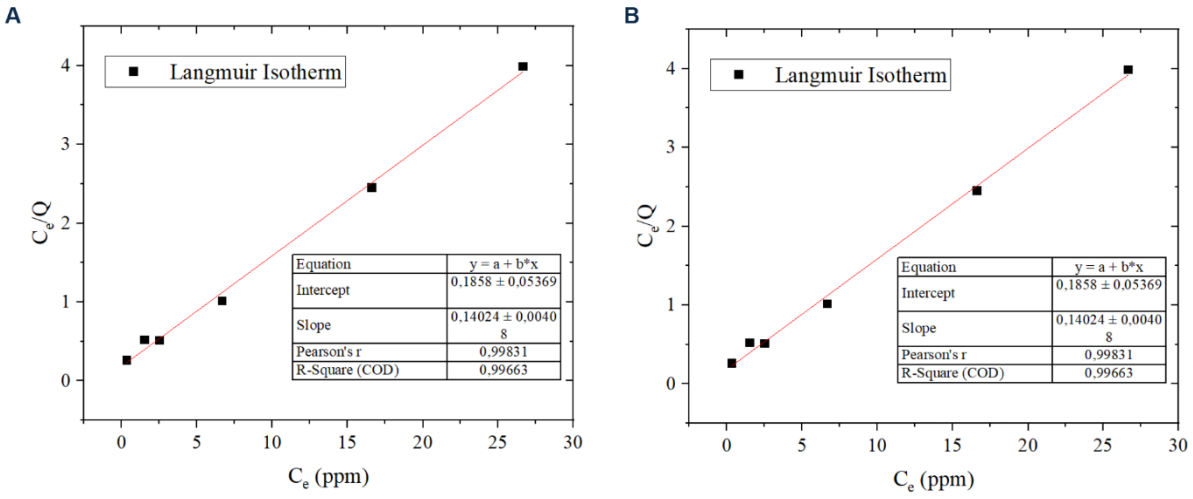
Effect of (A) solution pH, (B) adsorbent mass, (C) initial SMX concentration and (D) contact time on SMX adsorption by the MMIP and MNIP.



The equilibrium data were better described by the Langmuir model than by the Freundlich model, with coefficients of determination of 0.9966 and 0.8585, respectively. Based on the linearized Langmuir equation, the maximum adsorption capacity (q_{max}) was estimated as 7.13 mg g^{-1}, and the Langmuir affinity constant (K_L) was 0.755 L mg^{-1}. The better fit to the Langmuir model suggests predominantly monolayer adsorption at relatively homogeneous binding sites.

Figure 2

Linearized Langmuir and Freundlich isotherm models for SMX adsorption onto the MMIP.



Conclusions

A core–shell magnetic molecularly imprinted polymer was successfully synthesized for the adsorption of sulfamethoxazole from aqueous media. Spectroscopic, structural, morphological, textural, and magnetic characterization confirmed the successful functionalization of the magnetite nanoparticles, preservation of the Fe_3O_4 crystalline phase, formation of the polymer layer, and superparamagnetic behavior of the resulting material. The MMIP exhibited a higher BET specific surface area than the MNIP, with values of 174.73 and 122.49 $m^2\ g^{-1}$, respectively.

Adsorption optimization identified pH 4, an adsorbent mass of 5 mg, an initial SMX concentration of 20 mg L^{-1}, and a contact time of approximately 90 min as the selected experimental conditions. Under these conditions, the MMIP reached an experimental equilibrium adsorption capacity of 6.46 mg g^{-1}, compared with 3.45 mg g^{-1} for the MNIP. The MMIP adsorption capacity was approximately 1.87 times that of the MNIP, supporting a pronounced molecular imprinting effect.

The equilibrium data were better described by the Langmuir model ($R^2 = 0.9966$) than by the Freundlich model ($R^2 = 0.8585$). The Langmuir maximum adsorption capacity was estimated as 7.13 mg g^{-1}, with an affinity constant of 0.755 L mg^{-1}, suggesting predominantly monolayer adsorption at relatively homogeneous binding sites. In addition, the

superparamagnetic behavior of the MMIP enabled its rapid separation from the aqueous phase using an external magnetic field. These results indicate that the developed MMIP is a promising magnetically recoverable adsorbent for SMX removal. Competitive adsorption, regeneration, reuse, and real-sample studies should be conducted to further evaluate its selectivity and practical applicability.

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References

DE PAULA LUCAS, L.; HEILMANN, E. S.; BOCARDI, J. M. B.; COSTA, I. L., Evaluation of the TiO_2@SiO_2 Composite for the Removal of the Antibiotic Sulfamethoxazole in Aqueous Media Through Adsorption and Heterogeneous Photocatalysis Processes. **Revista de gestão social e ambiental**, 19(3), e011683, 2025

EALIAS, A. M.; MEDA, G.; TANZIL, K. Recent Progress in Sustainable Treatment Technologies for the Removal of Emerging Contaminants from Wastewater: A Review on Occurrence, Global Status and Impact on Biota. **Reviews of environmental contamination and toxicology**, 262(1), 2024

GKIKA, D. A.; TOLKOU, A. K.; LAMBROPOULOU, D. A.; BIKIARIS, D. N.; KOKKINOS, P.; KALAVROUZIOTIS, I. K.; KYZAS, G. Z. Application of molecularly imprinted polymers (MIPs) as environmental separation tools. **RSC Applied Polymers**, 2(2), 127–148, 2023

HUANG, W.; SI, H.; QING, Y.; ZHANG, L.; ZHANG, W.; SONG, F.; NI, X.; YANG, W. A Magnetic, Core–Shell Structured, pH-Responsive Molecularly Imprinted Polymers for the Selective Detection of Sulfamethoxazole. **Journal of inorganic and organometallic polymers and materials**, 31(5), 2054–2062, 2021

LÓPEZ, R.; KHAN, S.; WONG, A.; SOTOMAYOR, MDPT.; PICASSO, G. Development of a New Electrochemical Sensor Based on Mag-MIP Selective Toward Amoxicillin in Different Samples. **Frontiers in Chemistry**, 9, 2021