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ADVANCES IN MOLECULARLY IMPRINTED POLYMERS FOR SELECTIVE CHEMICAL SENSING

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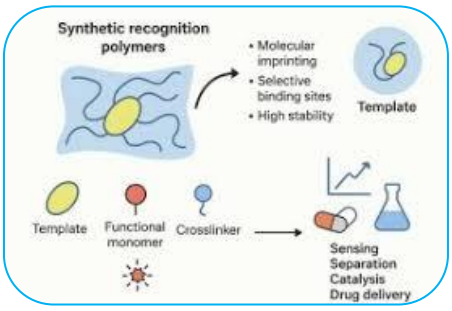
ABSTRACT:



Molecularly Imprinted Polymers (MIPs) represent a class of tailor‑made synthetic materials engineered with specific recognition sites complementary in shape, size, and functional group orientation to target analytes. Over recent years, significant advancements in MIP design, synthesis strategies, and signal transduction mechanisms have markedly enhanced their performance in selective chemical sensing applications. The integration of novel functional monomers, controlled polymerization techniques, and nanostructured templates has led to improved binding affinities, higher imprinting efficiencies, and faster response times. Additionally, coupling MIPs with diverse transducers—including electrochemical, optical, and mass‑sensitive platforms—has enabled highly selective, sensitive, and robust sensing systems capable of detecting a wide range of target compounds in complex environments. Recent research has focused on addressing traditional limitations of MIPs, such as heterogeneous binding site distribution and limited mass transfer, through innovations like surface imprinting, core–shell architectures, and computational design of monomer–template interactions. These developments have expanded the applicability of MIPs in environmental monitoring, biomedical diagnostics, food safety, and industrial process control. Furthermore, advancements in integrated sensing devices and real‑time monitoring systems have demonstrated the practical potential of MIPs for on‑site, rapid, and cost‑effective analysis. This review summarizes the latest progress in MIP technology for selective chemical sensing, highlighting key synthesis methodologies, transducer integration strategies, performance evaluation metrics, and emerging applications. The discussion emphasizes the future prospects of MIP‑based sensors, including multifunctional and adaptive recognition systems driven by advances in materials science and engineering.

KEYWORDS : *Molecularly Imprinted Polymers (MIPs); Selective chemical sensing; Functional monomers; Template recognition; Surface imprinting; Core–shell polymers.*

INTRODUCTION:

Molecularly Imprinted Polymers (MIPs) are synthetic polymers engineered with specific recognition sites that are complementary in shape, size, and chemical functionality to a target molecule or class of molecules. This “molecular memory” is created by polymerizing functional monomers in the presence of a template molecule, followed by removal of the template to leave behind cavities capable

of selective binding. MIPs combine the robustness and chemical stability of synthetic polymers with the high selectivity traditionally associated with biological receptors, such as antibodies or enzymes, making them highly attractive for chemical sensing applications. Over the past decades, significant advancements in MIP synthesis, functionalization, and integration with transducer technologies have dramatically expanded their utility in selective chemical sensing. Modern approaches, including surface imprinting, nanoimprinting, and computational design of monomer-template interactions, have addressed key limitations of conventional bulk MIPs, such as slow mass transfer, heterogeneous binding site distribution, and limited accessibility of recognition sites. These improvements have led to higher imprinting efficiency, faster binding kinetics, and enhanced sensitivity and selectivity. MIPs can be coupled with a variety of transduction mechanisms to convert selective molecular recognition into measurable signals. Electrochemical, optical, and mass-sensitive transducers are commonly employed, enabling MIP-based sensors to detect a wide range of analytes—including small molecules, ions, proteins, and environmental pollutants—in complex sample matrices. The combination of MIP selectivity with the versatility of modern transducers has facilitated the development of portable, real-time, and cost-effective sensing devices suitable for applications in environmental monitoring, food safety, medical diagnostics, and industrial process control.

Recent research has also emphasized the integration of nanomaterials, such as nanoparticles, nanotubes, and graphene derivatives, into MIP matrices to improve surface area, binding site accessibility, and signal amplification. These innovations have enhanced sensor performance, particularly in trace detection, and have paved the way for multifunctional and adaptive MIP-based sensing platforms. Overall, the continuous evolution of MIP technology highlights its potential as a robust, selective, and versatile platform for chemical sensing, bridging the gap between synthetic materials and biomimetic recognition systems, and offering promising solutions for real-world analytical challenges.

AIMS AND OBJECTIVES

Aim

The primary aim of this study is to explore recent advancements in molecularly imprinted polymers (MIPs) for selective chemical sensing, focusing on improvements in polymer design, synthesis strategies, and integration with sensing platforms to achieve high sensitivity, selectivity, and practical applicability.

Objectives

1. To examine the latest methodologies in MIP synthesis, including bulk polymerization, surface imprinting, nanoimprinting, and core–shell approaches, and their impact on binding site accessibility, imprinting efficiency, and sensor performance.
2. To investigate the role of functional monomers, crosslinkers, and template molecules in achieving selective recognition of target analytes.
3. To evaluate the integration of MIPs with diverse transduction techniques, including electrochemical, optical, and mass-sensitive sensors, and their effect on signal generation, sensitivity, and detection limits.
4. To analyze strategies for enhancing sensor performance, such as the incorporation of nanomaterials, optimization of polymer morphology, and computational design of monomer-template interactions.
5. To assess the application of MIP-based sensors in real-world scenarios, including environmental monitoring, food safety, biomedical diagnostics, and industrial process control.

REVIEW OF LITERATURE

Molecularly imprinted polymers (MIPs) have evolved substantially since their inception in the 1970s as synthetic recognition materials capable of mimicking the selectivity of biological receptors while offering greater chemical robustness and stability. Early work by Wulff and Mosbach laid the foundation for MIP synthesis, demonstrating that functional monomers could be polymerized in the

presence of a template molecule to create specific binding sites upon template removal. Initial applications focused on chromatographic separation and solid-phase extraction, but over time, the field expanded into sensing due to the potential for translating selective binding into measurable analytical signals. Conventional bulk MIPs were traditionally synthesized through free-radical polymerization, resulting in heterogeneous materials with binding sites distributed throughout the polymer matrix. Although these materials demonstrated selectivity, limitations such as slow binding kinetics, poor accessibility of recognition sites, and incomplete template removal motivated the development of alternative imprinting strategies. Surface imprinting and core–shell approaches emerged to address these challenges, enabling the creation of binding sites predominately on or near the polymer surface. This shift improved mass transfer and recognition site accessibility, significantly enhancing sensor response times and sensitivity. Recent advances have also capitalized on nanoscale materials and controlled polymerization techniques. Incorporation of nanoparticles, magnetic cores, and carbon-based nanostructures into MIP matrices has been shown to increase effective surface area and facilitate signal transduction. For example, magnetic molecularly imprinted polymers (MMIPs) enable rapid separation and preconcentration of target analytes, while conductive nanomaterials such as graphene and carbon nanotubes improve electron transfer in electrochemical sensing platforms. The development of solid-phase imprinting and the use of living/controlled radical polymerization methods, such as atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT), have provided greater control over polymer architecture and binding site uniformity.

The integration of MIPs with various transducers represents a major focus in recent literature. Electrochemical MIP sensors utilize changes in current, potential, or impedance upon target binding, achieving high sensitivity for small molecule detection in complex matrices. Optical MIP sensors based on fluorescence, surface plasmon resonance (SPR), and colorimetric responses have demonstrated real-time, label-free detection capabilities. Mass-sensitive platforms, such as quartz crystal microbalance (QCM) and microcantilevers, exploit changes in mass upon target binding for highly sensitive detection across diverse analyte classes. Computational design and molecular modeling have further refined MIP development by enabling in silico prediction of optimal monomer–template interactions, reducing experimental trial-and-error. Quantitative structure–activity relationship (QSAR) and density functional theory (DFT) studies assist in selecting monomers and optimizing imprinting conditions, enhancing specificity and binding affinity. Applications of MIP-based sensors have expanded to environmental monitoring (e.g., detection of pesticides, heavy metals, and organic pollutants), biomedical diagnostics (e.g., biomarkers, drugs, and disease indicators), food safety (e.g., contaminants, toxins, and additives), and industrial process control. Real-world implementation has been enhanced by miniaturization, integration with microfluidic systems, and development of portable sensing devices suitable for on-site analysis. Despite these advancements, challenges remain, including the need for improved selectivity in complex biological matrices, scalability of fabrication methods, and standardization of performance evaluation metrics. Nevertheless, the convergence of materials science, nanotechnology, and analytical chemistry continues to drive innovation in MIP-based selective chemical sensing, pushing toward multifunctional and adaptive recognition systems capable of meeting the demands of modern analytical applications.

RESEARCH METHODOLOGY

The research methodology for studying molecularly imprinted polymers (MIPs) in selective chemical sensing involves a comprehensive approach that integrates polymer design, synthesis, characterization, and performance evaluation. The process begins with the careful selection of a target analyte or template molecule along with appropriate functional monomers capable of forming stable non-covalent interactions such as hydrogen bonding, electrostatic interactions, and van der Waals forces. Computational modeling, including molecular docking and density functional theory (DFT), is often utilized to predict the optimal monomer–template interactions, ensuring high specificity and

binding affinity. Crosslinkers are chosen to provide structural rigidity while maintaining accessibility to the recognition sites, and the overall polymer architecture is tailored according to the desired sensor application. Polymer synthesis can be performed using conventional bulk polymerization or more advanced strategies such as surface imprinting, nanoimprinting, and core–shell polymerization. These approaches enhance the accessibility of binding sites and improve mass transfer kinetics. Controlled radical polymerization techniques, including atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT), are employed to regulate polymer chain growth and generate uniform binding cavities. Incorporation of nanomaterials, such as magnetic nanoparticles, graphene, or carbon nanotubes, within the polymer matrix further enhances surface area, facilitates electron transfer, and improves sensor performance in electrochemical or optical applications. Following polymerization, the template molecule is removed through solvent extraction, chemical degradation, or other appropriate techniques, leaving behind cavities complementary to the target analyte. Post-synthesis functionalization may be performed to improve affinity, selectivity, or compatibility with the chosen transducer. The polymers are then integrated with transducers that convert selective binding events into measurable signals. Electrochemical transducers detect changes in current, potential, or impedance, optical transducers monitor changes in absorbance, fluorescence, or refractive index, and mass-sensitive devices such as quartz crystal microbalance (QCM) or microcantilever sensors measure changes in mass or mechanical properties.

Characterization of MIPs is performed using techniques such as Fourier-transform infrared (FTIR) and Raman spectroscopy to verify functional group incorporation and monomer-template interactions, while scanning and transmission electron microscopy (SEM, TEM) provide information on morphology and nanoscale structure. Surface area and porosity are measured using Brunauer–Emmett–Teller (BET) analysis. The binding performance is evaluated through adsorption isotherms, selectivity tests against structural analogues, and kinetics studies to determine binding affinity, capacity, and response time. Sensor performance is assessed under controlled conditions and in real sample matrices, measuring parameters such as sensitivity, limit of detection, selectivity, reproducibility, and operational stability. Data obtained from these experiments are analyzed using statistical methods and binding models to establish correlations between polymer design features, monomer-template interactions, and transducer responses. Multivariate analysis and computational modeling support the prediction of sensor behavior and guide iterative improvements in polymer synthesis and device fabrication. This integrated methodology enables the rational development of MIP-based sensors that are highly selective, sensitive, and robust, suitable for applications in environmental monitoring, biomedical diagnostics, food safety, and industrial process control.

STATEMENT OF THE PROBLEM

Molecularly imprinted polymers (MIPs) have emerged as promising synthetic recognition materials due to their ability to selectively bind target molecules with high specificity and stability. Despite their potential, conventional MIPs face challenges such as heterogeneous distribution of binding sites, slow mass transfer, incomplete template removal, and limited accessibility of recognition cavities, which can reduce sensitivity, response time, and selectivity in chemical sensing applications. Furthermore, integrating MIPs with transducer platforms in a reproducible and scalable manner remains a significant challenge, particularly when detecting low-concentration analytes in complex matrices such as biological fluids, environmental samples, or industrial mixtures. The core problem lies in the need for optimized MIP design and synthesis strategies that ensure uniform, accessible binding sites while maintaining robust chemical and mechanical stability. Additionally, there is a demand for effective coupling of MIPs with diverse sensing platforms—electrochemical, optical, or mass-sensitive—to achieve reliable, real-time detection with high sensitivity and selectivity. Addressing these limitations requires a comprehensive understanding of polymer-template interactions, polymer morphology, and transducer integration, as well as innovative approaches such as surface imprinting, nanostructuring, and computationally guided monomer selection. Therefore, the primary problem is to develop advanced MIP-based sensors that overcome the inherent limitations of traditional MIPs,

achieving rapid, selective, and sensitive detection of target analytes in practical real-world applications, while providing a reproducible and scalable fabrication methodology.

DISCUSSION

Molecularly imprinted polymers (MIPs) have undergone significant evolution in recent years, with advances in design, synthesis, and integration strategies markedly enhancing their performance as selective chemical sensors. Traditional bulk MIPs, while demonstrating selectivity for target molecules, often suffered from heterogeneous binding site distribution, slow analyte diffusion, and limited accessibility to recognition sites. The development of surface imprinting and nanoimprinting techniques has addressed many of these limitations by creating recognition cavities predominantly on the polymer surface, improving mass transfer, response time, and binding efficiency. Core–shell architectures further allow for precise control of polymer thickness and porosity, providing enhanced binding site accessibility and better reproducibility. In addition to structural innovations, the choice of functional monomers and crosslinkers has a critical impact on MIP selectivity and affinity. Computational modeling and molecular docking studies have enabled the rational selection of monomers, predicting optimal template–monomer interactions and reducing trial-and-error experimentation. This has resulted in MIPs with higher imprinting efficiency, more uniform binding sites, and stronger target-specific interactions. Incorporation of nanomaterials, such as graphene, carbon nanotubes, and magnetic nanoparticles, has further enhanced sensor performance by increasing surface area, facilitating electron transfer in electrochemical sensors, and enabling rapid target preconcentration or separation. Integration with transducer technologies has been a major factor in the success of MIP-based sensors. Electrochemical sensors benefit from the conductive properties of nanomaterial-enhanced MIPs, allowing rapid and sensitive detection of analytes via current, potential, or impedance changes. Optical sensors, including fluorescence, colorimetric, and surface plasmon resonance (SPR) systems, provide label-free detection with high specificity, translating molecular recognition into measurable optical signals. Mass-sensitive devices, such as quartz crystal microbalances (QCM), detect subtle changes in polymer mass upon analyte binding, enabling real-time monitoring.

Recent studies have also highlighted strategies to overcome the challenges of complex sample matrices. Surface-imprinted MIPs and magnetic MIPs (MMIPs) facilitate selective recognition in environmental, biomedical, and food samples by reducing interference and improving analyte accessibility. Computationally guided design of MIPs ensures higher selectivity even in the presence of structurally similar compounds. Furthermore, integration into microfluidic platforms and portable devices has demonstrated the potential of MIP-based sensors for on-site, real-time analysis. Despite these advances, challenges remain in scaling up fabrication, standardizing performance evaluation, and achieving multifunctional MIP systems capable of simultaneous detection of multiple analytes. Nonetheless, the combination of advanced polymer synthesis, nanostructuring, computational design, and transducer integration has significantly improved the sensitivity, selectivity, and practical applicability of MIP-based sensors. These developments position MIPs as versatile and robust platforms for selective chemical sensing in a wide range of applications, including environmental monitoring, food safety, biomedical diagnostics, and industrial process control.

CONCLUSION

Molecularly imprinted polymers (MIPs) have demonstrated remarkable progress as highly selective and robust recognition materials for chemical sensing applications. Advances in polymer design, including surface imprinting, nanoimprinting, and core–shell architectures, have improved binding site accessibility, mass transfer, and response times, addressing the limitations of traditional bulk MIPs. Rational selection of functional monomers and crosslinkers, aided by computational modeling, has enhanced binding specificity and imprinting efficiency, while the incorporation of nanomaterials has further increased surface area, facilitated electron transfer, and enabled rapid analyte preconcentration. Integration of MIPs with diverse transducers—electrochemical, optical, and

mass-sensitive—has allowed effective conversion of selective molecular recognition into measurable signals, resulting in sensitive, rapid, and real-time detection of analytes in complex matrices. These innovations have expanded the applicability of MIP-based sensors to environmental monitoring, food safety, biomedical diagnostics, and industrial process control. Overall, the combination of advanced polymer synthesis, computational design, and transducer integration has established MIPs as versatile and reliable platforms for selective chemical sensing. Continued development in multifunctional and adaptive MIP systems promises to further enhance sensitivity, selectivity, and real-world applicability, supporting the creation of next-generation analytical devices capable of addressing complex sensing challenges.

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