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A Review on the Applications of Porous PolyHIPE and Molecularly Imprinted Polymeric Foams in Separation Processes

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1. ABSTRACT

This review provides a systematic analysis of two advanced material classes—porous polymer foams from high internal phase emulsions (polyHIPEs) and molecularly imprinted polymers (MIPs)—in separation science and related fields. It establishes that material performance is governed by the intrinsic synthesis-structure-property relationship. PolyHIPEs serve as robust, permeable scaffolds for applications requiring high capacity and convective flow, such as metal ion recovery, oil-water separation, and catalyst supports. MIPs provide exceptional molecular selectivity for targeted contaminant removal and controlled drug delivery. The core innovation of this review is its integrated framework highlighting the transformative potential of merging these technologies into MIP-polyHIPE hybrids. These systems combine the structural advantages of polyHIPEs with the recognition intelligence of MIPs, pointing toward next-generation smart materials for water treatment, resource recovery, and biomedical applications. Future challenges in scalable production, stability, and stimuli-responsive design are outlined.

Keywords: PolyHIPE Foam, Molecularly Imprinted Polymer, Separation, Hybrid Materials, Water Treatment.

2. INTRODUCTION

The demand for advanced porous polymers with tunable properties has grown significantly. Emulsion templating, particularly using high internal phase emulsions (HIPEs), is a prominent method for producing structured porous materials known as polyHIPEs. These foams feature interconnected porosity, high surface area, and mechanical stability, making them ideal for separation, catalysis, and absorption applications. Concurrently, molecularly imprinted polymers (MIPs) have emerged as materials with tailor-made molecular recognition sites, offering high selectivity for target molecules in complex matrices such as wastewater or biological fluids.

While significant research exists on each technology separately, a critical gap remains in systematically exploring their convergence. This review presents a unified framework arguing that combining the physical scaffold of polyHIPEs with the molecular intelligence of MIPs can yield hybrid materials with unprecedented functionality. Such integration addresses the need for materials that are not only highly permeable and robust but also selectively interactive.

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2.1 Fundamentals of Synthesis and Structure

2.2. PolyHIPEs: These materials are synthesized by polymerizing a HIPE, where the internal (dispersed) phase exceeds 74% volume, typically in a water-in-oil emulsion stabilized by surfactants (e.g., SMO, PGPR). Parameters like monomer type (commonly styrene with DVB crosslinker), surfactant concentration, internal phase ratio, and mixing conditions directly control pore size, window diameter, porosity, and mechanical strength. After polymerization and removal of the dispersed phase, a continuous open-cell network remains. Sustainable approaches like Pickering HIPEs, stabilized by solid particles (e.g., nanoparticles, protein microgels), offer greener alternatives [1].

2.3. MIPs: Synthesis involves polymerizing functional monomers and crosslinkers around a template molecule. Subsequent extraction leaves complementary cavities with "molecular memory." The choice of monomer (for interaction chemistry), crosslinker (for cavity rigidity), and porogen (for porosity) is crucial. Recent advances focus on green solvents (e.g., deep eutectic solvents) and stimuli-responsive designs [2].

3. Applications in Separation and Environmental Remediation

3.1. Metal Ion Separation and Water Purification

PolyHIPEs can be chemically functionalized to introduce ion-exchange sites (e.g., via sulfonation, amination). Their open structure enables rapid uptake of heavy metals like Cu(II), Pb(II), and Cr(VI), outperforming traditional resins in kinetics and capacity, even in complex separations such as plutonium recovery.

MIPs are designed for selective removal of specific contaminants, including pesticides, pharmaceuticals (e.g., diclofenac), and endocrine-disrupting compounds (EDCs), from water [3].

Synergy: Hybrid **MIP-polyHIPEs** merge fast convective transport with high selectivity. For example, a diclofenac-imprinted polyHIPE achieved complete pollutant removal in just 3 minutes [4].

3.2. Oil-Water Separation

PolyHIPEs can be engineered with controlled wettability. Creating superhydrophobic/superoleophilic surfaces (e.g., by incorporating Fe₃O₄ nanoparticles) allows them to selectively absorb oils and organic solvents with high capacity (up to 57 times their weight) and excellent reusability, ideal for spill remediation.

4. Applications in Catalysis

The porous, monolithic structure of polyHIPEs makes them excellent supports for heterogeneous catalysts, preventing issues like particle loss and clogging. Catalytic species can be incorporated as:

Functional groups tethered to the polymer (e.g., 4-vinylpyridine for Cu-catalyzed reactions).

Dispersed nanoparticles (e.g., Pt, Pt/Ru) stabilized within the foam. Such systems show high activity, selectivity, and stability over hundreds of cycles, with applications in fuel cells and green synthesis.

5. Applications in Controlled Drug Delivery

This domain is primarily advanced by **MIPs** due to their molecular recognition, enabling controlled release profiles.

Transdermal Delivery: MIP-based patches provide sustained release of drugs like nicotine and salicylic acid.

Oral Delivery: MIP nanoparticles enable controlled release of drugs such as risperidone.

Wound Dressings: MIPs loaded with antibiotics (e.g., vancomycin) in biopolymer matrices offer prolonged, localized release for chronic wound treatment.

Synergy Potential: PolyHIPE scaffolds could host MIP particles, creating implantable devices with combined structural support and targeted drug release.

6. Conclusion

The strategic integration of polyHIPEs and MIPs into hybrid materials represents a promising frontier for developing intelligent, multifunctional systems. Key future directions include:

Scalable and Sustainable Manufacturing: Developing cost-effective, green processes for hybrid material production.

Enhanced Stability: Improving the long-term chemical and mechanical stability of recognition sites within the porous matrix.

Stimuli-Responsive Design: Creating materials responsive to triggers like pH, temperature, or light for on-demand control over adsorption, release, or catalysis [5].

Multifunctional Integration: Designing platforms that combine separation, detection, and catalytic degradation.

In conclusion, the convergence of polyHIPE and MIP technologies holds significant potential for addressing critical challenges in environmental remediation, resource recovery, and precision medicine through the creation of efficient, selective, and smart material systems.

7. References

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