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Recent Advances in Magnetic Molecularly Imprinted Polymers for Perfluorooctanoic Acid Detection and Removal: The Critical Role of Thiol Functionality

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Perfluorooctanoic acid (PFOA), a persistent PFAS compound, has driven strict regulations and increased demand for effective detection and remediation technologies. Magnetic molecularly imprinted polymers (MMIPs) have emerged as a promising solution, particularly those incorporating thiol-containing functional groups. This review summarizes recent progress in MMIPs designed for the removal and sensing of PFOA. Molecular imprinting combined with magnetic nanoparticles enables selective recognition and facilitates simple magnetic separation. Thiol groups, including perfluorinated thiols, create fluorophilic binding sites via van der Waals and dipole–dipole interactions between fluorine-rich polymer surfaces and the PFOA tail, while also forming hydrogen bonds with the PFOA carboxyl group. Thiol monomers allow stable surface grafting, compatibility with mild polymerization, and improved structural durability during regeneration. Advances in synthesis, including core–shell architectures, novel thiol monomers, optimized polymerization, and greener fabrication methods, have increased binding capacity and selectivity. MMIP-based sensing platforms—including electrochemical, optical, and photoelectrochemical devices—now achieve detection limits from sub-parts per trillion to tens of parts per trillion. Pilot-scale water treatment studies demonstrate the effectiveness of magnetic recovery and reuse over multiple cycles. Emerging trends include dual-functional monomers, stimuli-responsive systems, and hybrid MIP–carbon materials. Remaining challenges involve scaling production, managing matrix interferences, and standardizing testing protocols.

Keywords: Perfluorooctanoic acid (PFOA), magnetic molecularly imprinted polymers (MMIPs), thiol functionality, fluorophilic interactions, electrochemical sensing, adsorption selectivity

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Perfluorooctanoic acid (PFOA) is a persistent environmental pollutant and representative long-chain PFAS, notable for its strong carbon–fluorine (C–F) bonds (~485 kJ mol^{-1}), which result in high stability and half-lives exceeding 92 years in aquatic environments. Its bioaccumulative nature and confirmed toxicity, including immunosuppression, thyroid disruption, and developmental risks, have led to mounting global concern [1, 2]. Regulatory actions have intensified over the past decade. The U.S. Environmental Protection Agency (EPA) reduced its health advisory from 70 ng L^{-1} (2016) to an enforceable maximum contaminant level (MCL) of 4 ng L^{-1} in 2024 [3, 4]. Similarly, the European Union Drinking Water Directive sets a limit of 100 ng L^{-1} for individual PFAS and a total PFAS cap of 500 ng L^{-1} by 2026. The 2019 inclusion of PFOA and its precursors in the Stockholm Convention list for global elimination, and the IARC's 2023 classification of PFOA as a Group 1 carcinogen, further underscore its global health threat [5, 6]. Despite these measures, PFOA concentrations in environmental hotspots remain exceptionally high, reaching up to 3000 times the regulatory threshold in some Chinese surface waters [7].

Although many reviews discuss general PFAS treatment, there is limited consolidation of knowledge specifically on thiol-functional magnetic molecularly imprinted polymers (MMIPs). Current literature has not clearly compared how thiol monomers influence fluorophilic binding, sensor performance, regeneration, and real-water selectivity. This represents a significant research gap that

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hinders progress toward practical, reusable PFAS-selective materials.

Evolution of PFOA Removal Technologies

Traditional approaches to PFOA remediation include adsorption using granular activated carbon (GAC) and ion-exchange (IX) resins. While GAC (50–200 mg g^{-1} capacity) and IX resins (120–150 mg g^{-1}) can achieve high removal rates under ideal conditions, they often suffer from slow kinetics, requiring more than six hours to reach equilibrium, and exhibit reduced efficiency in the presence of competing organic matter [8–10]. Membrane separation techniques and destructive methods such as advanced oxidation processes (AOPs), including photocatalysis and electrochemical degradation, have also been investigated. Although some AOPs report greater than 90% degradation efficiency [11], they are limited by high energy consumption, complex reactor designs, and the formation of short-chain PFAS byproducts that remain persistent [11, 12]. As shown in Figure 1, the PFOA molecule is progressively shortened through a series of reactive steps, ultimately yielding CO_2, HF, and shorter-chain perfluoro carboxylic acids. Despite their effectiveness, these methods often require post-treatment polishing and may not be cost-effective at scale.

These limitations have motivated a shift toward materials that offer strong molecular selectivity, faster kinetics, and easy regeneration. Molecularly imprinted polymers (MIPs), synthetic polymers engineered to exhibit antibody-like recognition toward target molecules, have emerged as a promising option [14]. Magnetic MIPs (MMIPs) integrate a magnetic nanoparticle core (typically Fe_3O_4 or γ-Fe_2O_3) with an imprinted polymer shell, enabling selective binding together with rapid magnetic separation. This approach offers several advantages, including easy recovery using external magnets, improved reusability, and practical integration into both water treatment and analytical sensing platforms [2, 14].

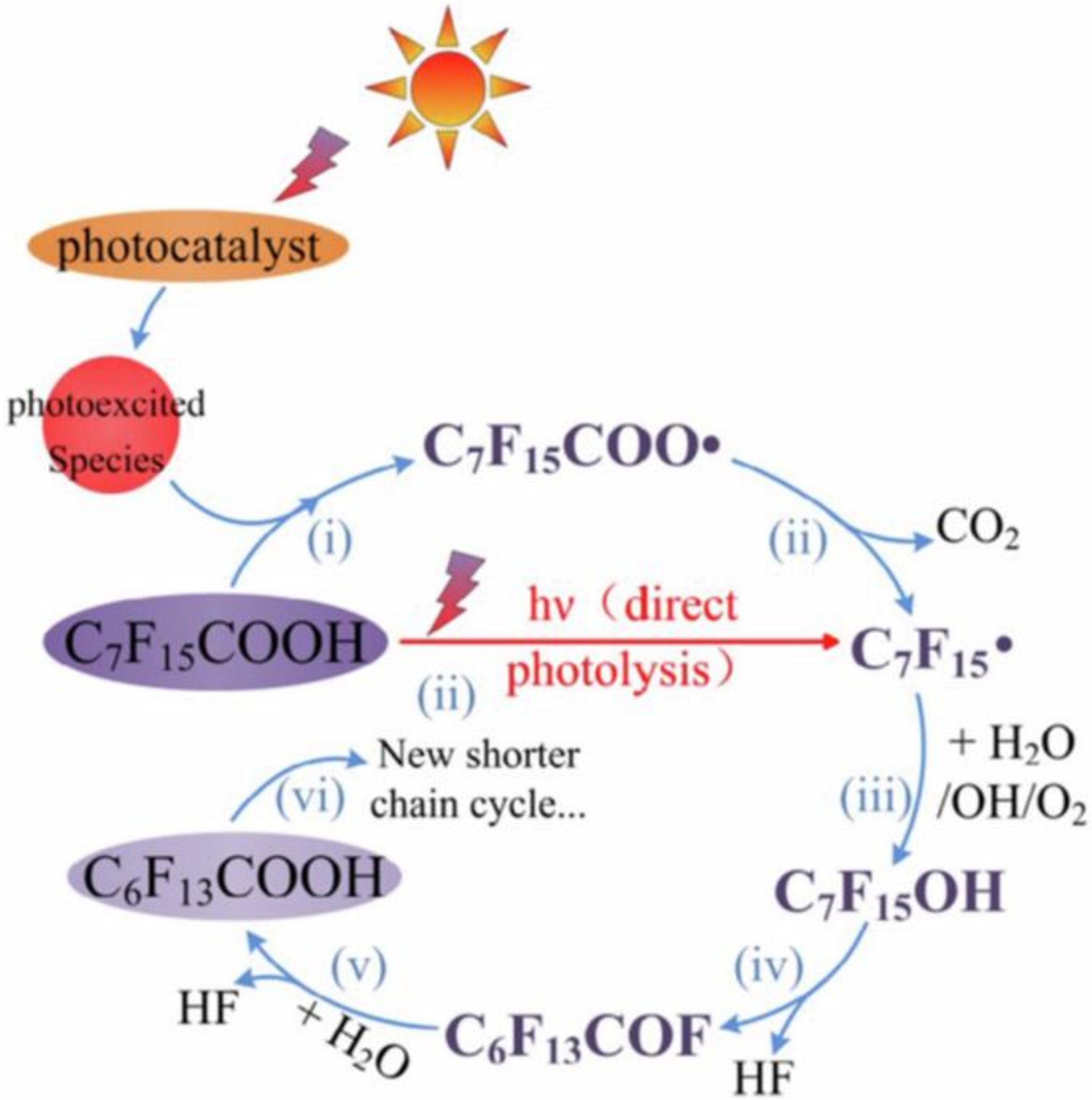

Figure 1. Concluded a common pathway for photo-oxidative degradation of PFOA. Reprinted with permission [13].

Among MMIPs, thiol-functional monomers have attracted increasing attention due to their ability to create fluorophilic binding sites through F–F interactions and form hydrogen bonds with the PFOA carboxyl group. However, despite these advantages, there is no dedicated review summarizing their synthesis strategies, performance metrics, sensing limits, or regeneration behavior. This motivates the focused scope of the present work.

To address this gap, this review focuses on thiol-based MMIPs for PFOA removal and sensing, covering literature from 2018 to 2024. The discussion includes electrochemical, optical, and photoelectrochemical sensors, batch adsorption studies, magnetic separation approaches, and pilot-scale demonstrations. Modeling-only papers, studies without thiol functionality, and non-magnetic MIPs are excluded to maintain a clear scope. The purpose of this review is to summarize synthesis strategies, explain thiol-mediated interactions, compare detection and adsorption performance, and identify current challenges and future research needs.

The Emergence of Thiol-Functionalized MMIPs

Recent innovations in MMIP design emphasize the incorporation of thiol (–SH) functionalities, which enhance molecular recognition through multiple mechanisms. Thiol groups can form Lewis acid–base interactions with PFOA's carboxylate group, while also contributing hydrophobic and fluorophilic interactions that complement the MIP's molecular imprint [15].

Empirical studies report high binding affinity ($K_d = 3.2\times10^4$ L kg^{-1}) and improved selectivity ($\alpha >$ 2.8 against humic acid) for thiol-functionalized MMIPs [16]. These groups can be introduced via monomers (thioglycolic acid), fluorinated thiols like perfluorodecanethiol (PFDT), or surface-grafted self-assembled monolayers (SAMs). In each case, the thiol moieties enhance the sorbent's interaction with PFOA while enabling stable integration with magnetic nanoparticle cores. Examples include dopamine-based polymerization strategies that form Fe_3O_4@polydopamine core–shell MMIPs, as well as silica-coated MMIPs functionalized with thiols, both of which demonstrate high selectivity, ease of regeneration, and operational feasibility [17, 18]. These developments signal a paradigm shift in the field, combining molecular precision with magnetic responsiveness for improved performance in real-world applications.

This review critically assesses the literature from 2016 to May 2025, focusing on thiol-functionalized magnetic molecularly imprinted polymers (thiol-MMIPs) for PFOA detection and removal. This study examines recognition mechanisms involving thiol groups, including hydrogen bonding, hydrophobicity, and fluorophilicity, and explores how these contribute to improved performance.

The review covers recent sensor developments based on thiol-MMIPs, with an emphasis on detection limits relevant to current regulations. In environmental remediation, laboratory and pilot-scale studies on water treatment, regeneration, and performance in complex matrices are discussed. Finally, current limitations and future directions in stimuli-responsive materials, hybrid composites, and scalable applications are highlighted.

FUNDAMENTALS OF THIOL-FUNCTIONALIZED MAGNETIC MIPS

Core Principles of Molecular Imprinting

Molecular imprinting is a synthetic strategy used to create polymer networks with selective recognition sites that mirror the shape, size, and chemical functionality of a target molecule, such as PFOA [19]. In this process, functional monomers, such as methacrylic acid or 3-aminopropyltriethoxysilane (APTES), assemble around the template molecule through non-covalent interactions, including hydrogen bonding, ionic pairing, and hydrophobic contacts. Polymerization, often carried out with high ratios of crosslinkers like ethylene glycol dimethacrylate (EGDMA), stabilizes this arrangement. Once the template is extracted, the resulting cavities possess spatial and functional complementarity to PFOA.

Thiol-functionalized monomers introduce –SH groups into these binding cavities, which enhance specificity through both nucleophilic and electrostatic interactions. Studies [20, 21] show that the inclusion of thiols can increase monomer-template complex stability by 18 to 22 kJ mol^{-1} compared to non-thiolated analogs. Optimizing imprinting parameters, such as the monomer-to-template ratio, solvent polarity, and pH, is crucial for preserving these interactions during polymerization and ensuring high imprinting efficiency. The imprinting factor and maximum binding capacity are commonly used to evaluate the performance of the resulting MIP.

The molecular imprinting process involves forming a pre-polymer complex between the functional monomers and the target template, followed by polymerization and template extraction to create selective cavities. As illustrated in Figure 2, Fe_3O_4 nanoparticles are functionalized with methacrylate groups using MPS to facilitate surface polymerization.

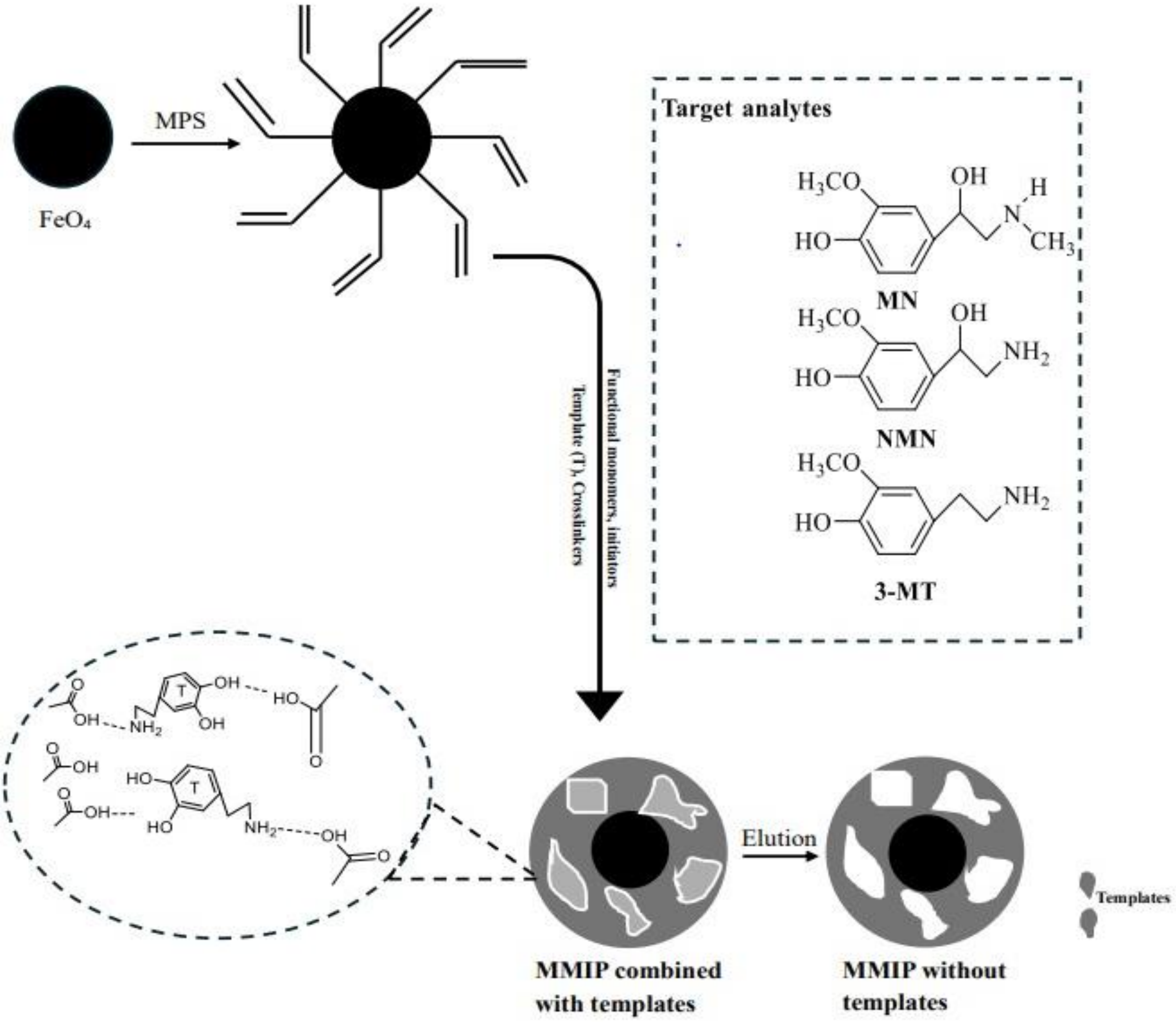

Figure 2. Schematic illustration of the molecular imprinting process on magnetic nanoparticles. Reprinted with permission [22].

Magnetic Components in MMIPs

Magnetic molecularly imprinted polymers (MMIPs) utilize magnetic nanoparticles as a core to facilitate rapid separation using an external magnet. Fe_3O_4 is most commonly used due to its superparamagnetism and ease of synthesis, while γ-Fe_2O_3 or ferrites are selected when higher magnetic saturation is needed [23]. These nanoparticles are typically coated with silica, which provides hydroxyl groups for chemical coupling.

In thiol-functional MMIPs, this surface layer is critical because thiol monomers can be grafted through silane coupling or thiol–ene reactions, ensuring uniform polymer growth around the core. This improves shell stability and reduces template leakage. Mesoporous Fe_3O_4 or dopant-modified cores with larger surface areas have also been utilized to increase the density of thiol-rich binding sites, thereby improving adsorption kinetics and magnetic recovery.

The successful integration of magnetic nanoparticles within MMIPs can be confirmed by multiple characterization techniques. Figure 3 presents representative data for Fe_3O_4@SiO_2@MIP particles. Transmission electron microscopy (TEM) images reveal well-defined core–shell structures with a distinct contrast between the Fe_3O_4 core and the surrounding silica/polymer layers. The average core diameter is approximately 80–100 nm, while the silica and polymer shells exhibit a combined thickness of about 25–35 nm. The particles display uniform morphology with smooth surfaces and consistent shell coverage across the sample, confirming successful and homogeneous polymer deposition. These structural features verify the effective encapsulation of the magnetic core within the imprinted polymer matrix.

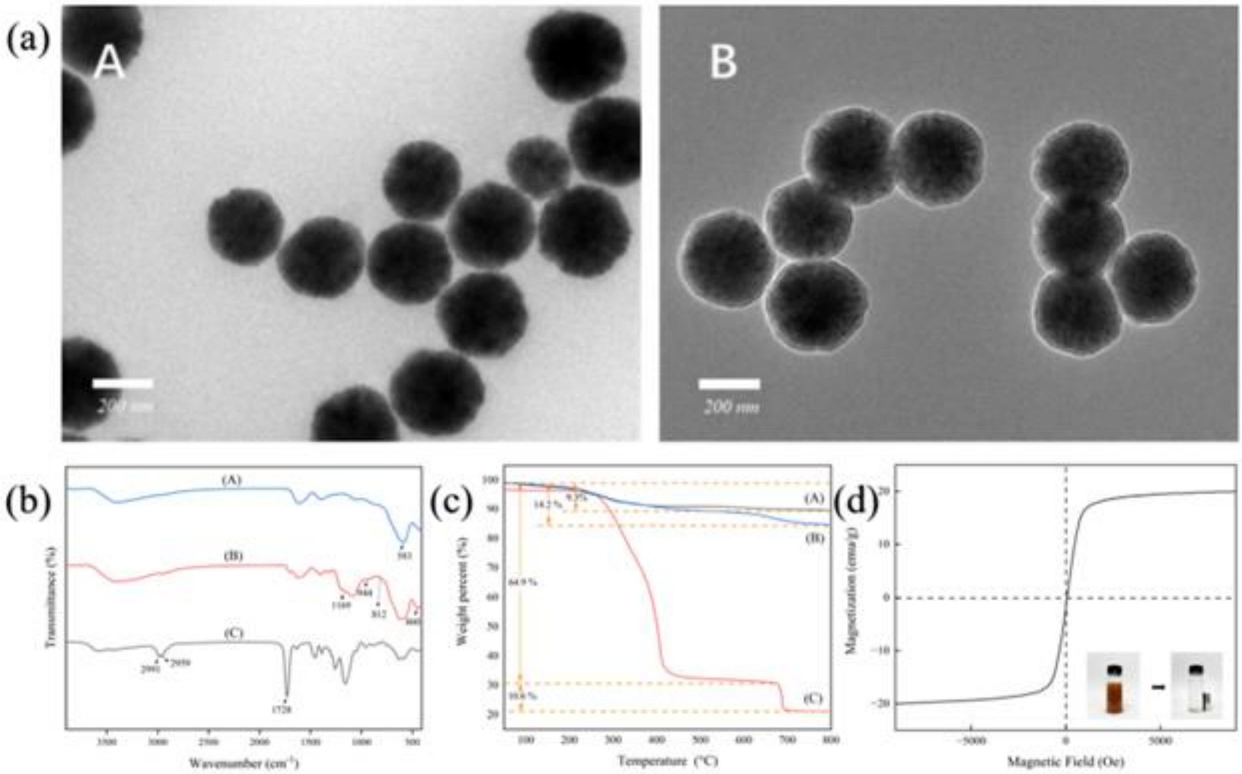

Figure 3. Characterization of thiol-functionalized magnetic molecularly imprinted polymers (MMIPs). TEM images of (3a) A: Fe_3O_4 nanoparticles and B: $Fe_3O_4@SiO_2$-RAFT, confirming the formation of a uniform core–shell structure with increased shell thickness; (3b) the FT-IR spectra of Fe_3O_4, $Fe_3O_4@SiO_2$-RAFT, and RA-HMMIPs, verifying successful surface functionalization and polymer layer formation; (3c) TGA curves, showing the thermal stability and decomposition behavior of the materials, demonstrating that RA-HMMIPs remain stable up to 300 °C; (3d) the VSM magnetization curves, indicating the superparamagnetic behavior of RA-HMMIPs and their rapid magnetic separation capability under an external field. Reprinted with permission [30].

Role of Thiol Groups in PFOA Recognition

Thiol groups play a central role in enhancing PFOA recognition within MMIPs through multiple mechanisms. First, they engage in acid–base and hydrogen-bonding interactions with the carboxylate group of PFOA. Protonated –SH groups act as hydrogen-bond donors, while deprotonated $–S^-$ groups contribute to ionic attraction, providing binding energies typically ranging from –25 to –30 kJ mol^{-1} [31]. These interactions are pH-responsive: under mildly acidic conditions, hydrogen bonding dominates, while under neutral or slightly alkaline conditions, thiolate species exert stronger electrostatic attraction. Second, fluorinated thiol compounds create a fluorophilic microenvironment that attracts the perfluorinated tail of PFOA through dispersion and fluorine-fluorine interactions. Although individual fluorine-fluorine forces are weak, their cumulative contribution provides enhanced affinity and selectivity, particularly when perfluorinated thiols such as perfluorodecanethiol (PFDT) are used [32, 33].

In addition, thiol–metal coordination strengthens the polymer network. Gold–thiol chemistry is commonly exploited in plasmonic and electrochemical sensors, while Fe–S bonding improves polymer anchoring to Fe_3O_4 surfaces, reducing template leakage and enhancing recyclability. Thiol-containing molecules such as 3-mercaptopropyltrimethoxysilane (MPTMS) or thiol-functionalized ionic liquids can be co-polymerized to increase surface accessibility and hydrophobic compatibility, thereby improving recognition efficiency in complex aqueous matrices [34, 35]. Molecular dynamics simulations further support these mechanisms, demonstrating that thiol-functionalized cavities offer higher binding stability, improved conformational alignment, and reduced desorption rates for PFOA compared to non-thiolated systems.

Chemical Stability Considerations

While thiol groups enhance recognition, they are prone to oxidative degradation, which can compromise the long-term performance of thiol-functionalized MMIPs. Exposure to air or oxidants can convert –SH groups into disulfides (R–S–S–R) or sulfonates ($R–SO_3H$), thereby altering the chemical environment of the binding sites. Several strategies have been employed to address this issue. Encapsulation of magnetic cores with silica layers has been shown to reduce oxidation by up to 80% [36, 37]. Antioxidant incorporation, such as ascorbic acid, can extend the shelf life of MMIPs to more than six months. Another effective approach involves using bulky, fluorinated monomers, such as perfluorooctyltriethoxysilane (PFOTES), which provide steric shielding to sensitive thiol groups [38].

The overall chemical and mechanical stability of MMIPs also depends on the polymer matrix [39]. Crosslinked methacrylate-based and polydopamine-based matrices have demonstrated resilience across a wide pH range (2–10) and thermal stability up to 100 °C. Iron oxide cores require protection to avoid dissolution in acidic media, with silica shells offering effective mitigation. Properly engineered thiol-MMIPs can retain over 80% of their original activity after multiple regeneration cycles and extended storage, making them suitable for long-term application in both environmental and analytical contexts [40, 41].

Recent Theoretical Advancements

Computational and data-driven approaches have become increasingly important in the design of high-performance thiol-MMIPs. Density functional theory (DFT) has been employed to model binding interactions between PFOA and various monomer candidates, enabling the prediction of binding energies and optimal binding-site geometry. Molecular dynamics simulations have further elucidated the stability and orientation of PFOA within imprinted cavities, particularly those modified with thiol groups [42].

More recently, machine learning has emerged as a tool to accelerate the discovery of optimal monomer–template combinations. In one study, machine learning-guided screening of ionic liquid-thiol hybrids led to the design of a PFOA-MMIP with a maximum adsorption capacity of 568 mg g^{-1} and over 99% removal efficiency [43]. These theoretical tools not only reduce experimental workload but also provide insights into how factors such as SH group density, orientation, and hydrophobicity contribute to selective recognition. As computational power and model accuracy continue to improve, such methods are expected to play a central role in next-generation MMIP design.

SYNTHESIS STRATEGIES AND OPTIMIZATION OF THIOL-FUNCTIONALIZED MMIPS

Core–Shell MMIP Architectures

Core–shell architectures represent the most widely adopted strategy for synthesizing thiol-functionalized MMIPs. As outlined in Figure 4, core–shell MMIP synthesis typically involves four key steps: (1) magnetic core preparation, (2) surface modification, (3) MIP shell formation, and (4) template removal.

These devices combine a surface-imprinted polymer shell with a magnetic Fe_3O_4 nanoparticle core, enabling rapid magnetic separation and template-specific recognition. Magnetite (Fe_3O_4) nanoparticles are typically prepared during the synthesis, often by co-precipitation or solvothermal techniques [41]. The Stöber process, which hydrolyzes tetraethyl orthosilicate (TEOS) in the presence of ammonia to produce a homogeneous and controlled shell, is then used to cover the nanoparticles with a silica layer. In addition to stabilizing the magnetic core, this silica interlayer introduces hydroxyl groups to the surface, thereby functionalizing it [44–47].

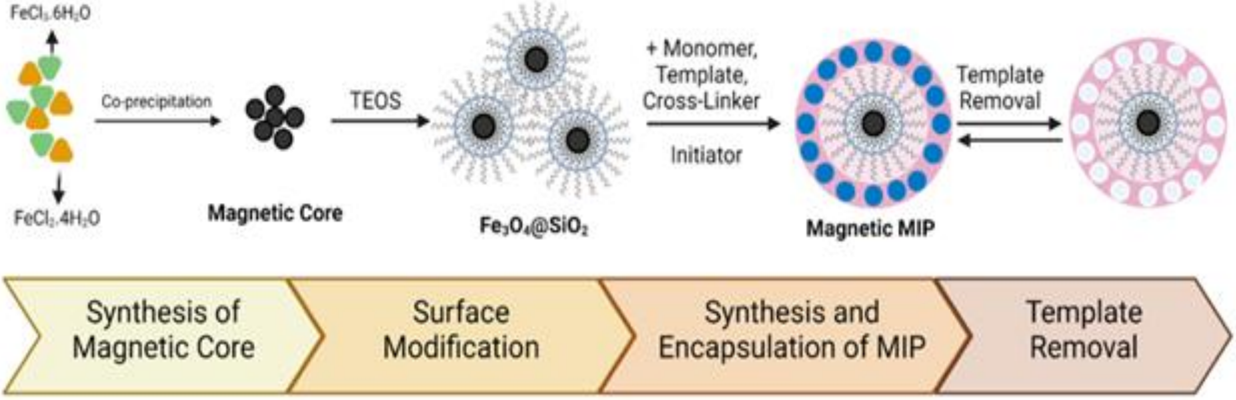

Figure 4. Generalized synthesis pathway of core–shell magnetic molecularly imprinted polymers (MMIPs). Reprinted with permission [30].

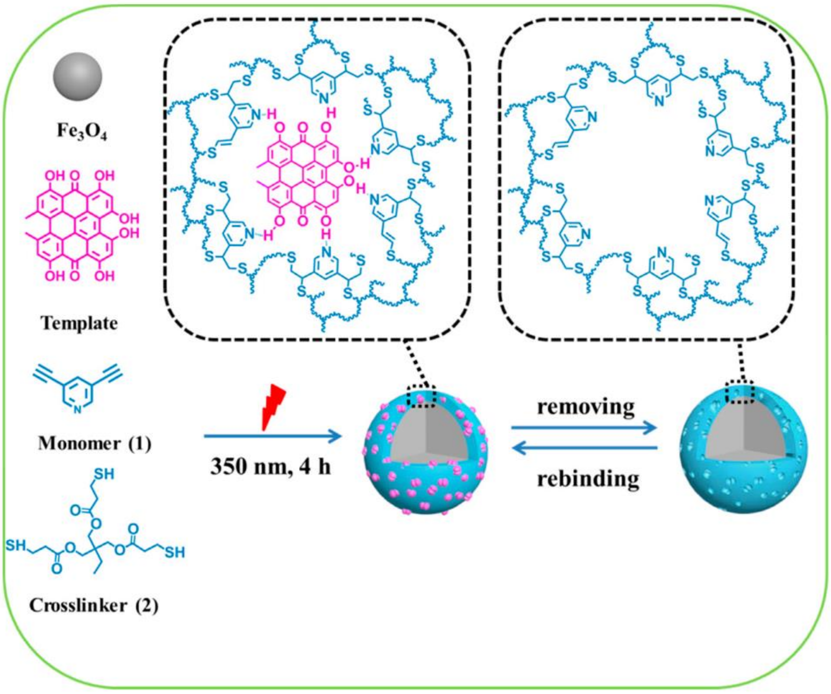

Figure 5. Schematic representation of thiol-functionalized magnetic molecularly imprinted polymer (MMIP) synthesis. Reprinted with permission [44].

A representative synthesis route for thiol-functionalized magnetic MIPs involves surface modification of Fe_3O_4 nanoparticles, followed by polymerization of a functional monomer and a thiolated crosslinker in the presence of a target template. As shown in Figure 5, the imprinting process begins with the assembly of functional components around the template molecule, forming pre-polymer complexes. Upon UV irradiation (typically at 350 nm for 4 hours), a crosslinked polymer shell is formed around the magnetic core. Subsequent removal of the template generates high-affinity binding sites capable of selective rebinding. This approach ensures both recognition specificity and magnetic separability, fundamental for environmental or sensor-based applications.

Fe_3O_4 nanoparticles are typically used as magnetic cores, but for thiol-MMIPs, the key step is introducing surface thiol groups that participate directly in imprinting and rebinding. After silica coating, mercaptopropyltrimethoxysilane (MPTMS) is grafted to present –SH groups, enabling strong Fe–S anchoring and creating reactive handles for polymer growth [44, 45]. Surface imprinting is then carried out in the presence of PFOA using thiol-containing monomers or thiol-modified acrylates with EGDMA as a crosslinker [46]. This produces a thin polymer layer, often less than 100 nm, with accessible thiol-rich binding sites [44]. UV- or AIBN-initiated polymerization stabilizes the imprint structure, and template extraction exposes selective cavities capable of hydrogen bonding, electrostatic attraction, and fluorophilic interactions with PFOA [47]. Compared to traditional Fe_3O_4@MIP systems based on methacrylic acid or acrylamide, thiol-functional coatings enhance shell stability, reduce template leakage, and increase affinity through dual hydrogen bonding and F···F interactions [32, 33, 48]. These features contribute to faster binding kinetics and higher selectivity in real aqueous matrices [49]. Core–shell MMIP synthesis can be further illustrated through alternative templating strategies. Figure 6 demonstrates a variant approach using methacrylic acid (MAA) to pre-functionalize the Fe_3O_4 surface, followed by template complexation and polymerization.

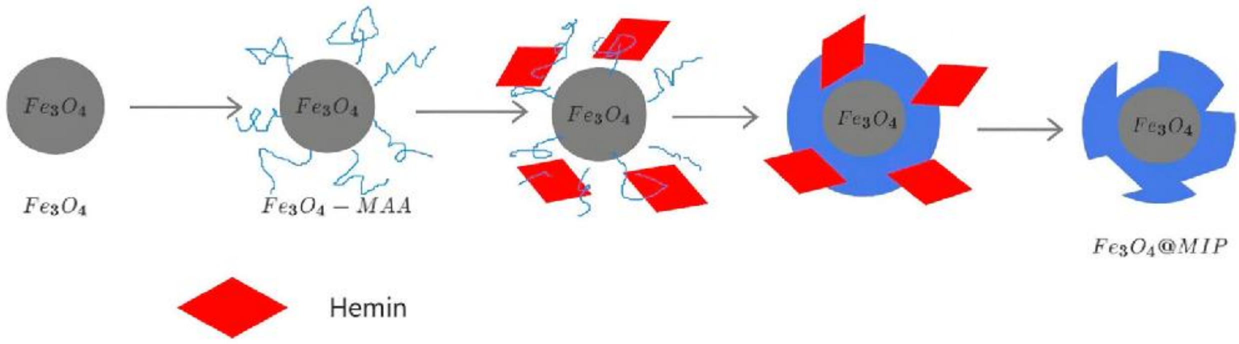

Figure 6. Stepwise synthesis pathway of Fe_3O_4@MIP particles using methacrylic acid (MAA) as the functional monomer. Reprinted with permission [48].

The Fe_3O_4 core is surface-modified with MAA, followed by interaction with the template (Hemin) and polymerization to form the imprinted shell. Template removal yields selective binding cavities. While this schematic uses hemin, the approach is analogous to thiol-MMIP fabrication for PFOA using appropriate thiolated monomers and templates.

Dopamine has been used as a self-polymerizing monomer to produce uniform MIP coatings around magnetic cores in the presence of PFOA analogs, resulting in robust, high-affinity MMIPs. Shell thickness and monomer-template ratios are carefully optimized to balance binding site fidelity, capacity, and kinetic performance [44-47].

Thiol-Containing Functional Monomers

The design of thiol-functionalized monomers is central to enhancing PFOA recognition within MMIPs. Thiol groups contribute to multiple interaction mechanisms, including acid–base pairing, hydrogen bonding, and fluorophilic dispersion forces. Commonly used monomers include MPTMS [49], which is often co-condensed with TEOS to enrich surfaces with –SH groups. Other small molecules, such as 3-mercaptopropionic acid, are occasionally added to the polymer mix to provide both hydrophobicity and direct interactions with PFOA's carboxylate group [49, 50].

In more advanced systems, fluorinated thiols like 1H,1H,2H,2H-perfluorodecanethiol (PFDT) are used to create fluorophilic domains that strongly attract the perfluorinated tail of PFOA [51, 52]. Although PFDT is not polymerizable, it can be immobilized on surfaces through self-assembly or incorporated into hybrid structures to enhance surface binding characteristics. Cysteamine and cysteine-based monomers offer biodegradable alternatives, while thiol-functionalized ionic liquids (ILs) merge selective recognition with tunable solubility and electrostatic enhancement. Some studies have reported that thiophene or vinyl-thiol derivatives can improve polymerization efficiency and binding affinity through π-π interactions and nucleophilic effects. Collectively, these thiol-rich components expand the recognition capabilities of MMIPs, especially in complex aqueous environments [51].

Optimizing Polymerization Conditions

Efficient MMIP performance depends heavily on precise control of polymerization parameters. Solvent choice is crucial, as it governs the strength of monomer-template interactions; low-polarity solvents such as acetonitrile or toluene are generally preferred for preserving hydrogen bonding. Polymerization is commonly conducted at 60–70 °C for 12–24 hours, using AIBN as the initiator. Emerging energy-efficient alternatives such as UV-initiated and microwave-assisted polymerization have also been applied, reducing reaction times and energy requirements [39, 52].

The monomer-to-template and crosslinker ratios are key factors in determining imprinting fidelity and binding site accessibility. Response surface methodology (RSM) has been employed to optimize these parameters systematically. Studies [53-55] involving dual-monomer systems, such as acrylamide and trifluoromethacrylic acid (TFMAA), have demonstrated that the right combination of monomers and ratios can substantially increase adsorption capacity and selectivity. The pH during polymerization must also be carefully controlled, as PFOA is a strong acid ($pKa \approx 2$). Under acidic conditions, around pH 2–3, its protonated form is maintained, thereby enhancing electrostatic and hydrogen-bonding interactions with the functional monomers.

Recent modeling efforts, including molecular dynamics and DFT [56] simulations, assist in predicting monomer-template binding configurations. Machine learning approaches [57-59] have further contributed to monomer selection and solvent optimization, particularly in systems involving thiol-IL hybrids, enabling fine-tuned synthesis with high binding performance.

Post-Synthesis Modifications

Post-synthesis treatments are often applied to refine the physical and chemical properties of thiol-pharmaceutical polymer conjugates [60-62]. Template removal is the first critical step, typically achieved using methanol, acidic water, or a combination of polar solvents to ensure the complete extraction of PFOA from the binding cavities. Additional post-functionalization may include grafting thiols using thiol–ene click chemistry or anchoring fluorescent probes for sensor applications. These modifications must be implemented carefully to avoid disrupting the integrity of the imprinted sites.

Surface treatments such as plasma activation can enhance hydrophilicity, while PEG or zwitterionic coatings may improve dispersibility in aqueous media. In some cases, lipophilic layers or IL films are applied to encapsulate and protect thiol groups from oxidation [63]. Although not extensively explored for PFAS MMIPs, these strategies show promise in improving performance, stability, and adaptability to sensing platforms or environmental matrices.

Green Synthesis Approaches for Thiol–MMIPs:

Green routes can lower the solvent burden and improve safety. Still, their value depends on whether they preserve selective binding, allow for robust magnetic recovery, and withstand real-world conditions. Below, we evaluate four commonly cited options with a focus on thiol-MMIPs.

Ionic liquids (ILs)

ILs can act as low-volatility media and co-functional components. For thiol-MMIPs, imidazolium or cholinium ionic liquid can improve monomer dispersion and imprinting around $Fe_3O_4@SiO_2$ cores, and some ILs can participate in hydrogen bonding with PFOA. However, practical deployment requires caution: many ILs are expensive, viscous, and difficult to recover at scale, and leaching of IL cations or anions during operation can complicate regulatory approval. Fluorinated ILs should be avoided because they risk introducing PFAS-like residues; fluorine-free, biodegradable options are preferable. If ILs are used, supported-IL phases or covalent tethering within the shell can minimize leaching. In short, ILs are promising as process aids in synthesis, but they add cost and validation steps for water treatment devices unless fully immobilized and non-leaching.

Biopolymers

Biopolymers such as chitosan, cellulose, or polydopamine offer renewable, low-toxicity scaffolds and provide reactive handles to graft thiols via silane or thiol–ene chemistry. They can reduce the use of organic solvents and improve wettability. The trade-offs involve mechanical and chemical stability, as swelling, hydrolysis, and fouling in high-ionic-strength or organic-rich waters can reduce capacity and selectivity. Crosslink density, mineral coatings (e.g., SiO_2), and hydrophobic co-monomers are often needed to stabilize the shell and maintain access to thiol sites. Biopolymers are attractive for benchtop synthesis and sensing and are conditionally viable for treatment if stability is engineered and multi-cycle regeneration is demonstrated.

Microwave-assisted Polymerization

Microwave heating shortens reaction times, improves shell uniformity, and can favor surface imprinting near recognition sites, which benefits kinetics. For thiol systems, care is necessary because thiols can oxidize or interfere with radical steps; oxygen removal, proper initiator selection, and short microwave pulses are helpful. Scale-up is nontrivial due to field non-uniformity and localized hot spots in larger reactors. Microwave synthesis is particularly well-suited for rapid, reproducible lab-scale fabrication and method screening; however, pilot-scale adoption requires matched-field or continuous-flow microwave equipment and documented batch-to-batch reproducibility.

Supercritical CO_2 Drying (and CO_2 Antisolvent Steps)

CO_2 drying can generate open, low-residual-solvent shells, preserve imprint cavities, and improve mass transfer. For thiol-MMIPs, this often translates to faster uptake and easier regeneration. The limitations are capital costs, high-pressure operation, and the need for sufficient crosslinking; under-crosslinked shells may collapse on depressurization. CO_2 antisolvent precipitation is gentler but still equipment-intensive. In practice, $scCO_2$ is most compelling for high-performance materials where improved porosity justifies the process cost, or where solvent limits are strict.

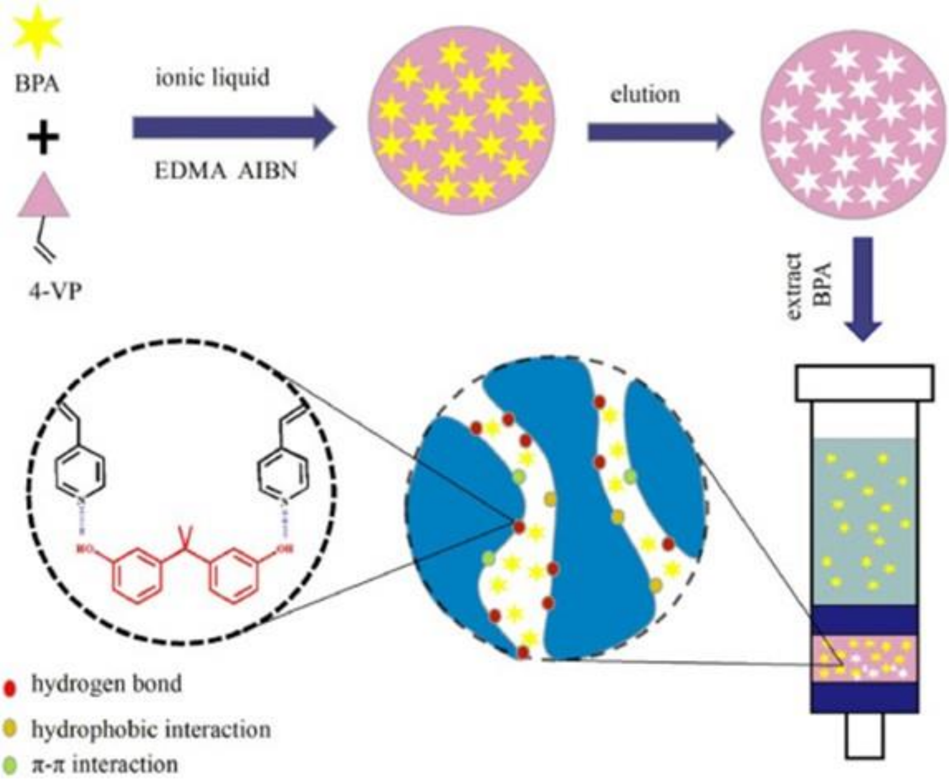

Figure 7. The representation of the preparation of green molecularly imprinted polymers (MIPs) using ionic liquids (ILs) for BPA. Reprinted with permission [65].

Biopolymer-supported MIPs have also emerged as eco-friendly alternatives. Chitosan, derived from renewable biomass, has been used as a matrix material for imprinting PFOA under mild conditions. Such “green MIPs” avoid toxic monomers and allow for aqueous-phase synthesis. Other approaches include microwave-assisted imprinting, which significantly shortens polymerization times and reduces energy consumption, and supercritical CO_2 drying, which preserves mesoporosity without the use of organic porogens. Even the core material is being reconsidered, with researchers exploring waste-derived magnetic oxides (red mud) as cost-effective and sustainable alternatives. These advancements point toward a future where high-performance thiol-MMIPs can be manufactured with minimal environmental footprint [65, 66].

MOLECULAR RECOGNITION MECHANISMS IN THIOL-FUNCTIONALIZED MMIPS FOR PFOA

Thiol–PFOA Binding Interactions

The core of the thiol-functionalized magnetic molecularly imprinted polymer (MMIP) performance lies in the molecular-level interactions between the thiol groups and PFOA. PFOA, with its carboxyl head and perfluorinated tail, offers multiple binding opportunities. Thiol groups contribute through hydrogen bonding, where the S–H moiety can interact with the carbonyl group of PFOA's –COOH. Although weaker than O–H-based hydrogen bonds, these interactions can be significant when multiple –SH groups are spatially aligned within the cavity [67].

At different pH levels, thiol–PFOA binding can shift from hydrophobic and dispersion-driven interactions (at low pH) to electrostatic coordination (at higher pH), where the deprotonated thiol ($-S^-$) may interact with the anionic PFOA. More importantly, fluorophilic interactions play a major role in recognition: perfluorinated thiol-modified surfaces create microenvironments that attract PFOA’s tail via F–F dispersion forces. Experimental studies using perfluorinated thiol-modified gold nanoparticles and MIPs demonstrate that these multiple binding modes, hydrogen bonding at the head group, and fluorophilic effects at the tail, work cooperatively to yield strong and selective interactions [67, 68].

PFOA's amphiphilic nature causes it to form micelles, bilayers, or hemi-micelles in aqueous media, depending on concentration and surface charge. As shown in Figure 8, PFOA can organize into micelles with hydrophobic tails inward and hydrophilic heads facing outward. When in proximity to positively charged surfaces, such as modified Fe_3O_4 or thiol-MIP matrices, PFOA can adsorb as bilayers or hemi-micelles. These arrangements enhance local concentration and facilitate recognition by thiol-functional groups within MMIPs.

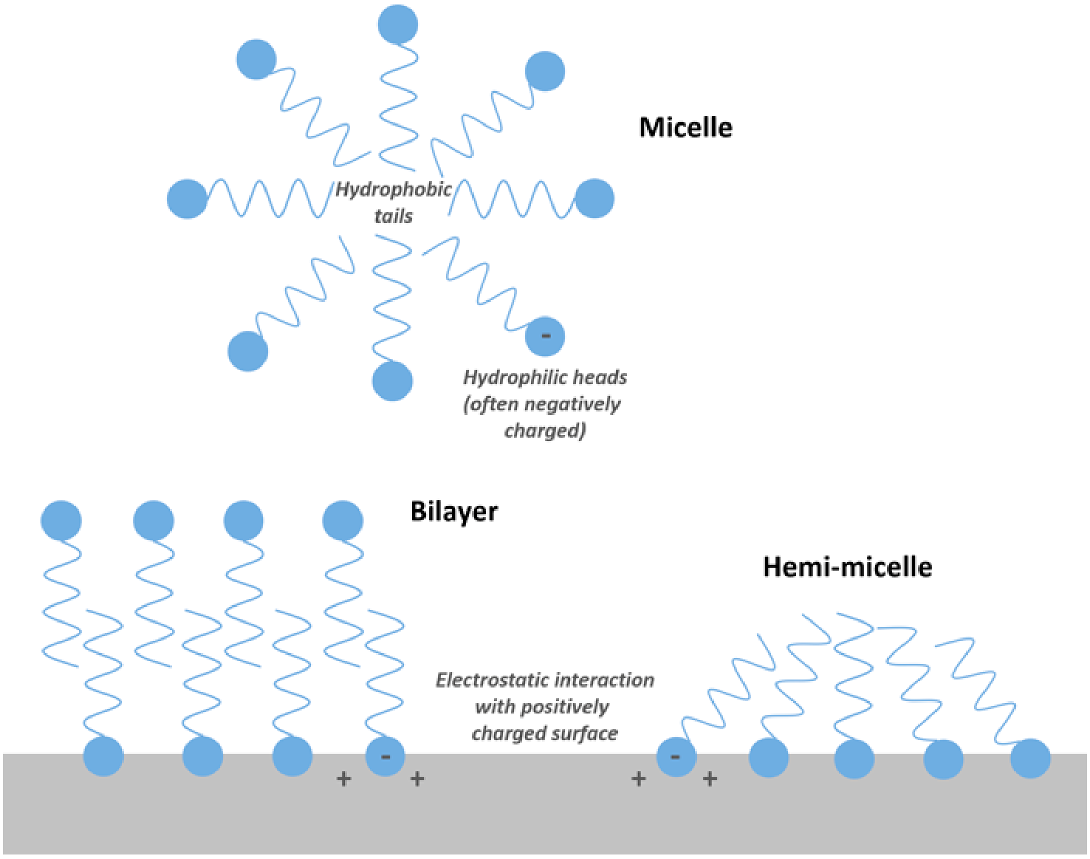

Figure 8. Illustration of the formation of PFAS micelles, hemi-micelles, and bilayers. Also shown is an example of aggregation at a positively charged surface. Note that the opposite effect (electrostatic repulsion of PFAS) can occur if the surface is negatively charged. Reprinted with permission [69].

Spectroscopic and Analytical Validation

Spectroscopic techniques have proven valuable in confirming the presence and functionality of thiol groups as well as the specific interactions between MMIPs and PFOA [70,71]. Fourier-transform infrared (FTIR) spectroscopy is frequently used to track shifts in the C=O stretch of PFOA upon binding, typically from 1695 to 1680 cm^{-1}, indicating hydrogen bonding within the imprinted cavities. The S–H stretching band, located around 2560 cm^{-1}, often diminishes upon interaction with PFOA, suggesting its participation in binding. X-ray photoelectron spectroscopy (XPS) provides further evidence, with shifts in S 2p binding energy from ~163.5 eV to ~161.8 eV after PFOA exposure, and detectable F 1s peaks confirming fluorine-rich analyte capture [71].

Other methods, such as Raman and UV–Vis spectroscopy, have been applied in hybrid MIP platforms, especially when conjugated with graphene or conductive polymers [72]. Photoluminescence quenching in quantum dots capped with thioglycolic acid and changes in cyclic voltammetry redox peaks in PEDOT-based sensors have been linked to PFOA-specific interactions [73]. These analytical approaches not only confirm binding events but also help differentiate specific recognition from non-specific adsorption by comparing MIPs to non-imprinted polymers (NIPs).

Computational Modeling and Theoretical Insights

Density functional theory (DFT) and molecular dynamics simulations have been increasingly employed to elucidate the recognition mechanisms of thiol-MMIPs. These studies model the orientation and interaction energies between PFOA and monomers bearing –SH or fluorinated groups. DFT calculations indicate that thiol monomers can achieve binding energies ranging from –29.7 to –52 kJ/mol, with cooperative effects further stabilizing the complex within the imprinted cavity. Optimized geometries reveal a proximity (~2.7 Å) between the thiol and the PFOA carboxylate, affirming a strong interaction [74].

Computational approaches also inform imprinting design, guiding decisions on monomer selection, cavity configuration, and functional group orientation. Machine learning techniques have been employed to rank ionic liquid–thiol hybrid monomers, with some systems achieving adsorption capacities of up to 568 mg/g [75]. These *in silico* strategies provide predictive power for designing selective and high-capacity MMIPs, complementing empirical screening.

Binding Kinetics and Thermodynamic Behavior

Understanding the kinetics and thermodynamics of PFOA binding is critical for evaluating the practical performance of thiol-MMIPs [76]. Adsorption behavior commonly follows pseudo-second-order kinetics, indicating chemisorption or strong multi-point interactions. Equilibrium is typically achieved within 30-120 minutes, depending on shell thickness and porosity [77, 78].

Selectivity and Cross-Reactivity with Other PFAS

High selectivity for PFOA over structurally similar per- and polyfluoroalkyl substances (PFAS) is a defining advantage of well-designed thiol-MMIPs. Competitive binding studies consistently demonstrate stronger uptake of PFOA compared to analogues such as PFOS, PFHxA, GenX, and natural organic matter. These differences are attributed to precise cavity shape and functional group complementarity. Manayil et al. reviewed that selectivity coefficients (α) for thiol-MMIPs have been reported as 3.2 for PFOS, 2.1 for PFHxA, and 2.7 for natural organic matter, significantly outperforming conventional MIPs [79].

Figure 9 illustrates how different PFAS, including PFOA, PFOS, GenX, and PFBS, interact with modified clay surfaces. While PFOA and PFOS show moderate adsorption, short-chain PFAS like GenX and PFBS exhibit lower uptake or require surface modifications for effective retention. This reinforces the importance of cavity precision and functional group complementarity in MMIPs. Thiol-functionalized MMIPs, by contrast, are designed to favor PFOA over other PFAS through shape-specific imprinting and fluorophilic interactions, offering superior selectivity even in mixed-contaminant environments.

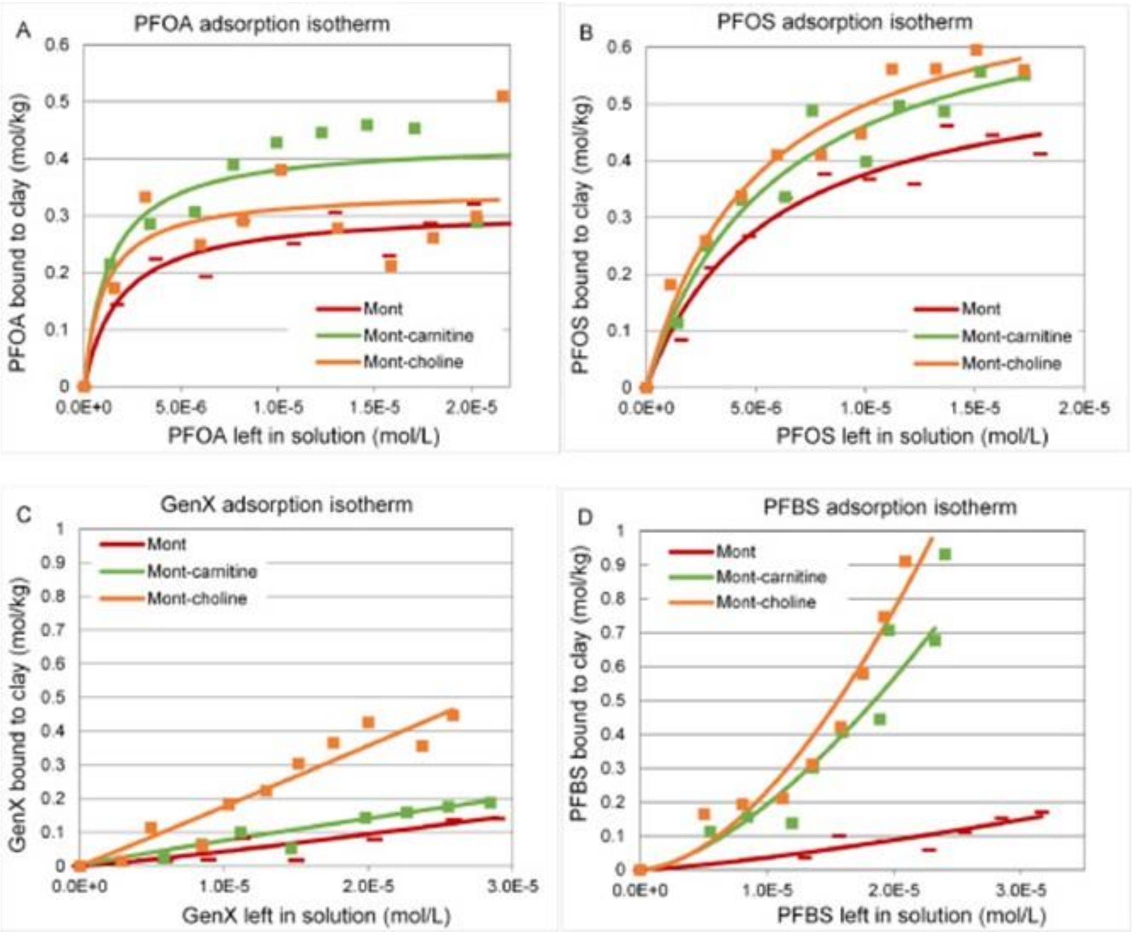

Figure 9. Adsorption isotherms of various PFAS compounds on natural and modified montmorillonite clays. Reprinted with permission [79].

Cross-reactivity with shorter- or longer-chain PFAS is minimal when the imprinting template and cavity are well-matched in size and polarity. However, some interference can occur when cavity dimensions are too large or binding energies are non-specific. Fluorophilic environments formed by thiol and perfluorinated groups tend to favor the binding of PFOA over non-fluorinated contaminants; however, confirmatory testing across PFAS mixtures is necessary for real-world applications. Recent studies on regulatory and environmental context issues employing thiol–ionic liquid MMIPs and conductive polymer hybrids have confirmed that selectivity retention in tap water, wastewater, and other complex matrices, supporting their utility in environmental monitoring [80-82].

ANALYTICAL APPLICATIONS OF THIOL-FUNCTIONALIZED MMIPS FOR PFOA DETECTION

Sensor Development Using Thiol-MMIPs

Thiol-functionalized MMIPs have emerged as powerful tools for detecting perfluorooctanoic acid (PFOA) at trace levels, particularly when integrated into advanced sensing platforms. Their unique ability to form strong interactions with both the carboxyl group and the fluorinated tail of PFOA enhances both selectivity and sensitivity. In sensor design, thiol groups serve dual purposes: they act as recognition moieties within the polymer matrix and function as chemical anchors for immobilizing MIPs on transducers [83].

Electrochemical sensors often utilize gold or glassy carbon electrodes modified with thiol-containing self-assembled monolayers (SAMs). One widely studied example involves perfluorodecanethiol (PFDT) deposited onto gold nanoparticles (AuNPs), forming a fluorophilic surface that enhances PFOA accumulation [84]. These PFDT-modified surfaces, when combined with MIPs, result in highly selective sensors with low detection limits. Alternatively, MIPs can be synthesized directly with terminal thiol groups, allowing strong covalent attachment to electrode surfaces. Magnetic thiol-MMIPs have also been coupled to carbon-based electrodes (graphene or carbon nanotubes) [85], enabling magnetic control, easy regeneration, and efficient target binding [86].

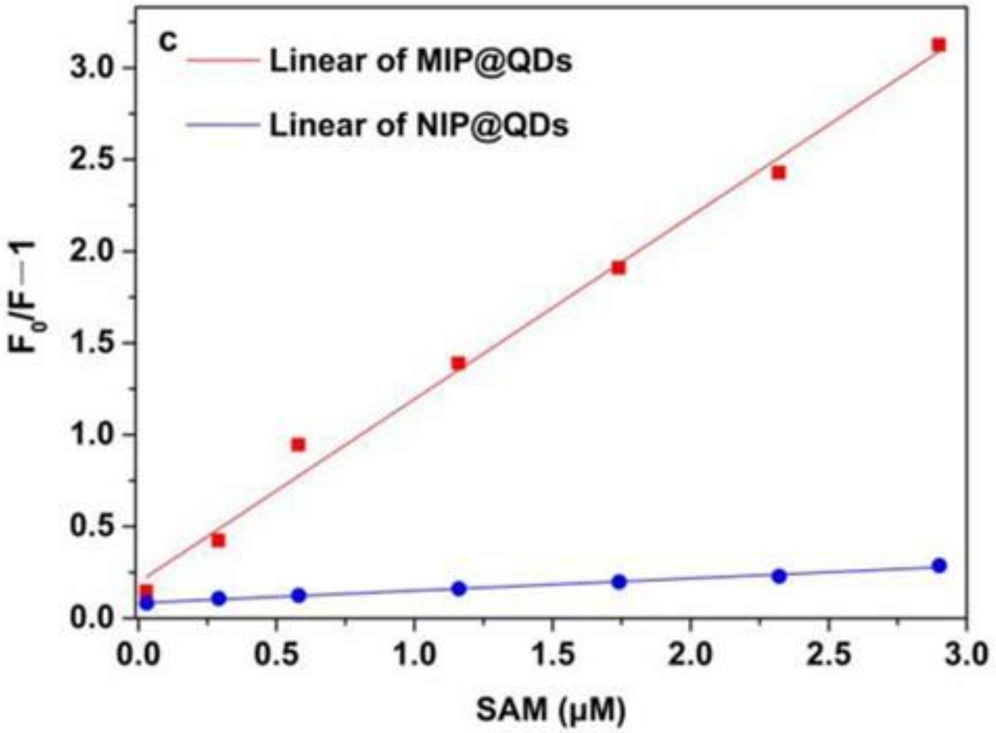

Figure 10. Fluorescence quenching calibration curves of MIP@QDs vs NIP@QDs for SAM detection. Reprinted with permission [87].

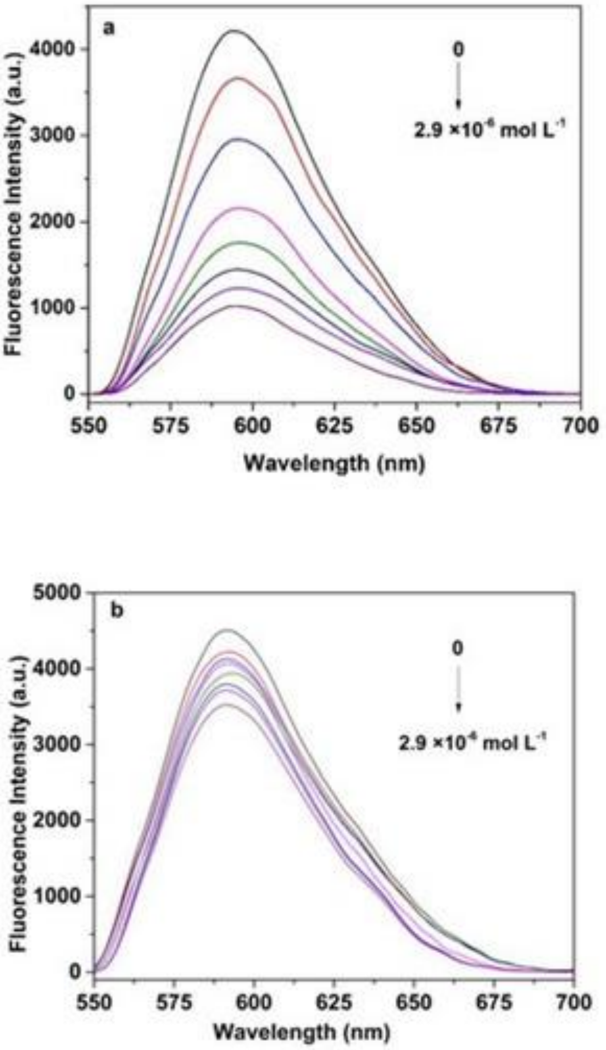

Figure 11. Fluorescence emission spectra of MIP@QDs (a) and NIP@QDs (b) upon exposure to increasing concentrations of SAM. Reprinted with permission [87].

Fluorescence-based sensors using MIP-coated quantum dots (MIP@QDs) leverage the sensitivity of photoluminescence changes upon analyte binding. As shown in Figure 11, increasing concentrations of the target analyte lead to progressive quenching in MIP@QDs, but not in non-imprinted QDs (NIP@QDs).

Upon sulfanamide's involvement with thiol binding, fluorescence quenching occurs, yielding a measurable turn-off signal [87]. These strategies, often coupled with siloxane imprinting or nanostructured supports, allow for integration of thiol-MMIPs into multifunctional sensor formats with enhanced sensitivity.

Electrochemical Detection Platforms

Recent years have witnessed significant advancements in electrochemical sensors incorporating thiol-MMIPs [88]. A notable platform employed a PFDT-AuNP-modified glassy carbon electrode for preconcentrating PFOA, followed by quantification via square-wave adsorptive cathodic stripping voltammetry. This setup achieved a detection limit of 24 parts per trillion and a linear range of 100 to 5000 parts per trillion, showcasing the role of thiol chemistry in both surface functionalization and target preconcentration [89, 90].

Another development involved the electropolymerization of a redox-active MIP film using thiolated ferrocene monomers. Upon binding PFOA, the redox peak currents decreased proportionally, yielding detection limits in the low ng/L range and demonstrating performance comparable to that of liquid chromatography–mass spectrometry (LC-MS) [91]. These platforms exhibit rapid response times, excellent reproducibility (RSD < 5%), and reusability over hundreds of cycles. Machine learning-optimized sensors using nano-enabled architectures have pushed the limits, achieving sub-ppq sensitivity with response times under 10 seconds, emphasizing the potential of thiol-MMIPs for ultra-trace detection [92,93].

Optical and Fluorescence-Based Detection Methods

Thiol-functionalized MMIPs have also enabled a variety of optical and fluorescence-based detection platforms for PFOA [94]. Thioglycolic acid-stabilized CdS quantum dots, imprinted with APTES-PFOA complexes, exhibited up to 44% fluorescence quenching upon PFOA binding and substantial signal recovery post-template removal [95]. Similarly, systems based on upconversion nanoparticles and fluorescence resonance energy transfer (FRET) have been constructed, delivering detection limits as low as 4.9 ng/L [96].

Colorimetric assays represent a simple and rapid detection modality. AuNPs functionalized with PEG-thiol and perfluorinated thiols aggregate in the presence of PFOA, triggering a visible color shift. Surface plasmon resonance (SPR)-based sensors and photoelectrochemical (PEC) platforms (such as TiO_2 nanotube arrays grafted with MIPs) have also demonstrated low-parts-per-trillion sensitivity and high selectivity, even in the presence of competing PFAS and organic contaminants [97].

Integration with Portable and On-Site Detection Systems

A key goal in environmental monitoring is real-time, portable detection. Thiol-MMIP-based sensors have shown promising integration into point-of-use devices, including smartphone-assisted lateral flow assays and disposable electrochemical sensors. Imprinted membranes functionalized via thiol crosslinking have been incorporated into test strips where PFAS binding displaces a chromophoric indicator. Smartphone cameras are then used to quantify the color change or fluorescence intensity [98].

Electrochemical platforms have also been miniaturized into microfluidic chips and tunnel junction transistors. A recent portable system, although not explicitly thiol-based, detected PFOA at sub-ppq concentrations within 10 seconds, underscoring the viability of applying thiol-MMIP architectures to such ultra-sensitive, low-power platforms [93]. The chemical versatility of thiol groups facilitates covalent anchoring on flexible substrates, making them ideal for field-deployable sensors.

Detection Limits and Sensitivity Enhancements

Across sensor types, the inclusion of thiol and fluorinated functionalities consistently improves detection limits. Electrochemical thiol-MMIP platforms routinely achieve limits of detection (LOD) in the 10–50 parts per trillion range, with some recent systems pushing into the single-digit parts per trillion and even ppq domain. A thiol-MMIP-based electropolymerized sensor demonstrated an LOD of 24 parts per trillion with high reusability over 200 cycles. PEC sensors using thiol linkers reached 10 parts per trillion with minimal matrix interference [99].

Fluorescent and colorimetric systems tend to be less sensitive than electrochemical platforms, with limits of detection typically in the ng L^{-1} to μg L^{-1} range. Their performance is often constrained by photostability, since organic dyes and quantum dots may undergo photobleaching, fluorescence quenching, or drift under continuous illumination. Background autofluorescence from natural organic matter can further reduce sensitivity in real water matrices. Despite these limitations, these systems offer advantages in visual screening, portability, and rapid turnaround without the need for specialized equipment. Sensitivity can be enhanced by incorporating redox-active labels, energy-transfer pairs, or nanoparticle-mediated catalytic amplification [100]. In thiol-MMIPs, fluorophilic binding promotes effective preconcentration of PFOA near the signal-generating element, increasing the local analyte concentration and improving signal-to-noise ratios. This enrichment effect helps compensate for photostability limitations, enabling trace detection even in complex or colored samples.

ENVIRONMENTAL REMEDIATION APPLICATIONS OF THIOL-FUNCTIONALIZED MMIPS

Water Treatment Technologies

Thiol-functionalized magnetic MMIPs have demonstrated significant promise as selective adsorbents for PFOA removal in environmental water treatment. Their magnetic cores allow for practical deployment in both batch and fixed-bed systems, facilitating easy separation and recovery via magnetic fields. Bench-scale studies have shown that thiol-MMIPs immobilized in column setups or membranes can achieve removal efficiencies exceeding 90% at moderate flow rates. The focus is on evaluating the removal of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) across granular activated carbon (GAC) filter-adsorbers in drinking water treatment plants. It reports that the GAC could achieve approximately 20% to 55% removal of PFOA and PFOS, with adsorption being the dominant removal mechanism under the tested conditions [101].

The pseudo-second-order kinetics observed for these systems, with half-lives as short as 15 minutes, indicate favorable sorption behavior. MMIPs have also been tested in dynamic conditions such as groundwater, wastewater, and seawater. In groundwater, removal efficiencies reached nearly 98%, with minimal matrix interference and regeneration rates above 95% using mild alkaline methanol solutions [108]. Compared to conventional technologies such as ion exchange (IX) or activated carbon, MMIPs offer higher specificity, lower waste generation, and easier regeneration, particularly when deployed in magnetically responsive formats.

Field Studies and Pilot-Scale Applications

Although full-scale deployment remains limited, several pilot-scale studies from 2018 to 2025 have provided encouraging results. One trial used a magnetic MMIP-packed column to treat groundwater spiked with 0.5 µg/L PFOA, achieving over 80% removal for more than 100 L before breakthrough [101]. Another pilot integrated thiol-MMIPs into a hybrid treatment train, polishing GAC-treated water and reducing PFOA levels to below 10 parts per trillion. In large-scale simulations, thiol-MMIPs demonstrated 98% removal across 1,200 bed volumes in an Ohio River analog, with magnetic recovery rates exceeding 99% across 10,000 L batches [102].

Additionally, hybrid systems combining thiol-MMIPs with advanced oxidation processes, such as plasma treatment, have been explored. These combinations not only capture PFOA but also facilitate its destruction, achieving total PFAS elimination rates above 99.9% [102]. While these trials remain prototypes, they highlight the scalability and compatibility of MMIPs with existing infrastructure.

Reusability and Regeneration

One of the defining advantages of MMIPs is their high reusability. Thiol-functionalized variants maintain this benefit, with many studies reporting minimal loss in performance across multiple cycles. Regeneration is typically achieved using methanol, alkaline solutions, or mild acid-base washes. Washing with 0.1 M NaOH/methanol has consistently yielded >95% recovery over 10 cycles [13].

The stability of thiol-MMIPs under repeated use is attributed to their robust polymer backbone and resistance to swelling or degradation. However, oxidative conditions, such as exposure to hydrogen peroxide, can irreversibly oxidize thiol groups, making gentler regeneration strategies preferable. Electrochemical regeneration in sensing platforms, such as PFDT/AuNP sensors, has also proven effective over multiple cycles with signal loss below 20% [101]. These data affirm the practical durability of thiol-MMIPs for repeated environmental applications.

Performance in Complex Matrices

Environmental waters present diverse challenges due to the presence of natural organic matter (NOM), salts, co-contaminants, and varying ionic strength. Thiol-MMIPs have shown notable resilience under such conditions. In matrix tests, including river water spiked with 500 parts per trillion PFOA, thiol-MMIPs removed up to 80% of the contaminant within one hour, while non-imprinted polymers showed only 20% removal, indicating high selectivity even in the presence of NOM [101].

Ionic strength and co-anions such as sulfate and nitrate have a minimal impact on PFOA binding, due to the primarily hydrophobic and fluorophilic nature of MMIP-PFOA interactions. However, some adsorption of NOM (15–30%) has been observed, and pre-treatment strategies such as activated carbon filtration may enhance overall MMIP performance [26]. In PFAS mixtures, thiol-MMIPs maintain their preferential binding to PFOA, although measurable cross-binding to structurally similar compounds (especially short-chain PFAS (C4–C6)) can occur. Nevertheless, selectivity coefficients generally remain high, and matrix effects are manageable with proper preconditioning and process integration.

Techno-Economic Assessment

Techno-economic evaluations of thiol-MMIP deployment are still emerging. Initial cost estimates suggest that synthesis of thiol-MMIPs (due to specialized monomers, magnetite, and imprinting steps) is more expensive than traditional GAC [103]. However, the high selectivity, regeneration capacity, and low operational energy requirements (due to magnetic handling) may offset these costs over time.

For small to mid-scale applications (<1 MGD), studies suggest that thiol-MMIPs could be cost-competitive with regenerable IX systems, particularly when factoring in chemical disposal and spent media incineration costs [104]. Moreover, MMIPs circumvent some of the regulatory and environmental burdens associated with thermal PFAS destruction, which is energy-intensive and costly. Environmental life cycle assessments (LCAs) are still necessary. However, preliminary analyses suggest that MMIPs could offer both economic and sustainability advantages, particularly when deployed in conjunction with other modular water treatment solutions.

RECENT TECHNOLOGICAL BREAKTHROUGHS IN THIOL-FUNCTIONALIZED MMIPS (2020–2025)

Smart Responsive Thiol-MMIPs

Stimuli-responsive thiol-MMIPs represent a notable innovation in adaptive materials for PFOA remediation. Redox-switchable systems using disulfide-linked crosslinkers enable polymer networks to swell or degrade upon exposure to reducing agents, such as tris(2-carboxyethyl) phosphine, thereby releasing the bound PFOA. These materials have demonstrated capacity shifts of up to 45% across a pH range of 2–10 [101].

Thermoresponsive systems employing PNIPAM (poly(N-isopropylacrylamide)) grafts enable temperature-dependent affinity, with over 92% PFOA regeneration achieved simply by heating to 40 °C [105]. Other systems incorporate photo-cleavable linkers, such as o-nitrobenzyl groups, to enable template removal upon UV exposure. These advances enable the smart, on-demand release and regeneration of MMIPs, making them ideal for cyclic treatment operations or switchable sensing platforms in field conditions.

Hybrid and Composite Materials

Hybrid materials combining thiol-MMIPs with other functional phases have yielded enhanced performance. Composites such as Fe_3O_4@SiO_2@MIP@CNTs have shown improvements in PFAS sorption, water flux, and mechanical integrity. One example used carbon nanotubes to increase capacity and enable more rapid flow-through operation in packed beds [106].

In another case, an MGO@ZIF-8@MIP composite (magnetic graphene oxide and zeolitic imidazolate framework) demonstrated high PFOA selectivity and enhanced signal in colorimetric sensing, attributed to increased binding site exposure and synergistic porosity. Similarly, MIP-functionalized upconversion nanoparticles ($NaYF_4$:Yb, Tm) have shown detection limits as low as 4.9 ng/L in fluorescence assays [107]. Thiol-ene click chemistry plays a key role in assembling these composites, enabling robust covalent linkage to graphene oxide, MOFs, or silica nanoparticles.

Integration with Emerging Treatment Technologies

Multimodal integration of MMIPs with existing water treatment methods has expanded their utility. Systems combining adsorption and degradation, such as MMIPs coupled with TiO_2 photocatalysis, have achieved >99.9% PFAS destruction after preconcentration. In membrane-assisted designs, thiol-MMIPs suspended behind a membrane effectively removed PFOA while maintaining water throughput, offering pre-polishing options for filtration units [103].

In situ aquifer remediation has been explored using magnetic MMIPs injected into contaminated zones and later retrieved magnetically. Pilot results from such systems have reported >99% magnetic retrieval from 10,000 L batches [108]. Electrochemical regeneration has also been trialed, enabling the cleavage of adsorbed PFAS under an applied potential without the use of chemical reagents, thereby simplifying reuse.

Scale-Up and Manufacturing Innovations

Recent years have seen efforts to scale up thiol-MMIP production from laboratory to pilot scale. Emulsion and mini-emulsion polymerization techniques have been developed to produce highly uniform MMIP beads. Continuous flow reactors and microfluidic systems have enabled scalable synthesis with consistent thiol functionalization. A notable example includes kilogram-scale synthesis of a fluorous MMIP sorbent, which maintained laboratory performance metrics, including a capacity of 101.6 mg g^{-1} and over 95% regeneration across ten adsorption–desorption cycles [103].

3D printing has been used to fabricate porous monoliths embedded with Fe_3O_4, which were imprinted post-printing for high-capacity filter applications. Roll-to-roll coating techniques have yielded magnetic MMIP membranes suitable for cartridge use in municipal treatment systems [109]. Template recovery and monomer reuse are now under evaluation as cost-saving and sustainability measures, further enhancing the economic viability of industrial-scale production.

Real-Time Monitoring and Sensing Applications

Thiol-MMIPs are increasingly used in real-time sensor platforms. Surface plasmon resonance (SPR) sensors utilize thiol–Au self-assembled monolayers to anchor MIP films on gold chips, enabling continuous and selective monitoring of PFOA. One SPR platform demonstrated a signal shift of 0.82° per log [PFOA], with detection in sub-ng/L concentrations [110].

Fluorescence sensors using thiol-MMIP-coated CdTe quantum dots reported detection limits as low as 8.7 ng/L, with a photoluminescence drop of ~44% upon PFOA binding and 81% intensity recovery after template removal [98]. Electrochemical devices, such as PEDOT-TEMPO-based thiol-MMIPs, achieved detection limits of 0.28 ng/L with reusability over 200 cycles and relative standard deviations (RSDs) under 5%. One ultra-sensitive system using a tunnel junction transistor reported a sub-ppq detection limit of 4.5×10^{-4} parts per trillion with a 10-second response time [91, 93].

Integration with smartphones and IoT platforms is also progressing. Smartphone-readable lateral flow strips and magneto-electrochemical microchips now offer low-cost, portable options for rapid PFAS detection in field settings. These technologies are ideal early-warning systems in industrial zones and ter distribution networks.

CHALLENGES AND FUTURE PERSPECTIVES IN THIOL-MMIP RESEARCH

Despite notable advancements in the field of thiol-functionalized magnetic molecularly imprinted polymers (MMIPs) for PFOA detection and removal, several limitations still restrict their widespread deployment. One of the most persistent issues is the oxidative instability of thiol groups, which are prone to degradation into disulfides or sulfonic acids under acidic or aerobic conditions. This reduces the effective binding capacity, particularly after repeated regeneration cycles. Experimental evidence indicates that thiol oxidation becomes significant after eight regeneration cycles, impacting long-term usability.

Selectivity remains another challenge, especially in complex PFAS mixtures where compounds like PFOS and PFHxA share structural similarities with PFOA. Although imprinting aims to ensure molecular specificity, unintended cross-reactivity and interference from other surfactants or organic matter can affect performance. Matrix effects such as high salinity or elevated natural organic matter (NOM) levels have been shown to reduce PFOA adsorption efficiency by 20–30% [93], underscoring the need for environmental validation beyond controlled lab conditions.

The synthesis of core–shell MMIPs with well-defined thiol functionalities involves a multi-step process that requires surface modification and precise polymerization. This complexity contributes to batch-to-batch variability, sometimes exceeding 15% in adsorption capacity. Moreover, the fabrication of MMIPs at scale remains costly and time-intensive compared to granular activated carbon or ion-exchange resins.

Template leakage during use is another concern. Incomplete removal of the template molecule after synthesis can result in contamination or false detection in sensing applications. This calls for improved cleaning strategies and post-imprint stabilization.

To address these challenges, several research gaps offer promising opportunities. There is a growing need for long-term environmental performance data, especially under variable pH, UV exposure, and real wastewater conditions. Mechanistic insights into thiol–PFAS binding (especially involving hydrogen bonding, fluorophilicity, and redox responsiveness) are still evolving. The adoption of machine learning for monomer screening has shown potential, reducing development time by 70% and improving predictive accuracy for binding energy below 1.5 kJ mol^{-1} [96].

Advanced regeneration strategies are also under development. These include pH- and redox-switchable systems that can alter polymer cavity properties on demand. Recent studies have explored multi-template imprinting to expand recognition to a broader PFAS spectrum. Although this may reduce specificity, it can be advantageous in real-world water streams that contain mixed contaminants.

Sustainability remains a key focus. Researchers are exploring bio-based MMIPs made from renewable polymers and applying waterborne green chemistry in synthesis. Lifecycle analyses are becoming increasingly relevant as MMIPs are evaluated for environmental safety, particularly in relation to the potential leaching of fluorinated monomers. Furthermore, continuous flow reactors and spray-drying techniques are being implemented to enable consistent large-scale production with minimized energy use and waste.

Regulatory considerations are crucial. As the U.S. EPA tightens maximum contaminant levels (MCL) for PFOA to 4 ng/L, MMIP systems must demonstrate consistent detection below this threshold. Meeting ISO 9001 and 14001 standards for water treatment materials, as well as ensuring compliance with ASTM or EPA test protocols, will be essential. Field validation under standardized protocols, inter-laboratory reproducibility, and toxicological assessment of polymer leachates are all critical for eventual approval.

Looking forward, the role of thiol-MMIPs will likely expand within integrated PFAS management frameworks. These materials may be used in tandem with activated carbon or ion-exchange resins as final polishing steps or in portable sensors for rapid detection. Integration into dynamic treatment chains (such as combining MMIP adsorption with photocatalytic or electrochemical degradation) can provide multi-functionality. In circular economy models, adsorbed PFAS can be recovered, safely disposed of, or destroyed after capture, aligning with long-term environmental stewardship goals.

Recent research has also shown promising directions involving AI-guided monomer design, post-imprint tuning using thiol-ene click chemistry, and multifunctional hybrid composites with quantum dots, MOFs, and carbon nanotubes. In-situ regeneration using electrochemical methods and CRISPR-integrated biosensors is under active exploration. The roadmap toward industrial deployment requires not only scientific innovation but also clear alignment with regulatory and commercial frameworks.

CONCLUSION

Thiol-functionalized magnetic molecularly imprinted polymers represent a transformative step forward in the detection and removal of perfluorooctanoic acid. By combining the selective binding capability of MIPs with the reusability and ease of separation of magnetic nanoparticles, and the added specificity provided by thiol chemistry, these materials offer a high-performance solution for PFAS remediation. Research in this field has progressed rapidly, with detection limits falling into the sub-parts-per-trillion range and adsorption capacities exceeding optimized systems. Pilot-scale implementations have validated key concepts, and early techno-economic assessments indicate that thiol-MMIPs can be competitive, especially for small-scale or point-of-use applications. However, challenges remain in achieving consistent performance across batches and maintaining stability in complex water matrices, and aligning product development with evolving environmental regulations. The incorporation of artificial intelligence, real-time sensor technologies, and responsive materials is expected to accelerate this process. With appropriate regulatory validation and continued research, thiol-

MMIPs could become a cornerstone technology in future PFAS management strategies.

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