

Review

Advanced Sorbents in Miniaturized Solid-Phase Extraction for Phenolic Compounds in Plant-Derived Food Matrices: A Systematic Critical Review of Sorbent Architecture, Interaction Mechanisms, and Analytical Trends

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Abstract

The compositional complexity of plant-derived food matrices and the structural diversity of phenolic compounds influence sample preparation, promoting miniaturized solid-phase extraction using advanced sorbents for their determination. This critical systematic review examines these sorbents over the 2016–2025 period, organizing the analysis according to their structural platform to investigate how their architecture is associated with the reported interaction mechanisms, to interpret analytical performance in the appropriate context, and to identify methodological trends, limitations, and knowledge gaps. Through a systematic search in Scopus and the application of predefined eligibility criteria, 37 studies were selected and included in the critical narrative synthesis. The analysis primarily covered molecularly imprinted sorbents, functionalized polymeric and carbon-based platforms, and layered inorganic materials. Magnetic separation using Fe₃O₄ emerged as the most widely employed operational strategy across the analyzed platforms, while flavonoids and phenolic acids were the predominant target subclasses. Identified gaps include the infrequent evaluation of matrix effects, the limited formal assessment of method sustainability, and the scarce experimental validation of the relative contribution of retention mechanisms in systems involving multiple simultaneous interactions. By organizing the available evidence according to sorbent structural platform, this review provides a critical framework for interpreting analytical performance, informing the rational design of advanced sorbents, and supporting the development of miniaturized solid-phase extraction techniques for food analysis.



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1. Introduction

Phenolic compounds constitute one of the most structurally diverse classes of plant secondary metabolites, characterized by the presence of at least one aromatic ring bearing one or more hydroxyl substituents. To date, more than 8000 structures have been identified within this family [1,2]. Widely distributed in plant-derived food matrices, including fruits,

vegetables, and cereals, these compounds are classified according to structural features such as the number of phenolic rings and the arrangement of hydroxyl groups, giving rise to subclasses including flavonoids, phenolic acids, and stilbenes, among others [3,4]. This structural diversity is associated with a broad range of biological activities, encompassing antioxidant, antimicrobial, and anti-inflammatory properties [4,5]. In plant-derived foods, phenolic compounds are closely linked to sensory attributes such as color, flavor, and overall quality [2], while also serving as markers of authenticity and nutritional value, as their profiles reflect factors including geographical origin, cultivation conditions, and processing methods [6,7]. Given their nutritional significance and their role as indicators of food quality, the accurate quantification and monitoring of phenolic compounds in plant-derived food matrices are essential. However, their determination remains analytically challenging due to the inherent complexity of these matrices.

Plant-derived food matrices exhibit an inherent compositional complexity that directly influences any analytical strategy aimed at the determination of phenolic compounds. The plant metabolome comprises primary metabolites, including sugars, proteins, lipids, and nucleic acids, together with specialized metabolites such as terpenoids, alkaloids, and phenolic compounds themselves. This complexity is further increased by the presence of photosynthetic pigments, which display a high affinity for the reversed-phase stationary phases commonly employed in HPLC, as well as lignocellulosic cell wall structures that hinder the efficient release of intracellular metabolites [8]. Phenolic compounds themselves introduce an additional analytical challenge due to their considerable variability in polarity, molecular weight, and stability. Some are thermolabile, volatile, or prone to oxidation, properties that influence their interactions with the matrix and directly affect their recovery during the extraction process [9].

Although chromatographic techniques such as high-performance liquid chromatography (HPLC), gas chromatography (GC), and hyphenated platforms such as liquid chromatography–mass spectrometry (LC–MS) provide robust analytical tools for the determination of phenolic phytochemicals in food matrices [10,11], their overall analytical performance depends largely on the sample preparation stage. This step represents one of the most critical components of the analytical workflow, as it must simultaneously isolate and preconcentrate the target analytes while removing coexisting matrix interferents that, if not adequately controlled, compromise the selectivity and reliability of the subsequent analysis [11]. Traditionally, this stage has relied on solvent-based methods and conventional solid-phase extraction formats. However, these approaches exhibit well-documented limitations, including labor-intensive procedures, the requirement for substantial volumes of solvents and samples, limited selectivity, insufficient cleanup of matrix co-interferents, and poor alignment with the principles of green analytical chemistry [9,12,13]. These limitations have driven the development of alternative approaches that are more efficient, selective, and environmentally sustainable.

In this context, the miniaturization of sample preparation procedures has emerged as a direct response to these limitations, leading to techniques that reduce resource consumption, simplify analytical workflows, and are fully compatible with modern analytical platforms [13,14]. Among these miniaturized approaches, solid-phase extraction (SPE)-based techniques have gained particular prominence because of their versatility and adaptability to diverse matrices, their efficiency in removing matrix interferents, and their ability to preconcentrate target analytes [11,13]. Nevertheless, regardless of the extraction format employed, the analytical performance of these methods is largely determined by the nature of the sorbent material, which governs analyte selectivity, sensitivity, retention, and preconcentration capacity [15,16]. This central role of the sorbent has directed consider-

able research efforts toward the development of materials with more precisely defined architectures and more specific interaction mechanisms.

Conventional sorbents used in sample preparation often exhibit limitations in selectivity and sensitivity when applied to complex matrices [17], prompting the development of advanced materials with enhanced sorption capacity, physicochemical stability, and, above all, improved selectivity [16,18]. These materials include molecularly imprinted polymers, metal–organic frameworks, covalent organic frameworks, layered double hydroxides, and carbon-based nanomaterials, all of which have been extensively investigated in the recent literature [19]. However, their representation in studies involving plant-derived food matrices remains variable and, in some cases, limited. The analytical performance of these materials is based on their ability to establish specific interactions with target analytes. Molecularly imprinted polymers enable selective molecular recognition through complementary binding cavities; carbon-based materials promote π – π interactions with aromatic compounds; and framework-structured materials provide additional interaction pathways through metal coordination sites or rationally designed porous cavities [8,18]. The combination of these interaction mechanisms, together with the possibility of tailoring sorbent architecture, has been associated with enhanced selectivity toward target analytes over matrix interferences, higher analyte recoveries, and improved analytical sensitivity [14,19].

These characteristics are particularly relevant for the determination of phenolic compounds in plant-derived food matrices, where the aromatic structure of the analytes promotes π – π interactions, while their structural diversity and the presence of closely related interferences require sorbents with high discriminatory capability. In this context, the synthesis of advanced sorbent materials has become an active area of research, driving the development of microextraction techniques and expanding their applicability to complex matrices [19,20]. Representative examples include the use of molecularly imprinted polymers for the determination of phenolic acids in fruit juice samples using microextraction formats [21], amino-functionalized covalent organic framework-modified Fe_3O_4 magnetic nanoparticles for the selective enrichment of flavonoid glycosides from plant fruit extracts [22], and Co–Al layered double hydroxide films for the determination of quercetin in fruit juices by thin-film microextraction [23].

Recent literature includes several reviews addressing specific aspects of this topic. Jano et al. [13] examined miniaturized solid-phase extraction techniques applied to food matrices, whereas Drabińska et al. [24] provided an overview of sorbent-based extraction techniques in food analysis, with particular emphasis on volatile compounds and contaminants. Nomngongo et al. [25] reviewed the development of advanced sorbent materials for analytical sample preparation without matrix-specific restrictions, while Lama-Muñoz et al. [26] discussed extraction systems and analytical techniques for phenolic compounds in foods. Similarly, Jin et al. [16] analyzed the application of advanced materials in solid-phase microextraction for natural products. However, to the best of the authors' knowledge, the available literature does not provide a critical synthesis integrating advanced sorbents, miniaturized solid-phase extraction techniques, and phenolic compounds in plant-derived food matrices within a framework organized according to sorbent architecture and the reported interaction mechanisms.

The present study aims to critically analyze, through a systematic review, the advanced sorbents employed in miniaturized solid-phase extraction techniques for the determination of phenolic compounds in plant-derived food matrices. The analysis is organized according to the structural platform of these materials in order to examine how sorbent architecture is associated with the reported interaction mechanisms and to interpret analytical performance within its appropriate context. Through this approach, the review seeks to identify

methodological trends, recurring limitations, and knowledge gaps in the literature, thereby contributing to a more comprehensive understanding of this research field.

2. Materials and Methods

2.1. Literature Search Strategy

A systematic literature search was conducted to identify studies reporting the application of advanced sorbents in miniaturized solid-phase extraction techniques for the determination of phenolic compounds in plant-derived food matrices. The retrieved studies were assessed for eligibility through a systematic selection process and subsequently analyzed using a structured narrative synthesis with a critical perspective. This review is reported in accordance with the PRISMA 2020 guidelines [27], adapted to the context of analytical chemistry reviews.

The literature search was performed in the Scopus (Elsevier, Amsterdam, The Netherlands) database on 9 March 2026 and was designed to cover the intersection of miniaturized solid-phase extraction techniques, advanced sorbent materials, phenolic compounds, and plant-derived food matrices. The search strategy was developed to maximize the retrieval of relevant studies by combining specific and general search terms. The term “food” was deliberately included to capture studies in which the food nature of the matrix was not explicitly stated in the title, abstract, or keywords. Specificity was subsequently addressed during the study selection phase.

The complete search strategy, including all search terms and Boolean operators used, is provided in the Supplementary Material S1 to ensure transparency and reproducibility of the search process. No restrictions were incorporated directly into the search query. Instead, filters for publication year (2016–2025), document type (research articles), and language (English) were applied using the Scopus filtering tools. The selected time frame was intended to capture the most recent scientific developments in this research area.

The initial search retrieved 135 records, which were reduced to 95 articles after applying the predefined filters. These records were subsequently subjected to the selection process described in Section 2.2. No additional searches were conducted in other databases or information sources. This review was not prospectively registered, and no review protocol was prepared. Due to variability in terminology and indexing practices, it is possible that some relevant studies were not retrieved if key concepts were not explicitly reported in the title, abstract, or keyword fields.

2.2. Study Selection and Eligibility Criteria

The study selection process was conducted in two stages. In the first stage, the titles, abstracts, and keywords of the identified records were screened using general eligibility criteria. Studies that could not be confidently excluded at this stage, either because they potentially met the eligibility criteria or because insufficient information was available for exclusion, were assessed in full text during a second stage using more specific inclusion criteria designed to ensure the methodological consistency and analytical relevance of the selected studies.

To be included, studies were required to simultaneously meet five predefined criteria: (I1) the presence of an actual solid-phase extraction step; (I2) implementation in a miniaturized format, assessed based on either explicit textual evidence of miniaturization within the study or recognition of the technique as miniaturized in the specialized literature [13,14], where the term miniaturized solid-phase extraction is used in a broad sense; (I3) naturally occurring phenolic compounds as the target analytes; (I4) plant-derived food matrices; and (I5) the use of advanced sorbents whose architecture, composition, or functionalization had been intentionally designed to provide targeted sorbent–analyte interactions, as established

from the recent literature on sorbent materials for miniaturized solid-phase extraction and functional nanomaterials [16,19]. The complete operational definitions of each criterion are provided in the Supplementary Material.

Studies involving both eligible plant-derived food matrices and non-eligible matrices were considered eligible provided that the plant-derived food matrix was clearly identified and independently analyzed. The extent to which results were reported separately according to matrix type was subsequently assessed during the data extraction stage. When a study failed to meet more than one full-text eligibility criterion, only a single primary reason for exclusion was assigned according to a predefined hierarchical order in order to avoid double-counting exclusion reasons.

2.3. Data Extraction

Data extraction was performed using a predefined structured template designed to ensure the consistency and traceability of the process. For each included study ($n = 37$), bibliographic, descriptive, operational, and analytical performance variables were recorded according to the definitions provided in Table S1.

Analytical performance parameters, including the limit of detection (LOD), recovery (%), and relative standard deviation (RSD), were extracted for descriptive purposes to support their contextual interpretation within the narrative synthesis. For LOD and recovery, only data reported for plant-derived food matrices were considered. In studies involving mixed matrices, only results that could be unequivocally attributed to the eligible plant-derived food matrix were included. For RSD, values considered representative of the overall analytical performance of the method were prioritized according to the criteria described in Table S1. Data were recorded at the study level; when multiple values were reported, they were summarized as minimum–maximum ranges, whereas the mean value reported by the authors was used when individual values were not provided. In addition, qualitative information was extracted regarding sorbent characteristics, reported interaction mechanisms, and other contextual aspects of the analytical methods, including matrix effect evaluation, sorbent reusability, and analytical sustainability, to support the critical interpretation of the findings.

Variables were coded according to the conventions described in Section S3 when they were not reported or when their extraction was not feasible under the conditions of the study. No inferences or imputations were made in cases of incomplete or ambiguous information. Categorical variables were coded using predefined operational criteria, the full details of which are presented in Table S1. Extraction techniques were grouped into major categories according to the terminology used by the original authors, with methodological variants classified under their corresponding extraction technique. The predominant phenolic subclass was assigned at the study level as the subclass representing $\geq 50\%$ of the phenolic compounds determined; studies that did not meet this threshold or presented a tie were classified as Mixed. Sorbents were classified according to their predominant structural platform, defined as the component primarily responsible for the dominant interaction with the target analytes. For composite materials, classification followed the decision hierarchy described in Table S2.

Regarding the distribution by food matrix, a single study could be represented in more than one matrix category when it included multiple eligible plant-derived food matrices. Consequently, the total number of occurrences may exceed the total number of included studies. Data extraction was performed by a single reviewer using a structured and reproducible procedure, without the use of automation tools or contact with the authors of the included studies.

2.4. Data Synthesis

Because of the substantial heterogeneity among the included studies, arising from differences in extraction techniques, sorbent types, plant-derived food matrices, target analytes, and experimental conditions, a quantitative synthesis was not considered appropriate, and therefore no meta-analysis was performed. Instead, the evidence was analyzed through a structured narrative synthesis with a critical perspective, without statistical aggregation across studies. For the same reason, no formal statistical methods were applied to explore heterogeneity, and no sensitivity analyses were conducted. Likewise, no formal methods were used to assess reporting bias arising from missing results.

For the overall characterization of the evidence base, the distributions of extraction techniques, sorbent structural platforms, predominant phenolic subclasses, and food matrix categories were calculated using the complete set of included studies ($n = 37$). For the distribution by food matrix category, because 8 of the 37 studies included matrices belonging to more than one category, percentages were calculated based on the total number of matrix assignments ($n = 48$). These results are presented in Section 3.2 as descriptive distribution figures.

For data analysis and interpretation, sorbent platforms were grouped into five analytical categories according to their frequency within the evidence base: molecularly imprinted sorbents ($n = 12$), functionalized polymeric sorbents ($n = 8$), functional carbon-based sorbents ($n = 6$), layered inorganic materials ($n = 3$), and underrepresented platforms ($n = 8$). Analytical performance parameters were reported in tables organized by sorbent category, presenting the values reported in each included study. Because the heterogeneity in extraction techniques, matrices, number of analytes, and experimental conditions precluded direct comparison, recovery and RSD values were additionally summarized as descriptive ranges derived from the studies within each sorbent category for illustrative purposes only, whereas LOD values were reported using the original units provided in each publication. Analytical performance was interpreted by considering the structural characteristics of the sorbent materials, the reported interaction mechanisms, the nature of the evaluated matrices and analytes, and, where relevant, the experimental conditions under which the reported performance was achieved, adopting an interpretative approach without inferring direct causal relationships between sorbent architecture and analytical performance.

The cross-sectional analysis presented in Section 3.8 was based on patterns observed across the entire set of included studies, considering variable distributions, relationships between categories, reporting limitations, and recurring patterns in sorbent architecture and their reported interaction mechanisms. The research gaps identified in Section 3.9 were derived from the distribution patterns of the included studies and the limitations identified during the analysis, complemented, where necessary, by references to the broader literature to contextualize their analytical relevance.

3. Results

3.1. Literature Search and Study Selection

The literature search and study selection process is summarized in Figure 1. Of the 95 records retrieved from the Scopus database, 37 were excluded during the initial screening stage, leaving 58 articles for full-text assessment. Following the second stage of evaluation, an additional 21 studies were excluded, and 37 studies were ultimately included in the review.

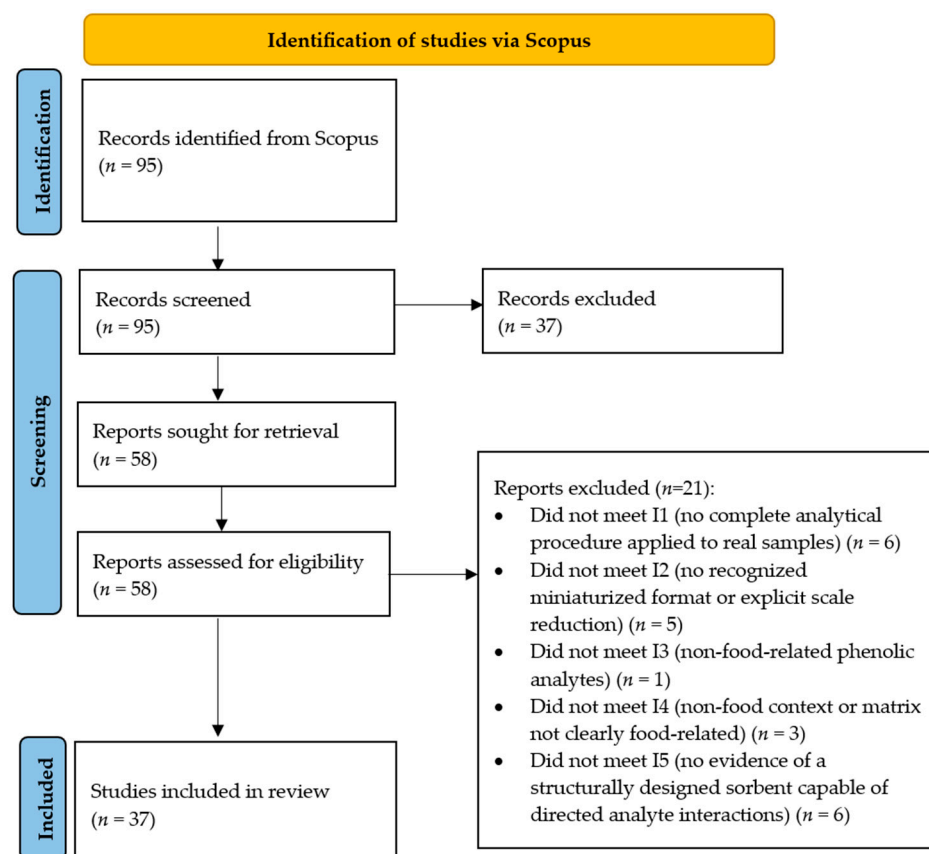


Figure 1. PRISMA flow diagram of the study selection process.

During the full-text assessment stage, inclusion criteria I1 and I5 accounted for the highest number of exclusions, with six studies excluded under each criterion. For I1, exclusions corresponded to studies that did not report a complete analytical procedure for the determination of analytes in real samples, as instrumental quantification was performed solely to characterize sorbent performance or extraction efficiency. Regarding I5, studies were excluded because the sorbents employed did not provide evidence of a deliberately designed structural and functional architecture capable of establishing targeted sorbent–analyte interactions. This included commercially available sorbents used without structural modification, as well as materials for which the reported information did not provide sufficient structural or functional evidence to reasonably support the existence of targeted sorbent–analyte interactions. Five studies were excluded under I2 because they employed extraction techniques that are not recognized as inherently miniaturized formats and did not explicitly report any scale reduction relative to conventional methods. Three studies were excluded under I4 because they investigated plant matrices exclusively in medicinal or pharmacological contexts, or because the matrices could not be unequivocally identified as food products. Finally, one study was excluded under I3 because the target analytes were contaminant phenolic compounds, which fell outside the scope of the present review.

To illustrate the operational application of the eligibility criteria during the full-text assessment, several representative examples are presented. Bagheri and Ghaedi [28] reported a dispersive solid-phase extraction method employing a solvothermally synthesized copper-based metal–organic framework (MOF), with comprehensive structural characterization and an explicitly described interaction mechanism for gallic acid in orange juice, thereby fulfilling criteria I1, I3, I4, and I5. However, the extraction technique did not correspond to any miniaturized format recognized under the eligibility criteria adopted in this review, nor did the authors report any reduction in scale relative to a conventional

procedure, resulting in exclusion under I2. Similarly, Wu et al. [29] applied magnetic solid-phase extraction for the determination of lignans in sesame oil using a $\text{Fe}_3\text{O}_4@\text{GO}$ sorbent prepared by physically mixing iron oxide nanoparticles with graphene oxide, without further functionalization of the graphene oxide. In this case, the reported information did not provide sufficient evidence of a purposefully designed functional architecture capable of supporting targeted analyte interactions, leading to exclusion under I5.

Overall, the final evidence base should be interpreted in light of the deliberately focused scope of this review. Because eligibility required the simultaneous fulfillment of all five predefined criteria, failure to meet any one criterion was sufficient to render a study ineligible for inclusion, regardless of whether other criteria were satisfied. Consequently, the resulting corpus of 37 studies reflects the scope of this review rather than a comprehensive account of the broader literature beyond it.

3.2. General Characteristics of the Included Studies

During the first half of the study period, the number of publications exhibited an increasing trend, rising steadily from 2016 ($n = 1$) to reach its highest level in 2019 ($n = 7$). This publication rate remained relatively stable in 2020 and 2021 ($n = 6$ for each year), followed by a marked decline in 2022 ($n = 1$) and a partial recovery over the subsequent years (2023: $n = 2$; 2024: $n = 3$; 2025: $n = 2$). Overall, the 2018–2021 period accounted for 65% of all included studies.

Descriptive distributions of extraction techniques, predominant phenolic subclasses, and sorbent structural platforms were calculated using the complete set of included studies ($n = 37$), whereas the distribution by food matrix category was calculated based on the total number of matrix assignments ($n = 48$), as some studies included matrices belonging to more than one category. These distributions are presented in Figure 2.

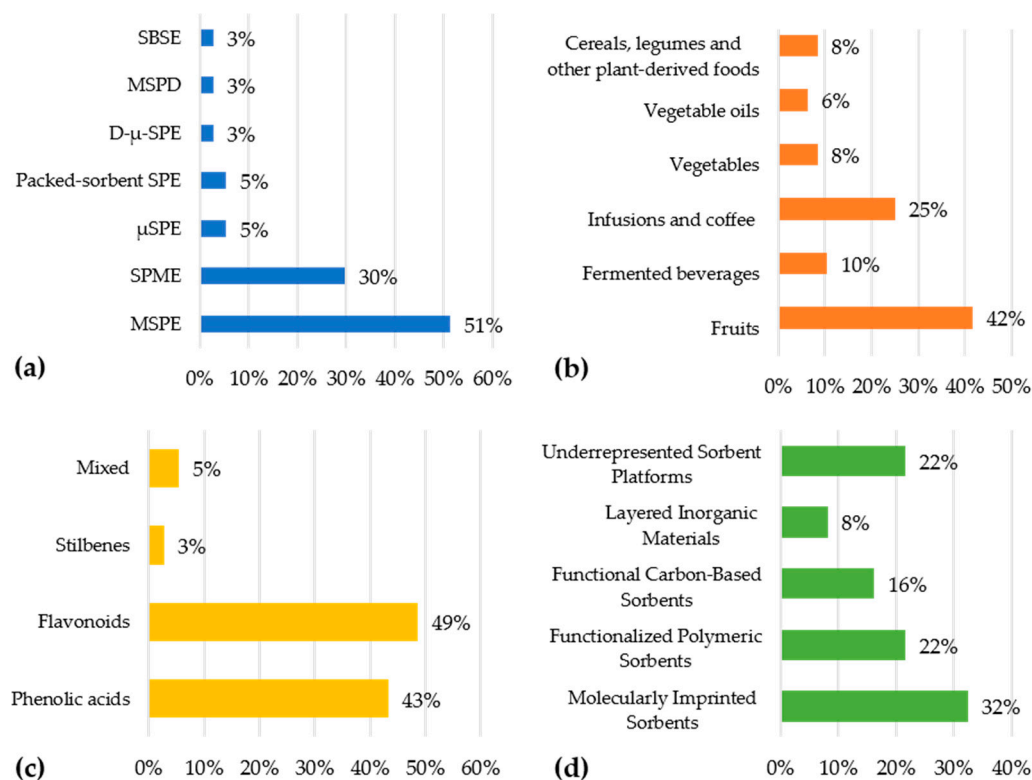


Figure 2. Distribution of the included studies according to (a) extraction technique, (b) food matrix category, (c) predominant phenolic subclass, and (d) sorbent structural platform.

The distribution of extraction techniques revealed a clear predominance of magnetic solid-phase extraction (MSPE), which was employed in 51% of the included studies, followed by solid-phase microextraction (SPME), accounting for 30%. The remaining extraction techniques identified—micro solid-phase extraction (μ SPE), packed-sorbent SPE, dispersive micro solid-phase extraction (D- μ -SPE), matrix solid-phase dispersion (MSPD), and stir bar sorptive extraction (SBSE)—each represented 5% or less of the included studies.

Fruit-based matrices, defined in this review as fresh fruits, natural and commercial fruit juices, and other edible fruit-derived fractions, represented the predominant food matrix category (42%), followed by tea infusions and coffee (25%). The remaining matrix categories each accounted for 10% or less of the total observations.

Flavonoids were the most frequently investigated phenolic subclass, representing 49% ($n = 18$) of the included studies, followed by phenolic acids (43%, $n = 16$). Stilbenes were the primary target analytes in only one study (3%), which focused on trans-resveratrol, whereas studies classified as Mixed accounted for the remaining 5% ($n = 2$).

Molecularly imprinted polymers (MIPs) constituted the most prevalent sorbent structural platform (32%, $n = 12$), followed by functionalized polymeric sorbents and under-represented platforms, each accounting for 22% ($n = 8$), functional carbon-based sorbents (16%, $n = 6$), and layered inorganic materials (8%, $n = 3$). Overall, 62% of the included studies ($n = 23$) employed sorbents incorporating a magnetic component. This strategy was distributed across multiple structural platforms, including MIPs (6 of 12 studies), functionalized polymeric sorbents (8 of 8), and carbon-based sorbents (5 of 6), whereas none of the included layered double hydroxide (LDH) materials incorporated magnetic functionality.

These findings suggest that magnetization represents a broadly applicable separation strategy that can be integrated into different sorbent architectures. This pattern is consistent with the predominance of MSPE as the most frequently employed extraction technique. This predominance may also reflect the operational advantages of magnetic separation, including the avoidance of cartridge packing and the associated risk of column blocking and high pressure, as well as a simpler and more rapid phase separation compared with centrifugation or filtration [30].

3.3. Molecularly Imprinted Sorbents (MIPs)

In the sections that follow, each sorbent platform is examined by tracing how its structural architecture gives rise to specific physicochemical features, how these features facilitate the reported interaction mechanisms, with their level of experimental support indicated where possible, and how these elements, together with the relevant extraction conditions, help interpret the analytical performance reported in the included studies.

Molecularly imprinted sorbents represent the most prevalent structural platform in this review, accounting for 12 of the 37 included studies (32.4%). Prepared through polymerization in the presence of a template molecule, these materials generate recognition cavities with shapes, sizes, and functional groups complementary to the target analyte [31]. Three main architectures were identified within this group: magnetic support-based sorbents, chitosan microspheres, and non-magnetic solid support-based sorbents.

Magnetic support-based sorbents were the most frequently reported. Those based on $\text{Fe}_3\text{O}_4/\text{SiO}_2$ employed different polymerization strategies for the molecularly imprinted layer, including bulk polymerization [32,33], precipitation polymerization [34], and sol-gel synthesis [35]. In contrast, other studies omitted the silica coating. Ma et al. [36] deposited the MIP layer by bulk polymerization directly onto chitosan-functionalized Fe_3O_4 (CS- Fe_3O_4), whereas Dramou et al. [37] prepared a surface-imprinted polymer on solvothermally synthesized magnetic graphene oxide.

Chitosan microsphere-based sorbents without a magnetic core were synthesized by emulsion polymerization [38,39]. Non-magnetic solid support-based sorbents comprised four different configurations: a sol–gel coating on stainless steel wire [40], a polymeric monolith inside a fused-silica capillary in a multicapillary fiber format [41], a polymeric monolith deposited on stainless steel wire in a microelectrode configuration [21], and an in situ synthesized silica monolith within a micropipette tip [42]. Collectively, these architectures illustrate design strategies aimed at combining molecular selectivity with either simplified sorbent recovery or direct integration into the extraction device.

Deep eutectic solvents (DESs) were incorporated into the imprinting systems with distinct functional roles, serving as the primary functional monomer [32,36], simultaneously as both functional monomer and template molecule [39], a co-monomer together with (3-aminopropyl)triethoxysilane (APTES) [38], or a modifier while methacrylic acid (MAA) served as the principal functional monomer [33]. In addition, several studies employed multi-template imprinting, using two or more template molecules [32,33,35].

Molecular recognition through specific binding cavities constituted the primary retention mechanism in all MIP-based sorbents. Hydrogen bonding between analyte functional groups and functional monomers such as APTES, (3-aminopropyl)trimethoxysilane (APTMS), or MAA was the most frequently reported complementary interaction. In systems where APTES or APTMS served as the principal functional monomer, analyte retention exhibited pH dependence associated with the protonation of amino groups: under highly acidic conditions, protonation reduced the ability of these groups to form hydrogen bonds with analyte hydroxyl groups, whereas moderately acidic conditions favored these interactions [40]. Asfaram et al. [34] reported a similar pH-dependent behavior attributed to protonation of the amino groups of APTES used to functionalize the support, irrespective of the use of MAA as the functional monomer.

Beyond this general pattern, several studies proposed additional mechanisms specific to their particular monomer or support configuration. In systems employing DESs as the principal functional monomer, analyte retention was attributed to the functional groups of the DES capable of participating in hydrogen-bonding interactions [32,36]. Li et al. [33] showed that the DES-modified MMIP exhibited higher adsorption capacity than the corresponding non-DES MMIP, supporting a beneficial effect of DES modification; the authors further proposed that ionic interactions and hydrogen bonding between the isoflavone analytes and the DES contributed to the observed pH-dependent extraction behavior, although the specific role of each interaction was not directly evaluated experimentally. Dramou et al. [37] attributed adsorption to the simultaneous contribution of π – π and hydrophobic interactions associated with the carbon-based support, whereas Zheng et al. [21] combined the specific recognition interactions proposed for the imprinted cavities—hydrogen bonding, dipole–dipole interactions, and ion exchange with the dissociated analytes—with an externally applied electric field that directed the ionized analytes toward the sorbent, a transport-enhancing strategy unique within this group. Overall, the selection of both the functional monomer and the support material shapes the interaction mechanisms available and, consequently, the potential for selective molecular recognition, although this relationship has not been systematically investigated.

A schematic summary of the MIP architectures and molecular recognition features discussed in this section is presented in Figure 3. The figure summarizes the three MIP architectures identified among the included MIP studies, their shared molecular recognition through complementary imprinted cavities, and the complementary interactions reported across the included MIP studies, including hydrogen bonding as the most frequently reported complementary interaction and additional interactions reported or proposed in specific systems.

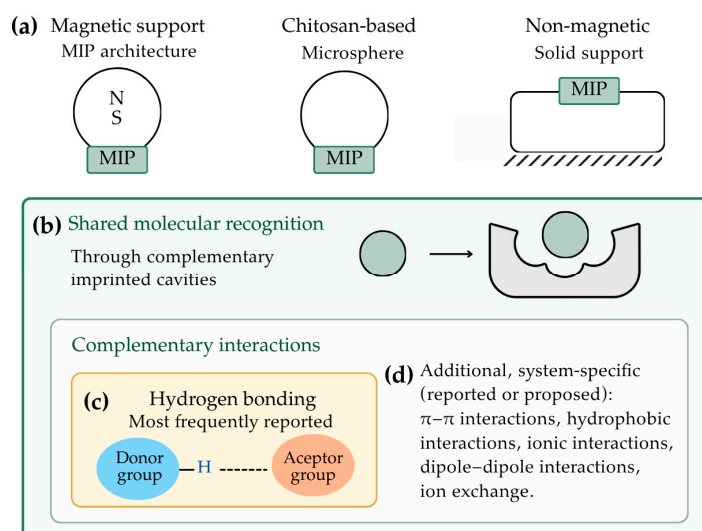


Figure 3. Molecularly imprinted sorbent (MIP) architectures and their shared molecular recognition mechanism. (a) The three MIP architectures identified among the included studies. (b) Shared molecular recognition through complementary imprinted cavities. (c) Hydrogen bonding as the most frequently reported complementary interaction. (d) Additional interactions reported or proposed in specific systems. The schematic does not assign specific interaction mechanisms to individual architectures.

Solid support-based sorbents are inherently associated with the SPME format, as the direct immobilization of the MIP onto the substrate is an intrinsic requirement of this technique [43]. This configuration was employed by Rahimi et al. [40], Chen and Huang [41], and Zheng et al. [21], the latter further incorporating electric field-assisted SPME (EE-SPME), in which an externally applied electric field promotes the migration of ionized analytes toward the sorbent and accelerates the extraction process. Arabi et al. [42], also using a solid support, employed pipette-tip solid-phase extraction (PT-SPE). In contrast, dispersed magnetic sorbents were used in extraction formats relying on magnetic separation with an external magnet, including MSPE [33,36,37], dispersive magnetic solid-phase microextraction (DM-SPME) [32], dispersive micro solid-phase extraction (D- μ -SPE) [34], and syringe-to-syringe magnetic solid-phase microextraction (SS-MSPME), a configuration designed to enhance sorbent–sample contact [35]. Chitosan-based sorbents without a magnetic core, by comparison, were applied in non-dispersive formats involving mechanical separation, namely pipette-tip μ SPE [37] and μ SPE with centrifugation-assisted separation [39].

As shown in Table 1, tea and fruit-derived matrices, including fruit juices and peels, were the most frequently investigated matrices within this group. The prominent representation of tea is consistent with its high polyphenol content and the increasing analytical interest in their determination [44]. Likewise, the well-established richness of fruits in phenolic compounds [45] likely explains their extensive representation. Other matrices investigated included vegetables [34], beer [41], coffee [40], and soybean [33]. Regarding the target analytes, flavonoids constituted the predominant phenolic subclass within this group, with quercetin and catechin among the most frequently investigated compounds, followed by phenolic acids. The abundance of hydroxyl groups in these molecules facilitates hydrogen-bond formation with the functional monomers of the MIP, which may account for their predominance in this sorbent platform. Most methods were designed for the selective determination of a predefined set of target phenolic compounds (typically 1–6 analytes per study), although Li et al. [33] and Li and Row [32] adopted a broader multiclass approach that also included non-phenolic compounds.

Table 1. Representative studies using MIPs to determine phenolic compounds in plant-derived food matrices.

Ref.	Sorbent	Extraction Technique	Matrix	Analytes (<i>n</i>)	Dominant Phenolic Subclass	LOD	Rec. (%)	Intraday RSD (%)	Interday RSD (%)	EF	Detection Technique
[41]	PIL/MIP	MMF-SPME	Fruit juice, beer	DBA, CA, VA, HFA, FA (5)	Phenolic acids	0.011–0.24 µg L ^{−1}	72.1–111	2.3–9.5	2.2–9.4	NR	HPLC-DAD
[42]	MISM	PT-SPE	Orange juice	GA (1)	Phenolic acids	7.0 µg L ^{−1}	92.5–101.0	2.7–4.5	1.6–4.5	120	HPLC-UV
[34]	Fe ₃ O ₄ @SiO ₂ @MIP	D-µ-SPE	Spinach, red and white onions, celery, broccoli, watercress, apple juice	Que (1)	Flavonoids	0.113–0.117 µg L ^{−1}	95.44–106.89	0.89–5.63	NR	97.41–101.09	HPLC-UV
[33]	DES-MMIP	MSPE	Glycine max (Linn.) merr, green tea	Gli, Gen, Dai, EC, EGCG, ECG (6)	Flavonoids	0.05 µg mL ^{−1}	ND	<4.62	NR	NR	HPLC-UV
[32]	Fe ₃ O ₄ -TDES-MIPs	DM-SPME	Green tea	(+)-Cat, CA (2)	Mixed	NR	86.17–92.32	<4.76	<4.76	NR	HPLC-UV
[40]	MIP-SS	DI-SPME	Black and green teas, coffee	Que (1)	Flavonoids	9.94 ng mL ^{−1}	94.20–98.50	2.09–4.03	2.58–4.83	NR	HPLC-UV
[37]	MGO-MIP	MSPE	Green tea	Que (1)	Flavonoids	0.09 ng mL ^{−1}	95.46–100	4.27–7.41	0.68–4.40	NR	HPLC-UV
[35]	Fe ₃ O ₄ @SiO ₂ -MDMIP	SS-MSPME	Pomegranate, grape, orange	p-CA, FA (2)	Phenolic acids	0.07–0.08 ng mL ^{−1}	85.12–94.96	2.73–3.36	4.19–4.80	104.2–113.8	HPLC-UV
[39]	MICSM	µSPE	Pear rind	PHBA (1)	Phenolic acids	0.08–0.24 µg mL ^{−1}	87.86–103.65	3.08–4.25	3.12–4.32	NR	HPLC-UV
[38]	HMICS	µSPE	Green tea	Cat (1)	Flavonoids	0.09–0.24 µg mL ^{−1}	90.02–101.45	2.78–4.53	3.08–5.04	NR	HPLC-DAD
[21]	MBM	EE-SPME	Fruit juices	VA, FA, HPPA, HMPA (4)	Phenolic acids	0.042–0.15 µg L ^{−1}	90.5–110	3.3–7.0	2.8–7.3	NR	HPLC-DAD
[36]	Fe ₃ O ₄ -CTS@DES-MIPs	MSPE	Black tea	(+)-Cat, (−)-EC, EGCG (3)	Flavonoids	0.15–0.50 µg mL ^{−1}	88.3–98.1	2.92–6.80	1.78–6.84	NR	HPLC-UV

Abbreviations: EF: Enrichment factor; PIL/MIP: molecularly imprinted polymer based on a polymeric ionic liquid; MISM: molecularly imprinted silica monolith; Fe₃O₄@SiO₂@MIP: core-shell magnetic molecularly imprinted polymer; DES-MMIP: multi-template magnetic molecularly imprinted polymer based on a deep eutectic solvent; Fe₃O₄-TDES-MIPs: ternary deep eutectic solvent-based magnetic molecularly imprinted polymer; MIP-SS: sol-gel molecularly imprinted polymer on stainless steel wire; MGO-MIP: molecularly imprinted polymer on magnetic graphene oxide; Fe₃O₄@SiO₂-MDMIP: double-template magnetic molecularly imprinted polymer; MICSM: molecularly imprinted chitosan microspheres; HMICS: hydrophilic molecularly imprinted chitosan microspheres; MBM: monolithic molecularly imprinted microelectrode; Fe₃O₄-CTS@DES-MIPs: deep eutectic solvent-based chitosan magnetic molecularly imprinted polymer; MMF-SPME: multiple monolithic fiber solid-phase microextraction; PT-SPE: pipette tip solid-phase microextraction; D-µ-SPE: dispersive micro solid-phase extraction; MSPE: magnetic solid-phase extraction; DM-SPME: dispersive magnetic solid-phase microextraction; DI-SPME: direct immersion solid-phase microextraction; SS-MSPME: syringe-to-syringe magnetic solid-phase microextraction; µSPE: micro solid-phase extraction; EE-SPME: electro-assisted solid-phase microextraction; DBA: 3,4-dihydroxybenzenepropanoic acid; CA: caffeic acid; VA: vanillic acid; HFA: hydroferulic acid; FA: ferulic acid; GA: gallic acid; Que: quercetin; Gli: glycitein; Gen: genistein; Dai: daidzein; EC: epicatechin; (−)-EC: (−)-epicatechin; EGCG: epigallocatechin gallate; ECG: epicatechin gallate; Cat: catechin; (+)-Cat: (+)-catechin hydrate; p-CA: p-coumaric acid; PHBA: p-hydroxybenzoic acid; HPPA: 3-(4-hydroxyphenyl)propionic acid; HMPA: 3-(4-hydroxy-3-methoxyphenyl)propionic acid. NR: not reported. ND: data in the main text not unambiguously attributable to an eligible matrix. The values correspond to ranges extracted at the study level in accordance with the criteria defined in Section 2.3.

The analytical performance data reported for this group are summarized in Table 1, following the extraction criteria described in Section 2.3. Recovery values ranged from 72.1% to 111%, whereas intra-day and inter-day RSDs ranged from 0.89–9.5% and 0.68–9.4%, respectively, based on the minimum–maximum values reported across studies. Only three studies reported enrichment factors, all exceeding 97, indicating a high preconcentration capability for matrices containing low analyte concentrations. However, differences in analytical conditions among studies preclude direct comparison of the reported performance values.

Overall, the data summarized in Table 1 indicate generally satisfactory analytical performance for MIP-based methods. These generally favorable extraction outcomes are consistent with the selective molecular recognition conferred by the imprinted cavities, with hydrogen bonding representing the most frequently reported complementary interaction, together with additional interaction mechanisms reported in specific systems. Nevertheless, differences among individual methods likely also reflect monomer chemistry, support configuration, analyte and matrix characteristics, and extraction conditions, rather than imprinting-related recognition alone. Furthermore, differences in analytical conditions and the incomplete reporting of selected validation parameters limit broader cross-study comparisons.

Regarding sorbent reusability, solid support-based systems exhibited the highest stability, remaining effective for 50 extraction cycles [21,41] and 25 cycles [40], whereas dispersed magnetic systems generally sustained between 4 and 9 cycles [34,35,37], potentially requiring more frequent replacement during routine analytical use. Yuan et al. [38], the only chitosan-based system reporting this parameter, remained reusable for 8 cycles. The remaining studies in this group did not report sorbent reusability.

With respect to the availability of analytical validation parameters, 10 of the 12 studies reported the LOD, recovery, and at least one measure of analytical precision. In the studies by Li et al. [33] and Li and Row [32], some analytical performance parameters could not be verified from the materials available for the present review.

Finally, none of the studies within this group performed a formal quantitative assessment of matrix effects, representing a significant limitation given that sugars, proteins, and organic acids commonly present in plant-derived food matrices may be co-extracted and interfere with analyte quantification [26]. Likewise, although several studies highlighted environmental advantages such as reduced solvent consumption [21,35,41], none employed formal analytical sustainability assessment tools such as AGREE [46], AGREEprep [47], or related metrics. The incorporation of these tools would enable a more systematic evaluation of the environmental impact of these analytical methodologies.

Overall, the analytical performance of MIP-based sorbents should be interpreted in light of monomer chemistry, support configuration, analyte and matrix characteristics, and extraction conditions, rather than attributed to molecular imprinting alone. The selectivity conferred by molecular recognition represents both the principal strength of this platform and its main limitation, as it may restrict applicability to other phenolic subclasses.

3.4. Functionalized Polymeric Sorbents

Functionalized polymeric sorbents were identified in 8 of the 37 included studies (21.6%). In these materials, the polymeric component, whose chemical composition determines the nature of the interactions with the target analytes, constitutes the active phase responsible for analyte retention.

In seven of the eight studies, stepwise surface modification of Fe₃O₄ served as the predominant synthesis strategy, giving rise to three principal architectural variants. The first comprised polymers deposited through oxidative polymerization, including poly-

dopamine [48], obtained by self-polymerization under alkaline conditions, and polypyrrole [49], synthesized in the presence of an oxidizing agent. The second included functional polymers incorporated by surface deposition or free-radical copolymerization, namely chitosan [50], deposited onto the magnetic surface during coprecipitation, a calixarene-based poly(ionic liquid) possessing a macrocyclic cavity [51], and a methacrylate copolymer bearing quaternary ammonium groups [52]. The third encompassed more structurally complex architectures, including a covalent organic polymer (COP) network containing imine linkages synthesized via a Schiff base reaction, which exhibited a porous structure within the lower mesoporous range and suboptimal crystallinity acknowledged by the authors as a design limitation [53], and the $\text{Fe}_3\text{O}_4\text{@PGMA@PNIPAAm}$ three-layer system, in which the poly(glycidyl methacrylate) (PGMA) layer was prepared by atom transfer radical polymerization (ATRP) to control the grafting degree of the thermoresponsive poly(N-isopropylacrylamide) (PNIPAAm) layer [54]. Chen et al. [55] represented the only exception to this synthetic approach, incorporating the nanoparticles directly during in situ polymerization inside a fused-silica capillary to produce a monolithic extraction format in which an external magnetic coil modulated the magnetic field throughout the extraction process.

Most studies described the simultaneous contribution of two or more interaction mechanisms between the sorbent and the target analyte. Hydrogen bonding and π – π interactions were the most frequently reported mechanisms, followed by hydrophobic interactions. Their relative contribution depended on the chemical composition of the polymeric coating. In the COP-based sorbent, the high density of aromatic rings and imine groups was proposed to enable the concurrent contribution of hydrogen-bonding, π – π , and hydrophobic interactions, consistent with the markedly higher adsorption capacity observed for the COP-coated material relative to the uncoated magnetic core [53]. In the calixarene-based system, these interactions were complemented by dipole–dipole interactions and potential host–guest molecular recognition [51]. For polydopamine, electrostatic interactions were proposed as the dominant mechanism among several concurrent interactions [48], whereas in the chitosan-based sorbent, hydrogen bonding constituted the principal retention mechanism, with a possible contribution from physical adsorption [50]. Chen et al. [55] reported that pH influenced the balance among the interaction mechanisms proposed to explain analyte retention, with π – π interactions predominating under acidic conditions and additional hydrophobic, hydrogen-bonding, and dipole–dipole interactions becoming relevant at higher pH values. A similar pH-dependent shift, from hydrophobic interactions toward possible electrostatic and ion-exchange mechanisms, was reported by Liu et al. [52]. Khosravi et al. [49] proposed electrostatic attraction as the principal driver of retention in light of the observed pH-dependent behavior, representing the only case in this group in which no other interaction mechanisms were considered. The system developed by Li et al. [54] exhibited a distinctive behavior governed by the thermoresponsive transition of PNIPAAm between hydrophilic and hydrophobic conformations at approximately 32 °C, with adsorption controlled by chemical interactions occurring at heterogeneous binding sites according to the adsorption models applied.

The diversity of interaction mechanisms identified within this group is consistent with the heterogeneity in the chemical composition of the polymeric coatings and may be associated with differences in the extraction performance of each sorbent platform. However, the variability in the experimental conditions among studies precludes drawing definitive conclusions regarding this relationship.

MSPE was the predominant extraction technique in this group, being employed in seven of the eight studies, which is consistent with a common structural characteristic of these sorbents: the polymeric functionalization of the Fe_3O_4 surface. Although the

polymer coating reduced the saturation magnetization relative to the uncoated magnetic core, all studies demonstrated sufficient magnetic responsiveness for efficient separation, as verified by vibrating sample magnetometry (VSM). Among these studies, Li et al. [54] employed a microwave-assisted magnetic solid-phase extraction (MAE-MSPE) approach that was particularly compatible with the thermoresponsive nature of the developed sorbent. Because the PNIPAAm layer requires thermal stimulation to trigger its hydrophilic-to-hydrophobic conformational transition, microwave irradiation provided a rapid and efficient heating mechanism, completing the process in approximately 1 min. By contrast, Chen et al. [55] employed magnetism-assisted in-tube solid-phase microextraction (MA/IT-SPME), a configuration well suited to the monolithic architecture of their sorbent, in which Fe_3O_4 nanoparticles were embedded within the fixed polymeric matrix of the capillary. Unlike dispersed magnetic systems, this format does not require particle recovery, and the externally applied magnetic field serves instead to modulate extraction efficiency.

As shown in Table 2, most of the investigated matrices were fruit-derived samples, primarily commercial fruit juices and fruit extracts. Their predominance is consistent with the pattern observed in other sorbent groups in this review and is likely attributable to the well-established abundance of phenolic compounds in fruits. Additional matrices included tea [49,51], wine [48], coffee [50], olive oil [54], purple rice [50], soybean, *Dioscorea bulbifera* L. [53], and vegetables such as spinach and tomato [50]. Regarding the predominant phenolic subclasses, flavonoids and phenolic acids were equally represented, each being the primary target in four studies. Both subclasses share aromatic rings and hydroxyl groups, structural features that are compatible with the dominant retention mechanisms observed for these sorbents. The number of target analytes ranged from 1 [49] to 11 [48], and all studies adopted a targeted analytical strategy focusing on predefined groups of phenolic compounds.

The analytical performance data for this group are summarized in Table 2. Recovery values ranged from 70.3% to 120.78%, excluding the study by Khosravi et al. [49], whose reported values could not be unequivocally attributed to eligible food matrices. Reported intra-day RSDs ranged from 0.57% to 9.8%, whereas inter-day RSDs ranged from 0.78% to 9.6% among the studies reporting these parameters. Among the available enrichment factors, the highest values were reported by Li et al. [54] (113–205), achieved through the combination of a 50 mL sample volume with a final reconstitution step in 200 μL , indicating a remarkable preconcentration capability. Nevertheless, methodological heterogeneity among studies limits the direct comparison of these analytical performance metrics.

Taken together, the performance data summarized in Table 2 indicate generally satisfactory analytical performance across this platform, consistent with the diversity of interaction mechanisms discussed above. Nonetheless, performance variability across individual studies also reflects differences in coating chemistry, support configuration, and extraction conditions.

Regarding sorbent reusability, Liu et al. [52] and Chen et al. [55] reported operational stability exceeding 30 extraction cycles, whereas Bian et al. [53], Hai et al. [50], and Li et al. [54] reported between 8 and 16 cycles, and Khosravi et al. [49] reported stable performance for more than 16 extraction cycles. The remaining studies did not provide reusability data. The monolithic configuration developed by Chen et al. [55] avoided the repeated dispersion and recovery steps characteristic of dispersed sorbents. However, the similarly high reusability reported for the dispersed magnetic system of Liu et al. [52] suggests that operational stability may be influenced by factors beyond support configuration alone.

Table 2. Representative studies using functionalized polymeric sorbents to determine phenolic compounds in plant-derived food matrices.

Ref.	Sorbent	Extraction Technique	Matrix	Analytes (n)	Dominant Phenolic Subclass	LOD	Rec. (%)	Intraday RSD (%)	Interday RSD (%)	EF	Detection Technique
[48]	Fe ₃ O ₄ @pDA	MSPE	White grape and lychee wines	GA, CGA, CA, p-CA, FA, SA, Cat, EC, Rut, Que, Hes (11)	Phenolic acids	0.01–0.29 ng mL ^{−1}	80.03–120.78	NR	NR	NR	LC-MS/MS
[53]	Fe ₃ O ₄ @TAPM-TFPB	MSPE	Orange, soybean, <i>Dioscorea bulbifera</i> L.	Hes, Nar, Pin, Dai, Fmn, Lqg (6)	Flavonoids	ND	80.0–114.8	0.57–4.41	1.24–7.67	NR	LC-MS/MS
[55]	MCC@Fe ₃ O ₄	MA/IT-SPME	Fruit juices	CA, VA, DPA, HMPA, FA (5)	Phenolic acids	0.012–0.061 µg L ^{−1}	80.1–116	1.9–9.8	3.8–9.1	NR	HPLC-DAD
[49]	Fe ₃ O ₄ @PPy	MDSPE	Black tea	Que (1)	Flavonoids	ND	ND	4.44	NR	NR	IMS
[50]	CS@Fe ₃ O ₄	MD-µSPE	Coffee beans, purple rice, spinach, tomato, orange, kiwi	GA, Cat, CA, FA (4)	Phenolic acids	0.02–0.16 µg mL ^{−1}	95.0–99.4	0.9–3.3	1.4–4.9	NR	HPLC-UV
[54]	Fe ₃ O ₄ @PGMA@PNIPAAm	MAE-MSPE	Olive oil	VA, SiA, p-CA, FA, t-CA (5)	Phenolic acids	0.005–0.030 µg L ^{−1}	84.6–108.1	1.36–3.98	0.78–4.85	113–205	UPLC-MS/MS
[52]	Fe ₃ O ₄ @MDHM	MSPE	Grape juice	Que, Lut, Kae, Api (4)	Flavonoids	0.080–0.12 µg L ^{−1}	70.3–120	1.4–9.6	2.5–9.6	60–69	HPLC-DAD
[51]	poly(CalixIL)-MNPs	MSPE	Grape juice, green tea	Myr, Que, Lut, Kae, Api (5)	Flavonoids	0.15–0.75 ng mL ^{−1}	92.5–104.8	1.5–4.5	2.3–5.2	NR	HPLC-DAD

Abbreviations: EF: Enrichment factor; Fe₃O₄@pDA: magnetic nanoparticles coated with polydopamine; Fe₃O₄@TAPM-TFPB: magnetic nanoparticles with tetraamine and trialdehyde ligands; MCC@Fe₃O₄: monolithic capillary column with magnetic nanoparticles; Fe₃O₄@PPy: magnetic nanoparticles coated with polypyrrole; CS@Fe₃O₄: chitosan-coated magnetic nanoparticles; Fe₃O₄@PGMA@PNIPAAm: magnetic nanoparticles with a thermosensitive methacrylate-acrylamide polymer; Fe₃O₄@MDHM: magnetic nanoparticles functionalized with long-chain amine; poly(CalixIL)-MNPs: magnetic nanoparticles with poly(calixarene ionic liquid); MSPE: magnetic solid-phase extraction; MA/IT-SPME: magnetically assisted in-tube solid-phase microextraction; MDSPE: magnetic dispersive solid-phase extraction; MD-µSPE: magnetic dispersive micro-solid-phase extraction; MAE-MSPE: microwave-assisted magnetic solid-phase extraction; GA: gallic acid; CGA: chlorogenic acid; CA: caffeic acid; p-CA: p-coumaric acid; FA: ferulic acid; SA: sinapic acid; Cat: catechin; EC: epicatechin; Rut: rutin; Que: quercetin; Hes: hesperetin; Nar: naringenin; Pin: pinocembrin; Dai: daidzein; Fmn: formononetin; Lqg: liquiritigenin; VA: vanillic acid; DPA: 3-(3,4-dihydroxyphenyl)propionic acid; HMPA: 3-(4-hydroxy-3-methoxyphenyl)propionic acid; SiA: syringic acid; t-CA: trans-cinnamic acid; Lut: luteolin; Kae: kaempferol; Api: apigenin; Myr: myricetin. NR: not reported. ND: existing data not unambiguously attributable to an eligible matrix or phenolic analyte.

With respect to analytical performance reporting, five studies provided all three parameters considered in this review. The remaining three studies presented only partial information: one did not report RSD values [48], another reported LOD values that could not be unequivocally attributed to eligible food matrices [53], and in the third, most analytical performance parameters could not be extracted for the same reason [49].

Evaluation of matrix effects was absent in half of the studies [49,51,52,55], representing an important limitation given that the compositional complexity of the investigated matrices increases the likelihood of co-extracting interfering substances that may affect analyte quantification [56].

Regarding analytical sustainability, only one study applied a formal sustainability assessment tool, obtaining a score of 72 points according to the Analytical Eco-Scale [50,57]. Three additional studies made qualitative claims regarding the environmental advantages of their methods without performing quantitative sustainability assessments [51–53], whereas the remaining four studies did not address this aspect.

Functionalized polymeric sorbents exhibited diverse interaction profiles that reflected the specific chemical composition of the polymeric coating, while analytical performance also varied according to support configuration and extraction conditions. Owing to this chemical and methodological heterogeneity, the available evidence precludes establishing generalizable relationships between coating composition, proposed retention mechanisms, and analytical performance.

3.5. Functional Carbon-Based Sorbents

Functional carbon-based sorbents were reported in 6 of the 37 studies analyzed (16.2%). These materials share a carbonaceous phase as the dominant retention component while differing in both the type of carbon structure employed and the surface functionalization strategy adopted.

Three main structural variants were identified within this group: functionalized graphene oxide (GO)-based materials, multi-walled carbon nanotube (MWCNT)-based materials, and velvet-like graphitic carbon nitride (V-g-C₃N₄). In all cases, the carbonaceous phase constituted the principal active component responsible for analyte retention, whereas the specific surface modification defined the structural identity of the sorbent.

The GO-based variant, represented by three studies, employed distinct functionalization strategies. Tashakkori et al. [58] deposited GO onto a stainless-steel wire through successive coating layers and subsequently immobilized the imidazolium-based ionic liquid [APMIM][NTf₂] onto the GO surface using the same layer-by-layer approach. Jafari and Hadjmohammadi [59] synthesized GO using the Hummers method, formed Fe₃O₄ nanoparticles in situ on the GO surface by coprecipitation, and subsequently incorporated chitosan to produce the ternary Fe₃O₄–CS–GO nanocomposite. Wu et al. [60] employed commercially available amino-functionalized graphene oxide (NH₂/GO) and reacted it with Fe₃O₄ precursors through a one-step hydrothermal synthesis to obtain an amino-functionalized graphene oxide magnetic nanocomposite (AGMN).

The MWCNT-based variant, represented by two studies, shared the tubular carbon framework but differed in architectural complexity. Wu et al. [61] prepared c-MWCNT-MNPs by depositing Fe₃O₄ onto carboxylated MWCNTs through hydrothermal synthesis. In contrast, Ulusoy et al. [62] developed a more sophisticated architecture by combining MWCNTs with nanodiamonds through hydrothermal synthesis, followed by Fe₃O₄ deposition via coprecipitation and the application of an external SiO₂ coating. This core–shell architecture integrates sp² and sp³ carbon domains and was associated by the authors with enhanced adsorption capacity.

The third structural variant, represented by a single study, consisted of V-g-C₃N₄, synthesized through the thermal condensation of urea and subsequently combined with Fe₃O₄ prepared by coprecipitation [63]. Its two-dimensional layered structure has promoted its application in analytical extraction processes [64].

The incorporation of Fe₃O₄ was reported in five of the six studies, where its primary function was to enable magnetic separation. The only exception was the study by Tashakkori et al. [58], whose fiber-based solid-support configuration eliminated the need for magnetic recovery using an external magnet.

In terms of sorbent–analyte interactions, the reported retention mechanisms reflect the functional diversity of the carbon-based platforms employed. π – π interactions were the most consistently reported mechanism. Wu et al. [61] attributed these interactions to the affinity between the aromatic systems of the phenolic compounds and the carbon framework of carboxylated MWCNTs, referring to them as π – π electrostatic interactions. Ulusoy et al. [62] related them to the combined sp²–sp³ electronic distribution of the MWCNT@ND architecture, noting that quercetin exhibits a similar electronic distribution, thereby promoting its affinity toward the sorbent. Fan et al. [63] attributed retention to π – π interactions arising from V-g-C₃N₄, together with hydrophobic interactions associated with the same component and hydrogen bonding provided by Fe₃O₄. The authors additionally reported that the addition of water as a co-solvent altered the solvent polarity, thereby promoting analyte transfer onto the sorbent and enhancing extraction efficiency.

The interaction profile was broader in the functionalized GO-based systems. Tashakkori et al. [58] proposed that electrostatic interactions between the imidazolium cation and ionized phenolic compounds at pH 8, together with π – π and dipole–dipole interactions between the GO–ionic liquid system and the polar functional groups of the analytes, contributed to the observed extraction performance. Wu et al. [60] proposed that the interaction pattern was pH-dependent, with π – π and hydrophobic interactions predominating under acidic conditions and ion-exchange and hydrogen-bonding interactions becoming increasingly relevant as pH approached the optimal extraction value. Jafari and Hadjmohammadi [59] reported hydrogen-bonding and π – π interactions mediated by the Fe₃O₄–CS–GO nanocomposite, in which GO and chitosan provided complementary contributions to analyte retention: GO supplied the principal active surface, whereas chitosan increased the availability of binding sites within the composite.

The wide variety of functional groups present in these materials—including epoxide, hydroxyl, carbonyl, and carboxyl groups in GO; oxygen-containing and amino groups in the amino-functionalized GO precursor of AGMN; carboxyl groups in MWCNTs; and imidazolium moieties in the ionic liquid—is consistent with this mechanistic diversity and suggests that the specific modification introduced onto the carbonaceous phase modulates the retention profile in a system-dependent manner. Although this mechanistic diversity may contribute to differences in extraction capacity and selectivity among sorbent systems, the lack of experimental evaluation of the relative contribution of each proposed interaction in studies involving multiple retention mechanisms prevents definitive conclusions.

MSPE was the predominant extraction technique within this group, being employed in five of the six studies, which is consistent with the nearly universal incorporation of Fe₃O₄ nanoparticles. These particles can be dispersed throughout the sample under agitation to maximize analyte–sorbent contact and subsequently recovered using an external magnet, thereby eliminating the centrifugation or filtration steps [30]. The study by Tashakkori et al. [58] represented the only exception, employing direct immersion solid-phase microextraction (DI-SPME), a configuration inherently suited to the fiber-based architecture of the sorbent, where direct immersion and thermal desorption constitute the intrinsic extraction operations [43].

As shown in Table 3, tea was the most frequently investigated plant-derived food matrix in this group, which may be attributed to its well-established abundance of phenolic compounds and the growing analytical interest in their determination [44]. Tashakkori et al. [58] and Wu et al. [60] investigated fermented beverages, both focusing on wine, a matrix characterized by both a high concentration and a broad diversity of phenolic compounds [65], which may explain its representation in studies of this type. Other matrices included sesame oil [61], fruit juices, and onion juice [59]. Regarding the target analytes, flavonoids constituted the predominant phenolic subclass, followed by phenolic acids, a pattern consistent with the presence of aromatic rings that favor π - π interactions with the carbonaceous phases characteristic of these sorbent platforms. The number of analytes ranged from 1 to 23. Four studies focused on relatively small groups of 1–6 compounds, whereas Tashakkori et al. [58] analyzed 12 analytes, and Wu et al. [61] analyzed 23 analytes, the latter representing the only multiclass analytical profile within this group. Nevertheless, even in studies involving larger analyte panels, the methodological design remained fundamentally targeted.

The analytical performance data for this group are summarized in Table 3. Recovery values ranged from 72.8% to 125.9%. Reported intra-day RSDs varied between 0.5% and 14.82%, whereas inter-day RSDs, reported in only two studies, ranged from 0.8% to 13.2%. Two studies reported particularly high enrichment factors (Wu et al. [60]: 110–201; Ulusoy et al. [62]: 103.7), indicating a high preconcentration capacity for matrices containing low analyte concentrations. Differences in analytical conditions among studies limit direct comparison of these values, which are therefore presented here solely as a descriptive characterization of the overall performance of functional carbon-based sorbents.

Collectively, the results summarized in Table 3 indicate generally satisfactory extraction outcomes across this platform, consistent with the diversity of interaction mechanisms discussed above. However, individual differences in performance likely also reflect the specific carbon framework, surface functionalization strategy, and extraction conditions employed in each study, rather than the reported interaction mechanisms alone.

The incorporation of Fe_3O_4 as a magnetic component represents the most common design strategy within this group, and its close correspondence with the predominance of MSPE suggests that the architectural decision to incorporate magnetic functionality is strongly associated with the selected extraction format.

Regarding sorbent reusability, a clear pattern emerged according to the support configuration. The wire-immobilized system developed by Tashakkori et al. [58] remained effective for 150 extraction cycles, substantially exceeding the 4–50 cycle range reported for nanoparticle-based dispersed systems [60–63]. Jafari and Hadjmohammadi [59] did not report this parameter. This difference may be attributed to the greater mechanical stability conferred by immobilization on a solid support, which avoids the repeated dispersion and magnetic recovery cycles experienced by nanoparticle-based sorbents and which may progressively contribute to material degradation.

With respect to analytical performance reporting, all studies provided LOD, recovery, and intra-day RSD values. However, this group also presents important limitations. A formal evaluation of matrix effects was performed only by Wu et al. [61] and Jafari and Hadjmohammadi [59], using different calculation approaches that preclude direct comparison. The remaining four studies did not assess matrix effects, despite the fact that endogenous components of the investigated food matrices may be co-extracted and interfere with analyte quantification [26]. Furthermore, none of the studies proposing multiple retention mechanisms experimentally evaluated the relative contribution of each interaction, thereby limiting the mechanistic validation of the proposed adsorption models.

Table 3. Representative studies using functional carbon-based sorbents to determine phenolic compounds in plant-derived food matrices.

Ref.	Sorbent	Extraction Technique	Matrix	Analytes (<i>n</i>)	Dominant Phenolic Subclass	LOD	Rec. (%)	Intraday RSD (%)	Interday RSD (%)	EF	Detection Technique
[58]	GO-[APMIM][NTf ₂]	DI-SPME	Red, white, black mulberry, blueberry, melon, and red plum wines	SiA, PCA, CnA, p-CA, SA, FA, CA, Res, GA, Kae, Que, CGA (12)	Phenolic acids	0.02–0.1 µg L ^{−1}	72.8–99.9	0.71–14.82	NR	NR	GC-MS
[63]	V-g-C ₃ N ₄ /Fe ₃ O ₄	MSPE	Black, green, red, and white teas	Que, Api, Kae, Myr (4)	Flavonoids	0.075–0.1 µg mL ^{−1}	88.2–107.2	0.62–2.53	NR	NR	HPLC-UV
[61]	c-MWCNT-MNPs	MSPE	Sesame oil	HPE, CnA, DHBA, p-CA, 2-HCA, VA, GA, CA, FA, SiA, SinAlc, SA, t-Res, Api, Lut, Cat, EC, Que, Dai, Gen, Dzn, Gtn, Ses (23)	Mixed	0.01–13.60 µg kg ^{−1}	80.0–125.9	0.5–10.0	0.8–13.2	NR	LC-MS/MS
[59]	Fe ₃ O ₄ -CS-GO	MSPE	Natural orange and apple juice, commercial apple juice, onion juice, green tea	Api, Mor, Nar, Que (4)	Flavonoids	0.03–0.14 µg L ^{−1}	90–102	4.1–4.8	NR	19–19.6	HPLC-UV
[60]	AGMN	MSPE	Wines derived from Tieguanyin tea	DPA, CA, VA, HPPA, HMPA, FA (6)	Phenolic acids	0.031–0.23 µg L ^{−1}	84.6–116	2.2–8.9	1.8–7.2	110–201	HPLC-DAD
[62]	MWCNT@ND	MSPE	Black and green teas	Que (1)	Flavonoids	1.46 ng mL ^{−1}	92.8–105.2	3.2	NR	103.7	HPLC-DAD

Abbreviations: EF: Enrichment factor; GO-[APMIM][NTf₂]: graphene oxide modified with amino-functionalized methylimidazolium ionic liquid; V-g-C₃N₄/Fe₃O₄: velvet-like magnetic graphitic carbon nitride; c-MWCNT-MNPs: carboxylated magnetic multi-walled carbon nanotubes; Fe₃O₄-CS-GO: chitosan–graphene oxide magnetic nanoparticles; AGMN: aminated graphene oxide-functionalized magnetic nanocomposite; MWCNT@ND: core–shell carbon nanotube@nanodiamond magnetic nanocomposite; DI-SPME: direct immersion solid-phase microextraction; MSPE: magnetic solid-phase extraction; SiA: syringic acid; PCA: protocatechuic acid; CnA: cinnamic acid; p-CA: p-coumaric acid; SA: sinapic acid; FA: ferulic acid; CA: caffeic acid; Res: resveratrol; t-Res: trans-resveratrol; GA: gallic acid; Kae: kaempferol; Que: quercetin; CGA: chlorogenic acid; Api: apigenin; Myr: myricetin; HPE: 2-(4-hydroxyphenyl)ethanol; DHBA: 3,4-dihydroxybenzoic acid; 2-HCA: 2-hydroxycinnamic acid; VA: vanillic acid; SinAlc: sinapyl alcohol; Lut: luteolin; Cat: catechin; EC: epicatechin; Dai: daidzein; Gen: genistein; Dzn: daidzin; Gtn: genistin; Ses: sesamin; Mor: morin; Nar: naringenin; DPA: 3-(3,4-dihydroxyphenyl)propionic acid; HPPA: 3-(4-hydroxyphenyl)propionic acid; HMPA: 3-(4-hydroxy-3-methoxyphenyl)propionic acid. NR: not reported.

Regarding analytical sustainability, only Jafari and Hadjmohammadi [59] and Wu et al. [60] included qualitative statements concerning the environmental aspects of their methods; however, none of the studies performed a formal quantitative assessment of environmental sustainability.

The carbonaceous phase constituted the dominant retention component across these architectures, while the specific surface modifications introduced were associated with system-dependent retention profiles. Accordingly, the resulting retention behavior should be interpreted in light of the complete functional architecture of each sorbent, rather than attributed in isolation to the carbonaceous phase or to a particular surface modification.

3.6. Layered Inorganic Materials (LDHs)

The three-layered inorganic materials included in this group exploit the permanent positive charge of their brucite-like layered structure and the presence of exchangeable interlayer anions to retain ionizable phenolic compounds through anion-exchange mechanisms [66].

These sorbents share a common synthesis strategy based on the in situ hydrothermal growth of the LDH layer on electrochemically anodized aluminum, which simultaneously acts as the structural support and as the source of Al^{3+} ions, thereby eliminating the need for an external aluminum precursor. The materials differ in the divalent metal cation incorporated into the layered structure— Co^{2+} [23,67] or Zn^{2+} [68]—as well as in the geometry of the supporting substrate. Rezaei and Matin [67] employed a cylindrical aluminum–polylactic acid (Al–PLA) composite fiber fabricated by fused deposition modeling (FDM) 3D printing, followed by surface anodization. Alipour et al. [23] used an anodized aluminum sheet (10×15 mm), whereas Ghani [68] prepared an anodized aluminum rod (5 mm diameter, 2 cm length) incorporating an iron core to enable magnetic stirring during extraction. Despite these differences in metallic composition and substrate geometry, all three materials preserved the characteristic layered architecture of LDHs.

Rezaei and Matin [67] reported spectroscopic evidence consistent with CO_3^{2-} , HCO_3^- , and OH^- acting as the exchangeable interlayer anions displaced by phenolic analytes in their anionic form during extraction. The presence of ionized analyte species was therefore essential for efficient retention, explaining the critical role of pH as an operational parameter in all three methods. Alipour et al. [23] reported an increase in extraction efficiency as the pH was raised from 5 to 8, which they attributed to the increased deprotonation of quercetin ($\text{pK}_a = 7.04\text{--}13.06$). Ghani [68] observed a similar trend for the investigated phenolic acids ($\text{pK}_a = 4.26\text{--}4.54$), although extraction efficiency decreased at $\text{pH} > 7$, which was attributed to competition from OH^- ions for the available ion-exchange sites. Rezaei and Matin [67] established pH 6 as the optimum extraction condition, noting that both strongly acidic media, owing to LDH dissolution, and highly alkaline media were unsuitable for microextraction, although the specific mechanism underlying the decline in efficiency at alkaline pH was not discussed by the authors. They further proposed hydrogen bonding between hydroxyl groups on the sorbent surface and functional groups of the phenolic acids, together with a pore-filling effect associated with the Co–Al LDH, as complementary retention mechanisms in addition to anion exchange. The dependence of anion-exchange retention on the ionization state of the analyte is consistent with the cationic layered architecture of LDHs and suggests that both selectivity and extraction efficiency vary according to the acid–base properties of the analytes and the pH conditions employed, potentially resulting in different extraction efficiencies among analytes within the same analytical method.

A schematic summary of the retention mechanism discussed in this section is presented in Figure 4. The figure summarizes the positively charged layered structure of LDHs

together with the exchangeable interlayer anions and the localized anion-exchange process underlying the retention of ionized phenolic analytes.

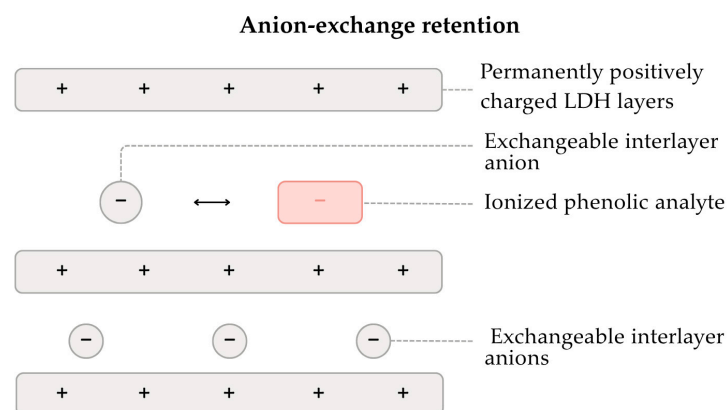


Figure 4. Layered double hydroxide (LDH) architecture and the common anion-exchange mechanism. Positively charged layers, exchangeable interlayer anions, and the retention of ionized phenolic analytes through anion exchange are shown. The double-headed arrow indicates the localized anion-exchange process involving the exchangeable interlayer anion and the ionized phenolic analyte. The identities, charges, numbers, and exchange stoichiometry of the represented species are schematic and do not correspond to a specific interlayer anion or phenolic analyte. A single interlayer exchange site is shown for clarity and does not imply that anion exchange is restricted to one location within the LDH structure.

The physical configuration of each sorbent dictated the corresponding extraction technique. Rezaei and Matin [67] employed SPME, a configuration well suited to the cylindrical geometry of the printed fiber, which was mounted onto a holder and directly immersed in the sample solution. Alipour et al. [23] applied thin-film microextraction (TFME), in which the flexible metallic sheet provides a larger active extraction surface than a conventional fiber [69], a feature highlighted by the authors as advantageous for routine analytical applications. Ghani [68] adopted stir bar sorptive extraction (SBSE), a configuration made possible by incorporating an iron core into the anodized aluminum rod, thereby allowing simultaneous magnetic stirring and extraction, with the device functioning both as a stir bar and as the immersed sorbent [70].

As summarized in Table 4, fruit-derived matrices, represented in all three studies by commercial and freshly prepared fruit juices, constituted the common eligible food matrices within this group, with non-alcoholic beer additionally investigated by Ghani [68]. The liquid nature of these matrices is fully compatible with the direct-immersion extraction formats employed. Regarding the target analytes, phenolic acids represented the predominant phenolic subclass [67,68]. As weak acids, these compounds readily adopt an anionic form under moderately alkaline conditions, making them naturally compatible with anion-exchange sorbents such as LDHs. All three studies adopted a targeted analytical approach focused on a predefined group of analytes, which is consistent with a sorbent whose retention efficiency depends on the acid–base properties of the target compounds.

The analytical performance data are summarized in Table 4. Across the three studies, recovery values ranged from 80.20% to 108.93%, whereas intra-day RSDs ranged from 1.35% to 10.31%. Inter-day RSDs, reported in two studies, ranged from 4.1% to 4.5%. Regarding preconcentration capability, Alipour et al. [23] reported an enrichment factor of 152, the highest value within this group, reflecting the substantial volume reduction achieved by the TFME format. As in the previous groups, differences in analytical conditions among studies preclude direct comparison of these performance metrics.

Table 4. Representative studies using layered inorganic materials to determine phenolic compounds in plant-derived food matrices.

Ref.	Sorbent	Extraction Technique	Matrix	Analytes (<i>n</i>)	Dominant Phenolic Subclass	LOD	Rec. (%)	Intraday RSD (%)	Interday RSD (%)	EF	Detection Technique
[67]	Co-Al LDH-PLA	SPME	Apple juice, red grape juice, pineapple juice	VA, FA, p-CA, PHBA, PCA, CA (6)	Phenolic acids	0.03–0.15 µg L ^{−1}	80.20–108.93	1.35–10.31	NR	12.81–35.21	HPLC-DAD
[23]	Co-Al LDH	TFME	Commercial pomegranate juice, commercial and natural apple juices	Que (1)	Flavonoids	0.18 µg L ^{−1}	96–103	3.2–3.6	4.1	152	HPLC-UV
[68]	Zn-Al LDH	SBSE	Commercial grape juice, natural white and red grape juices, commercial cranberry juice, non-alcoholic beer	GA, DHBA, PHBA (3)	Phenolic acids	0.06–0.26 µg L ^{−1}	90–105	3.4–4.3	4.1–4.5	46–50	HPLC-DAD

Abbreviations: EF: Enrichment factor. Co-Al LDH-PLA: Co-Al layered double hydroxide on a 3D-printed composite fiber; Co-Al LDH: Co-Al layered double hydroxide on anodized aluminum; Zn-Al LDH: Zn-Al layered double hydroxide on an anodized aluminum stir bar; SPME: solid-phase microextraction; TFME: thin-film microextraction; SBSE: stir bar sorptive extraction; VA: vanillic acid; FA: ferulic acid; p-CA: p-coumaric acid; PHBA: p-hydroxybenzoic acid; PCA: protocatechuic acid; CA: caffeic acid; Que: quercetin; GA: gallic acid; DHBA: 3,4-dihydroxybenzoic acid. NR: not reported.

Across the three included studies, the performance data summarized in Table 4 indicate generally satisfactory extraction outcomes across this platform, consistent with the anion-exchange mechanism common to all three sorbents and its dependence on the ionization state of the target analytes. Still, the observed variation among the three sorbents is likely influenced not only by substrate geometry and divalent cation identity but also by differences in the extraction technique and experimental conditions under which the methods were evaluated.

Reported sorbent reusability varied considerably, ranging from 43 extraction cycles without significant loss of efficiency [23] to only 2 effective cycles, after which progressive performance deterioration was attributed to reduction in the LDH coating on the printed surface [67]. Ghani [68] did not report sorbent reusability. All three studies reported LOD, recovery, and at least one precision parameter. However, none performed a formal quantitative evaluation of matrix effects, representing an important limitation given the compositional complexity of plant-derived food matrices, as discussed for the other sorbent platforms included in this review [26]. Likewise, none of the studies applied formal analytical sustainability assessment tools or explicitly evaluated the environmental sustainability of the developed analytical methods.

Both selectivity and extraction efficiency varied according to the acid–base properties of the analytes and the pH conditions employed. Accordingly, retention behavior should be interpreted in light of the cationic layered architecture of LDHs and the resulting analyte ionization state.

3.7. Underrepresented Sorbent Platforms

The characteristics of the studies included in this section are summarized in Table 5. Because each platform is represented by a single study, with the exception of surface-functionalized Fe_3O_4 nanoparticles ($n = 3$), it is not possible to identify consistent within-group trends. Consequently, each system is discussed individually. The architectural heterogeneity of this group—ranging from zeolitic imidazolate framework metal–organic frameworks (ZIF-MOFs) to calixarenes, multicomponent hybrid materials, and ionic liquid-functionalized clays—illustrates the diversity of design strategies that have not yet achieved substantial representation in applications targeting phenolic compounds in plant-derived food matrices.

Jafari and Hadjmohammadi [71] developed the hierarchical hybrid CY-PPy-LDH-ZIF8, which was employed as a thin-film sorbent in TFME for the determination of quercetin in apple and pomegranate juices. Analyte retention was primarily attributed to hydrogen bonding, π – π interactions, and hydrophobic interactions between the imidazolate rings of ZIF-8 and the target analyte. This represents the only study among those included in the present review in which a MOF functioned as the active sorbent. Although ZIF materials are increasingly recognized as promising sorbents for food analysis [72], their application in analytical methods targeting phenolic compounds in plant-derived food matrices remains limited, possibly owing to the relatively complex multicomponent synthesis required for these materials. Furthermore, the study evaluated only a single analyte, limiting assessment of the platform’s applicability to multiclass analytical methods.

Alipanahpour Dil et al. [73] synthesized the multicomponent hybrid nanocomposite $\text{CuO}/\text{ZnO}@\text{Fe}_3\text{O}_4\text{-CNTs}$, which was employed as a sorbent in magnetic dispersive micro solid-phase extraction coupled with HPLC–UV (MDMSPE–HPLC–UV) for the determination of chlorogenic acid in broccoli, tomato, and eggplant. The sorbent architecture integrates mixed metal oxides (CuO/ZnO) with Fe_3O_4 magnetic nanoparticles anchored onto functionalized carbon nanotubes, thereby combining polar and non-polar adsorption sites, magnetic separation capability, and a high specific surface area. The authors

attributed analyte retention primarily to hydrogen bonding and π - π stacking between the aromatic structure of the carbon nanotubes and chlorogenic acid. Their direct comparison between CuO/ZnO@Fe₃O₄-CNTs-NC and CuO/ZnO@Fe₃O₄-NC demonstrated a substantial increase in sorption capacity after incorporating carbon nanotubes, which they associated with the resulting increase in specific surface area, although no definitive causal relationship was established. Because the study focused exclusively on a single phenolic acid, the behavior of this sorbent toward structurally diverse phenolic compounds remains uncertain.

Yang et al. [74] employed calix[8]arene as the dispersive sorbent in matrix solid-phase dispersion (MSPD) coupled with ultra-high-performance liquid chromatography–quadrupole time-of-flight mass spectrometry (UHPLC–Q-TOF/MS) for the simultaneous determination of five organic acids, including phenolic acids, in the fruit of *Chaenomeles speciosa*. Retention was attributed to π - π interactions and hydrogen bonding between the benzene framework of the calixarene and the analytes. The ionic liquid 1-dodecyl-3-methylimidazolium bromide ([Domim]Br), used as the eluent, contributed complementary π - π stacking and hydrogen-bonding interactions that facilitated analyte desorption from the sorbent. This dual functionality—calixarene as the dispersive sorbent and ionic liquid as a cooperative eluent—constitutes one of the most distinctive features of the proposed analytical system. However, because the study focused on organic acids, its findings cannot be readily extrapolated to structurally more complex phenolic compounds.

Da Silva and Lanças [75] prepared the three-component material β -CD@GO@Si, consisting of β -cyclodextrin (β -CD) coupled to graphene oxide supported on aminopropyl-functionalized silica. This sorbent was applied in microextraction by packed sorbent (MEPS) coupled with LC–MS/MS for the determination of isoflavones in soybean juice. The architecture combines the high adsorption capacity of graphene oxide toward aromatic compounds with the molecular selectivity provided by β -cyclodextrin through host–guest interactions. The authors reported that although the non-functionalized GO@Si sorbent exhibited higher extraction efficiency, incorporation of β -CD substantially reduced matrix effects, demonstrating that β -cyclodextrin functionalization improved analytical selectivity at the expense of a reduction in overall extraction capacity. This behavior is consistent with previous observations reported for cyclodextrin–nanomaterial composites [76].

Tashakkori et al. [77] prepared SPME fibers coated with a composite consisting of sulfuric acid-activated montmorillonite (KSF) intercalated with the aminopropyl benzylimidazolium ionic liquid (KSF-[H₂N-C₃bim]). Multiple anionic variants and two coupled detection techniques, GC–MS and HPLC–DAD, were evaluated. Among the tested combinations, the KSF-[H₂N-C₃bim][BF₄] fiber coupled with GC–MS provided the lowest LODs and the widest linear range, and therefore corresponds to the data presented in Table 5. The method was applied to the simultaneous determination of 16 phenolic compounds belonging to several subclasses, including phenolic acids, flavonols, flavanols, and stilbenes, in fresh fruit juices. The authors attributed analyte retention to π - π interactions between the benzyl group and the imidazolium ring of the cation and the aromatic rings of the analytes, hydrogen bonding with phenolic hydroxyl groups, and electrostatic and coordination interactions involving the clay fraction of the composite. A comparison between fibers coated with KSF alone and KSF–ionic liquid composites demonstrated that incorporation of the ionic liquid improved extraction efficiency, although the relative contribution of each component of the composite to the overall retention mechanism was not experimentally resolved. The simultaneous determination of 16 phenolic compounds from different subclasses in six fruit juices represents the broadest analytical scope among the sorbent platforms discussed in this section.

The following three studies employed Fe_3O_4 nanoparticles directly functionalized at the surface with organic modifiers (salicylic acid, sodium alendronate, and an ammonium-based ionic liquid, respectively), which served as the active extraction phase. In each case, the chemical nature of the functionalizing agent determined the interaction properties of the sorbent.

Yari and Rashnoo [78] employed silica-coated magnetite nanoparticles functionalized with salicylic acid (SA-SCMNPs) as the sorbent in MSPE–HPLC–UV for the determination of anthocyanins in cherry, sour cherry, pomegranate, and barberry. The sorbent architecture consisted of a Fe_3O_4 core, a silica coating serving as the structural support, and surface-immobilized salicylic acid as the functional phase responsible for analyte retention. Surface functionalization with salicylic acid was confirmed by FT-IR spectroscopy; however, the authors did not explicitly describe the sorbent–analyte interaction mechanism, limiting interpretation of the specific role of this functionalization in the observed extraction performance.

Zhao et al. [79] modified mesoporous Fe_3O_4 nanoparticles with sodium alendronate ($\text{Fe}_3\text{O}_4\text{@ANDS}$) through Lewis acid–base interactions under mild aqueous conditions. The resulting sorbent was applied in MSPE–HPLC–UV for the determination of trans-resveratrol in peanut oil. The retention mechanism was explicitly described by the authors: the amino group of sodium alendronate formed hydrogen bonds with the phenolic hydroxyl group of the analyte in a non-polar medium, whereas the triglycerides constituting the bulk of the oil matrix remained dissolved in n-hexane because of their non-polar character. This selective behavior was supported experimentally by comparison with non-functionalized Fe_3O_4 , with the functionalized material exhibiting markedly superior extraction performance, demonstrating that surface functionalization with sodium alendronate played a decisive role in analyte retention.

Rezaeinejad et al. [80] functionalized Fe_3O_4 nanoparticles with 2-hydroxyethylammonium chloride, producing $\text{Fe}_3\text{O}_4\text{@IL}$ magnetic nanoparticles, which were employed in a narrow-bore tube magnetic solid-phase extraction (NBT-MSPE) format coupled with HPLC–UV for the determination of catechin in grape juice. The retention mechanism was attributed to the formation of hydrogen bonds between the hydroxyl groups of the ionic liquid and the phenolic hydroxyl groups of catechin, an interaction favored under acidic conditions. Desorption was achieved under basic conditions using a phosphate buffer, in which catechin exhibited reduced affinity for the sorbent according to the authors. The NBT configuration, in which the nanoparticles descend by gravity through the narrow tube into a collection vial, represents a distinctive operational adaptation that eliminates the need for either mechanical or magnetic agitation during adsorption, thereby differing substantially from the conventional dispersive extraction formats employed in the other two studies.

Overall, a recurring characteristic observed among several of the systems discussed in this section is the tendency toward architectural multifunctionality, with multiple platforms combining two or more components performing complementary functions. However, this feature is not common to all of the sorbent systems included in this category.

Regarding analytical performance reporting, all studies provided recovery values and intra-day RSDs. LOD values could not be unequivocally attributed to eligible food matrices only in the study by Alipanahpour Dil et al. [73]. Inter-day RSDs were reported in only five studies. Formal evaluation of matrix effects was uncommon: only Da Silva and Lanças [75] performed a quantitative assessment; Zhao et al. [79] addressed matrix effects indirectly by comparing recoveries obtained in matrix and solvent without explicitly reporting ME%; and Jafari and Hadjmohammadi [71] reported ME%, although it was calculated jointly for honey and beverage samples without separating the two matrix categories, preventing its

attribution exclusively to eligible plant-derived food matrices. The remaining five studies did not evaluate matrix effects.

With respect to analytical sustainability, Alipanahpour Dil et al. [73], Zhao et al. [79], Rezaeinejad et al. [80], and Yang et al. [74] explicitly highlighted environmental advantages associated with their methods but did not apply formal sustainability assessment tools, whereas the remaining four studies did not address this aspect.

Overall, the individual systems summarized in Table 5 reported generally satisfactory analytical performance for the specific matrix and analyte combination examined in each case. However, given that most platforms are represented by a single study, the current evidence does not permit the identification of consistent relationships between sorbent architecture and analytical performance across this category, and the observed diversity of design strategies should instead be regarded as illustrative of emerging directions warranting further investigation.

3.8. Cross-Cutting Trends and Critical Considerations Across the Evidence Base

3.8.1. Cross-Cutting Architectural Features

Magnetic recovery using Fe_3O_4 represents the most widespread operational strategy among the included studies, being employed in 62% of the evidence base ($n = 23/37$). This approach was identified in four of the five sorbent groups analyzed: molecularly imprinted sorbents (6/12), functionalized polymeric sorbents (8/8), functional carbon-based sorbents (5/6), and underrepresented platforms (4/8), whereas it was absent from the layered inorganic materials. Its occurrence across sorbent groups exhibiting markedly different retention architectures suggests that magnetic recovery is primarily an operational strategy that can be readily integrated into structurally diverse sorbent platforms.

Multifunctional architectures, in which different components perform complementary roles within the same sorbent, were observed across all sorbent groups analyzed. Representative examples include molecularly imprinted polymers incorporating deep eutectic solvents as functional elements within the sorbent architecture [36], carbon-based sorbents combining multiple functional phases with distinct interaction mechanisms [62], layered inorganic materials synthesized in situ on structurally differentiated supports [67], and composite sorbents in which individual components contribute complementary adsorption capacity and molecular selectivity [75].

3.8.2. Interaction Mechanisms: Cross-Cutting Patterns

Hydrogen bonding was the most consistently reported retention mechanism, being identified across all sorbent groups included in this review. π - π interactions were likewise highly recurrent, although they were less frequently reported for layered inorganic materials, in which anion exchange constituted the dominant retention mechanism. The widespread occurrence of these two interaction mechanisms is consistent with the chemical structure of phenolic compounds. On the one hand, the hydroxyl groups of phenolic molecules readily participate in hydrogen bonding [81] with functional groups present on the sorbents, including functional monomers, oxygen-containing groups, and amino groups. On the other hand, their aromatic rings promote π - π interactions [81] with carbonaceous phases and aromatic structural motifs incorporated into the sorbent materials. Hydrophobic and electrostatic interactions were also frequently proposed as complementary retention mechanisms, although their relative importance varied according to sorbent composition.

Table 5. Underrepresented Platforms.

Ref.	Sorbent	Extraction Technique	Matrix	Analytes (n)	Dominant Phenolic Subclass	LOD	Rec. (%)	Intraday RSD (%)	Interday RSD (%)	EF	Detection Technique
[78]	SA-SCMNPs	MSPE	Cherry, sour cherry, pomegranate, barberry	Cld-Cl, Plg-Cl (2)	Flavonoids	0.02–0.03 $\mu\text{g g}^{-1}$	72.9–97.6	2.1–2.5	NR	NR	HPLC-UV
[73]	CuO/ZnO@Fe ₃ O ₄ -CNTs-NC	MDMSPE	Broccoli, tomato, eggplant	CGA (1)	Phenolic acids	ND	94.07–107.59	1.67–5.27	2.20–6.94	102.43–123.76	HPLC-UV
[77]	KSF-[H ₂ N-C ₃ bim][BF ₄]	DI-SPME	Natural juices of orange, quince, grape, mandarin, apple and pear	CnA, p-CA, VA, FA, SiA, SA, PCA, CA, GA, CGA, Res, Que, Kae, Cat, EC, Rut (16)	Phenolic acids	0.01 $\mu\text{g L}^{-1}$	84.6–101.7	0.9–3.2	NR	NR	GC-MS
[71]	CY-PPy-LDH-ZIF8	TFME	Commercial pomegranate juice, commercial and natural apple juices	Que (1)	Flavonoids	0.04 $\mu\text{g L}^{-1}$	90–93	3.5–5.6	2.5–4.8	95	HPLC-UV
[79]	Fe ₃ O ₄ @ANDS	MSPE	Peanut oil	t-Res (1)	Stilbenes	0.3 ng g^{-1}	78.6–118.9	1.8–3.3	1.9–15.2	78	HPLC-UV
[80]	Fe ₃ O ₄ @IL MNPs	NBT-MSPE	Grape juice	Cat (1)	Flavonoids	0.141 $\mu\text{g mL}^{-1}$	93.4–99.5	1.63	NR	3.3	HPLC-UV
[74]	Calix[8]arene	MSPD- μE	Fruit of <i>Chaenomeles speciosa</i>	CGA, PCA, CA, GA (4)	Phenolic acids	0.202–1.056 ng mL^{-1}	82.19–113.36	0.43–0.67	0.57–2.30	NR	UHPLC-Q-TOF/MS
[75]	β -CD@GO@Si	MEPS	Soy-based juice	Dai, Gen, Fmn, Bio (4)	Flavonoids	0.5–1.5 $\mu\text{g L}^{-1}$	93.3–123.3	3.0–15.5	5.0–12.8	NR	UHPLC-MS/MS

Abbreviations: EF: Enrichment factor; SA-SCMNPs: salicylic acid-functionalized silica-coated magnetite nanoparticles; CuO/ZnO@Fe₃O₄-CNTs-NC: CuO/ZnO magnetic carbon nanotube nanocomposite; KSF-[H₂N-C₃bim][BF₄]: KSF montmorillonite modified with amino-functionalized ionic liquid; CY-PPy-LDH-ZIF8: cotton yarn-polypyrrole with layered double hydroxide and ZIF-8; Fe₃O₄@ANDS: mesoporous magnetic nanoparticles with sodium alendronate; Fe₃O₄@IL MNPs: ionic liquid-modified magnetic nanoparticles; Calix[8]arene: calix[8]arene; β -CD@GO@Si: β -cyclodextrin on graphene oxide over aminopropyl silica; MSPE: magnetic solid-phase extraction; MDMSPE: magnetic dispersive solid-phase microextraction; DI-SPME: direct immersion solid-phase microextraction; TFME: thin-film microextraction; NBT-MSPE: narrow-bore tube magnetic solid-phase extraction; MSPD- μE : matrix solid-phase dispersion microextraction; MEPS: microextraction by packed sorbent; Cld-Cl: cyanidin chloride; Plg-Cl: pelargonidin chloride; CGA: chlorogenic acid; CnA: cinnamic acid; p-CA: p-coumaric acid; VA: vanillic acid; FA: ferulic acid; SiA: syringic acid; SA: sinapic acid; PCA: protocatechuic acid; CA: caffeic acid; GA: gallic acid; Res: resveratrol; Que: quercetin; Kae: kaempferol; Cat: catechin; EC: epicatechin; Rut: rutin; t-Res: trans-resveratrol; Dai: daidzein; Gen: genistein; Fmn: formononetin; Bio: biochanin A. NR: not reported. ND: existing data not unambiguously attributable to an eligible matrix or phenolic analyte.

The dependence of extraction efficiency on pH emerged as a recurring pattern throughout the reviewed studies, although the underlying mechanisms differed substantially among sorbent platforms. In MIPs containing amino-functional monomers, pH regulates the protonation state of the functional monomer, thereby influencing its ability to establish hydrogen bonds with the target analyte. In layered inorganic materials, pH determines the degree of analyte ionization, a prerequisite for efficient anion exchange. In functional carbon-based sorbents, pH modulates the relative contribution of the different interaction mechanisms proposed for each system. Consequently, although similar pH-dependent extraction behaviors are observed across different sorbent platforms, the underlying mechanistic basis differs and should therefore be taken into account when comparing the optimum pH ranges reported in the literature.

The proposal of multiple simultaneous retention mechanisms without experimentally evaluating their relative contribution represents a recurring pattern across the reviewed studies, particularly among carbon-based sorbents, functionalized polymeric materials, and hybrid platforms. The absence of such mechanistic validation constitutes an important opportunity for future research and is discussed further in Section 3.9.

3.8.3. Reporting of Analytical Performance Data and Comparability Across Studies

Reporting of analytical performance parameters was common throughout the included studies, although substantial differences in reporting practices were observed. Thirty-one of the 37 studies simultaneously reported the LOD, recovery, and at least one indicator of analytical precision according to the extraction criteria defined in Section 2.3. In contrast, inter-day RSD was reported less frequently, appearing in only 25 studies, thereby limiting the assessment of intermediate precision across a considerable proportion of the evidence base. In several studies, recovery and RSD values were reported within the analytical application section rather than as part of an independent validation procedure, making it difficult to distinguish between formally validated analytical performance and operational performance obtained during the analysis of real samples.

These observations reflect a lack of uniformity in reporting practices within the field. Among the six studies with incomplete analytical performance data, the underlying reasons were heterogeneous and included the absence of matrix-specific data disaggregation, reporting precision exclusively as recovery $\pm$ standard deviation (SD) without explicit RSD values, and presenting validation parameters only in Supplementary Materials, irrespective of the overall analytical rigor of the individual studies.

Formal evaluation of matrix effects was infrequent. Only seven studies performed a quantitative assessment, one study addressed matrix effects indirectly by comparing recoveries obtained in matrix and solvent without explicitly reporting ME%, and 28 studies did not evaluate matrix effects at all. An additional study conducted a quantitative assessment on a mixed sample set that could not be unequivocally attributed exclusively to eligible plant-derived food matrices. The widespread absence of formal matrix-effect evaluation limits comparability across studies because it prevents assessment of the extent to which the reported recoveries are influenced by matrix-induced signal suppression or enhancement rather than by extraction efficiency alone.

With respect to analytical sustainability, only one study applied a formal assessment tool, namely the Analytical Eco-Scale. Twelve studies included explicit qualitative statements highlighting environmental advantages, primarily based on reduced solvent consumption or favorable comparisons with previously reported methods, but without quantitative sustainability metrics. The remaining 24 studies did not provide sustainability statements specifically related to the developed analytical method. In several cases, only

general properties of the sorbent material or extraction technique were mentioned without explicitly linking them to the environmental performance of the analytical procedure.

The predominance of qualitative descriptions over formal sustainability assessments indicates that the environmental dimension has not yet achieved a level of standardization comparable to that of conventional analytical performance parameters, thereby limiting systematic comparison of the environmental performance of analytical methods across studies.

3.8.4. Practical Implications of Sorbent Platform Design

Beyond analytical performance, comparison across the reviewed sorbent platforms revealed several practical considerations relevant to their operational use. The most consistent pattern concerned the relationship between sorbent architecture and extraction format. Magnetically recoverable configurations were typically implemented in MSPE-type formats, whereas sorbents immobilized on fibers, films, rods, wires, or capillary supports were directly integrated into device-based formats such as SPME, TFME, or SBSE, avoiding a separate particle-recovery step. The less frequently represented non-magnetic particulate systems required mechanical separation. Among the underrepresented platforms, a comparable architecture–format correspondence was evident at the level of individual systems, although their structural diversity precluded its interpretation as a common platform-level trend.

Reusability represented a second practical dimension, although the evidence does not support a consistent hierarchy among platforms. Some of the highest reusability values were reported for immobilized configurations; however, a dispersed magnetic polymeric sorbent achieved reusability comparable to that of a monolithic system [52,55], while two immobilized layered double hydroxide sorbents showed markedly different numbers of effective extraction cycles [23,67]. These findings indicate that support configuration alone does not explain operational stability and that the available reusability data do not support ranking the platforms in terms of practical durability.

A qualitative contrast in analyte scope was supported only for MIPs and LDHs, the two platforms for which the evidence explicitly addressed this aspect. Template-directed recognition in MIPs favors compounds structurally related to the template but can limit applicability to dissimilar phenolic structures, whereas the dominant anion-exchange mechanism in LDHs makes retention strongly dependent on analyte ionization, although complementary interactions may also contribute. The mechanistic heterogeneity of the functionalized polymeric and carbon-based platforms prevented an equivalent platform-level comparison.

For the underrepresented systems, the available evidence was too limited and heterogeneous to support the identification of common practical advantages or limitations; as discussed in Section 3.7, these systems are better regarded as emerging design directions than as a basis for generalized comparisons. Taken together, the available evidence suggests that the practical implications of the reviewed sorbents are more closely associated with their specific architecture, extraction format, and dominant retention mechanism than with broad platform classification alone.

3.8.5. Limitations of the Evidence Base and the Review Process

The substantial heterogeneity of the evidence base with respect to extraction techniques, sorbent materials, food matrices, target analytes, and experimental conditions limited direct comparability among studies and restricted the interpretation of the findings to patterns observed within each analytical category. Consequently, robust comparative generalizations across different sorbent platforms could not be established. Data extraction was inherently dependent on the level of detail reported in the primary publications. When-

ever the available information was insufficient to allow unequivocal attribution according to the criteria defined in Section 2.3, the corresponding values were neither extracted nor imputed. Although this approach reduced the amount of data available for analysis, it ensured the methodological consistency of the review process. In several studies, certain analytical performance parameters were reported exclusively in Supplementary Materials that were not accessible during the review process, preventing their extraction in accordance with the predefined protocol. Furthermore, the literature search was restricted to studies indexed in Scopus; therefore, the possibility that relevant studies indexed elsewhere were not retrieved cannot be excluded. Finally, several sorbent categories were represented by only a single study, limiting the identification of within-platform trends for these materials, as discussed in Section 3.7.

3.9. Research Gaps and Future Perspectives

3.9.1. Standardization of Analytical Validation and Sustainability Assessment

The gaps identified in matrix-effect evaluation and in the standardization of analytical reporting indicate that future studies should incorporate quantitative matrix-effect assessment as a systematic component of method development rather than as an optional element. Likewise, future research should adopt standardized analytical validation protocols to ensure the generation of reliable and reproducible results [10]. Such protocols should include matrix-specific reporting of validation parameters, a clear distinction between formal method validation and operational performance evaluation, and the systematic reporting of both intra-day and inter-day precision to facilitate method comparison and improve the interpretation of analytical performance.

In parallel, the environmental characterization of analytical methods requires a comparable level of methodological rigor. The systematic implementation of formal sustainability assessment tools, such as AGREE [46], AGREEprep [47], and the Analytical Eco-Scale [57], would enable the empirical verification of the environmental advantages claimed by newly developed methods while facilitating objective comparisons of the sustainability profiles of different sorbent platforms.

3.9.2. Expanding Analytical Coverage: Phenolic Subclasses and Food Matrices

The strong concentration of the reviewed studies on flavonoids and phenolic acids contrasts with the absence or very limited coverage of other phenolic subclasses that are well documented in plant-derived food matrices. Among these, stilbenes comprise a family of more than 30 compounds, occurring predominantly in grapes and wine, which represent their principal dietary sources [82]. However, within the studies included in this review, stilbenes were represented only by trans-resveratrol in peanut oil [79] and resveratrol as part of a multiclass analytical panel in wine matrices [58]. Lignans, which are naturally present in oilseeds, nuts, vegetables, fruits, and beverages [83], were likewise minimally represented, being limited to sesamin among the 23 analytes determined by Wu et al. [61] in sesame oil. Other important phenolic subclasses, such as tannins, recognized for their antioxidant properties and contribution to the nutritional value of foods [84], and coumarins, naturally occurring in foods including citrus fruits, cinnamon, carrots, and parsley [85], were not represented in the analyzed studies. Collectively, these underrepresented subclasses highlight specific analytical opportunities for the development of advanced sorbents in miniaturized extraction formats dedicated to their determination.

Furthermore, most studies adopted targeted analytical approaches focused on relatively small panels of predefined analytes. Nevertheless, the studies by Wu et al. [61], which determined 23 analytes in sesame oil, and Tashakkori et al. [77], which analyzed 16 analytes in fruit juices, both encompassing multiple phenolic subclasses, demonstrate

that broad phenolic profiling is technically feasible using miniaturized extraction formats. These examples point to a promising methodological direction that remains only sparsely explored within the current literature.

With respect to food matrices, the predominance of beverages such as fruit juices and tea contrasts with the limited representation of other plant-derived matrices, including vegetable oils, vegetables, cereals, and legumes. The application of advanced sorbents in miniaturized solid-phase extraction techniques to these underrepresented matrices therefore represents an important opportunity for future methodological development.

3.9.3. Experimental Validation of Sorbent Retention Mechanisms

The frequent proposal of multiple simultaneous retention mechanisms without explicit experimental validation of their relative contributions, particularly among carbon-based sorbents, functionalized polymeric materials, and hybrid platforms, highlights the need for experimental designs capable of isolating and quantifying the contribution of each proposed interaction. Such mechanistic validation would strengthen the rational basis for sorbent design and provide a more robust experimental foundation for the development of new sorbent platforms with improved selectivity and extraction efficiency.

3.9.4. Emerging Trends in Sorbent Design

The evidence synthesized in this review and recent developments in sorbent and sample-preparation research point toward several directions that may shape future sorbent design for the miniaturized extraction of phenolic compounds from plant-derived food matrices.

One direction involves external stimuli, although mechanisms differ. In the $\text{Fe}_3\text{O}_4@\text{PGMA}@\text{PNIPAAm}$ sorbent of Li et al. [54], thermal stimulation reversibly changes the coating's conformation, directly modulating its affinity for the analyte. By contrast, the electric field in the EE-SPME system of Zheng et al. [21] acts mainly on analyte transport rather than on the sorbent itself. These approaches reflect a broader shift toward externally controlled extraction; thermoresponsive systems specifically align with the development of smart adsorbents exhibiting tunable, reversible responses to stimuli [86]. However, the potential toxicity and high molecular weight of certain thermoresponsive carriers, together with the fact that each strategy is currently represented by a single study, limit generalization to other analytes and matrices.

A second direction concerns deep eutectic solvents (DESs) as functional components during synthesis, identified within the MIP group as functional monomers, templates, comonomers, or modifiers. Tuning DES composition through hydrogen-bond donor/acceptor combinations allows adjustment of solvent properties [87], which may be particularly relevant given the recognition cavities characteristic of molecularly imprinted systems [31]. This should not be equated with inherent sustainability: a DES's environmental profile depends on the identity of its components, and formal sustainability assessment remained uncommon among the included studies. Available studies generally report only a limited number of extraction–desorption cycles, leaving long-term durability insufficiently established [87]; moreover, for at least one DES-based system in this review, the specific contribution of individual interactions was not evaluated experimentally [33].

A third direction reflects the widespread occurrence of multifunctional architectures across the evidence base, where distinct components contribute complementary properties within a single sorbent (Section 3.8.1), and points toward deliberately engineered sorbents, with each component assigned a defined analytical function rather than combined primarily through empirical optimization. This interpretation is consistent with recent liter-

ature identifying multifunctional hybrid materials as a key priority for advanced sample preparation [88].

A further direction, largely absent from the studies included here, concerns green-by-design sorbents based on renewable or biodegradable materials and less resource-intensive synthesis routes. A biological origin, however, is not sufficient on its own: recent critical assessments of green extraction phases for food analysis note that incorporating a biopolymer into a composite does not automatically render the overall procedure environmentally preferable, as reagent toxicity and reusability are seldom assessed systematically [89]. Their contribution to greener sorbent design for phenolic compounds therefore requires application-specific evaluation of both analytical performance and environmental impact.

A related opportunity follows directly from the gap discussed in Section 3.9.3: the frequent proposal of multiple retention mechanisms without experimental validation of their relative contribution. Computational tools—molecular mechanics, molecular dynamics, and DFT calculations—have been applied to select functional monomers and model pre-polymerization complexes in molecularly imprinted systems before synthesis [90]. Machine learning and other artificial intelligence approaches have also been explored alongside these methods, although their integration into routine practice remains limited [91]. For phenolic-targeted sorbents in food matrices, such strategies were absent from the included evidence base; in adjacent MIP-design applications, they have been used to narrow experimental search spaces and generate hypotheses about candidate interactions, but they inform, rather than replace, the experimental validation still required.

Taken together, the convergence of stimulus-controlled extraction, tunable chemical microenvironments, multifunctional architectural integration, sustainability-oriented material selection, and computationally guided design may support future strategies for advanced sorbents in this field. Building on the gaps identified throughout this review, the design of next-generation sorbents should prioritize experimentally isolating the relative contribution of individual mechanisms and structural components while validating computational predictions, together with the routine use of standardized sustainability metrics, applied in only a minority of the included studies. The design of such platforms may further benefit from assigning a specific, testable analytical function to each component of a multifunctional architecture from the outset, with design decisions informed, where appropriate, by computational screening, to help translate this observed architectural integration into deliberately engineered systems.

4. Conclusions

Across the sorbent platforms examined, analytical performance was interpreted considering sorbent architecture and the reported interaction mechanisms, alongside analyte properties and extraction conditions, rather than inferred as a direct causal outcome. Within this framework, two cross-cutting features emerged across the evidence base: the incorporation of Fe_3O_4 for magnetic separation, present across most sorbent groups and compatible with structurally diverse architectures, and the development of multifunctional designs in which distinct components fulfilled complementary roles. However, the substantial methodological heterogeneity across studies limited direct comparability, and no definitive relationship between sorbent architecture and analytical performance could be established.

Several gaps remain in the current evidence base. Matrix effects were rarely evaluated quantitatively, whereas most studies focused on a limited number of phenolic subclasses and food matrix categories, leaving other relevant subclasses and matrices underrepresented. Sustainability claims were predominantly qualitative, in the absence of formal environmental assessment metrics. A further gap concerns the limited experimental valida-

tion of the relative contributions of proposed retention mechanisms, particularly where multiple interactions were proposed simultaneously.

Future work should address these gaps along two complementary lines. Methodologically, quantitative matrix-effect assessment should become a standard component of method development; the relative contributions of individual retention mechanisms and structural components should be experimentally isolated through experimental designs that also validate computational predictions against experimental evidence; and standardized sustainability metrics should be routinely applied. In terms of scope, extending the development of advanced sorbents and analytical methods targeting underrepresented phenolic subclasses and food matrices, together with assigning a specific, testable analytical function to each component of multifunctional architectures at the design stage, may help translate the architectural integration observed across the included studies into deliberately engineered systems. Taken together, the findings of this review provide a structured basis for the rational design of sorbents with clearly defined analytical functions and the development of extraction methods whose performance metrics are more directly comparable across studies and whose sustainability is systematically assessed for the determination of phenolic compounds in plant-derived food matrices.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations13080219/s1>, Table S1: Extracted variables and operational definitions, Table S2: Decision Hierarchy for the Classification of the Sorbent Structural Platform.

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