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Extraction of Methylparaben and Propylparaben Using Magnetic Nanoparticles

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Abstract

Parabens, notably methylparaben (MP) and propylparaben (PP), are being extensively utilized as preservatives in pharmaceuticals, cosmetics, and personal care products because of their antimicrobial characteristics. Their widespread application and persistence in environmental systems have, however, raised important issues regarding human health and environmental stability, such as endocrine disruption and bioaccumulation. There is therefore a growing demand for the development of extraction methods that are efficient, selective, and environment-friendly for parabens. Magnetic nanoparticles (MNPs) were found to be useful materials for paraben extraction because they have a large surface area, simple functionalization procedures, and fast magnetic separation features. The current paper reviews the application of MNPs for the extraction and elimination of methylparaben (MP) and propylparaben (PP) from pharmaceutical and environmental samples. The review covers different functionalization procedures such as surfactant-coated MNPs and magnetic solid-phase extraction, detailing their efficiency, selectivity, and sustainability. The paper also mentions novel methods such as green magnetic molecularly imprinted polymers and syringe-to-syringe magnetic fluid phase microextraction. By comparative analysis of various MNP-based methodologies, this article tries to find the best approaches to paraben contamination mitigation and environmental safety enhancement.

Keywords: Methylparaben, Propylparaben, Magnetic Nanoparticles, Extraction of Parabens, Environmental Pollution, Magnetic Solid-Phase Extraction (MSPE), Endocrine Disrupting Chemicals, Green Chemistry Principles

1. Introduction

1.1 Background on Parabens

Parabens, being synthetic esters of para-hydroxybenzoic acid, are extensively utilized as stabilizers in pharmaceuticals, cosmetics, personal care items, and foods because of their wide range of antimicrobial activity, cost-effectiveness, and stability over time (Nguyen et al., 2021). Methylparaben (MP) and propylparaben (PP) are the most frequently employed parabens, inhibiting microbial growth and maintaining product integrity. Methylparaben, having a comparatively shorter alkyl chain, is more water-soluble and is frequently incorporated into aqueous formulations. Propylparaben, having a longer alkyl chain, provides higher activity in inhibiting the growth of fungi and yeast (Chen, Chiou, & Chang, 2017). The widespread application of these chemicals across numerous industries has led to their ubiquitous presence in environmental matrices such as surface water, wastewater, and even drinking water sources (Mashile et al., 2020).

The heightened application and subsequent environmental release of parabens have generated considerable alarm regarding their health and environmental hazards. The compounds have been ubiquitously detected in aquatic and terrestrial matrices, pointing to their stability and resilience to traditional wastewater treatment systems (Nguyen et al., 2021). Accordingly, the advancement of effective and green extraction protocols for the extraction and determination of parabens has been a key research front.

1.2 Environmental and Health Implications of Parabens

Notwithstanding their prevalent application, parabens have been linked to adverse health and environmental impacts. Parabens have been reported to display endocrine-disrupting activity through their capacity to imitate estrogen, thus possibly interfering with hormonal balance and reproductive well-being in wildlife and human populations (Nguyen et al., 2021). The bioaccumulating nature of such chemicals heightens concerns, given that they have been found in human urine, breast tissue, and amniotic fluid, indicating ongoing exposure from cosmetics and personal care product use (Mashile et al., 2020).

Environmental contamination with parabens is also of concern given their presence in wastewater effluent and natural aquatic environments will impact aquatic organisms. Parabens can disrupt the endocrine activity of fish and amphibians and cause reproductive and developmental abnormalities (Nguyen et al., 2021). Their partial biodegradation during wastewater treatment processes also leads to their environmental persistence, necessitating the use of more effective removal measures to mitigate such risks (Mashile et al., 2020).

Due to concerns like these, effective, selective, and green extraction methods for parabens have been an expanding field of interest. One promising candidate is magnetic nanoparticles (MNPs) due to their beneficial properties like high surface area, easy surface functionalization, and magnetic separation efficiency (Antoniou & Samanidou, 2022).

1.3 Role of Magnetic Nanoparticles in Paraben Extraction

Magnetic nanoparticles (MNPs) transformed analytical chemistry through the provision of extremely efficient and selective extraction methods. The superparamagnetic behavior of MNPs allows for the rapid and effortless isolation of target analytes from intricate matrices using an external magnetic field, thereby minimizing the time used for sample preparation and decreasing solvent consumption (Antoniou & Samanidou, 2022). Due to the large surface area of MNPs, they are capable of adsorbing huge quantities of impurities, thereby improving extraction efficiency even at trace levels (Chen, Chiou, & Chang, 2017).

Functionalization of magnetic nanoparticles (MNPs) with various organic and inorganic molecules enhances their selectivity and adsorptive capability for certain analytes, i.e., methylparaben and propylparaben. For example, MNPs surface-modified by surfactants, i.e., Sylgard 309 modified MNPs, have been shown to display high extraction efficiency in pharmaceutical and aqueous samples (Ariffin et al., 2019). Likewise, phenyl-functionalized MNPs show intense hydrophobic interactions towards parabens, thereby enhancing their adsorptive efficiency (Chen, Chiou, & Chang, 2017).

New extraction methods involving magnetic nanoparticles (MNPs), such as magnetic solid-phase extraction (MSPE) and syringe-to-syringe magnetic fluid phase microextraction, are several steps ahead of traditional methods. The methods have the features of high selectivity, minimal solvent consumption, and the capacity to concentrate multiple analytes at the same time (Dil et al., 2021). Moreover, the preparation of green magnetic molecularly imprinted polymers (MIPs) is aligned with the concept of green chemistry, which serves as a green solution for paraben removal (Ramin, 2023).

With the growing demand for green and efficient extraction techniques, magnetic nanoparticle utilization for the extraction of methylparaben and propylparaben from pharmaceutical and environmental matrices is an attractive approach. This study discusses the synthesis, surface modification, and utilization of magnetic nanoparticles for paraben extraction and highlights the potential of magnetic nanoparticles in mitigating the existing environmental and health issues caused by paraben contamination.

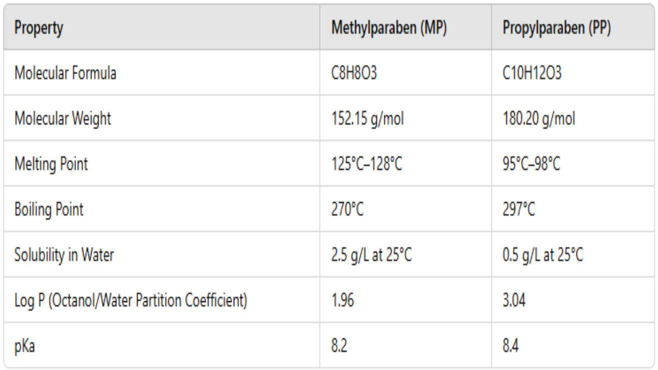
2. Methylparaben and Propylparaben: Characteristics and Attributes

Parabens, such as methylparaben (MP) and propylparaben (PP), are extensively utilized because of their potent antimicrobial activity, low cost, and chemical stability. Their complete physical, chemical, and environmental study is crucial to creating effective processes for removal and extraction. Here, their physical, chemical, and environmental properties, behavior, and effects are discussed in detail, with magnetic nanoparticles (MNPs) being presented as an innovative extraction technique.

2.1 Molecular Structure and Physical Properties

MP and PP are both esters of para-hydroxybenzoic acid, and they primarily differ in the length of their alkyl chain. The variation in the length of the chain plays an important role in determining their solubility, adsorption characteristics, and interaction with extraction substrates, such as magnetic nanoparticles (Chen, Chiou, & Chang, 2017).

Table below presents a comparative examination of their basic physical and chemical properties:



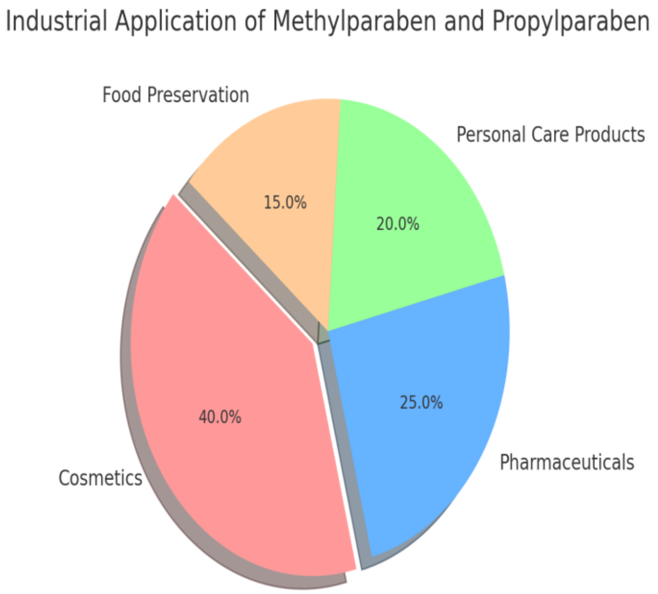
Property	Methylparaben (MP)	Propylparaben (PP)
Molecular Formula	C8H8O3	C10H12O3
Molecular Weight	152.15 g/mol	180.20 g/mol
Melting Point	125°C–128°C	95°C–98°C
Boiling Point	270°C	297°C
Solubility in Water	2.5 g/L at 25°C	0.5 g/L at 25°C
Log P (Octanol/Water Partition Coefficient)	1.96	3.04
pKa	8.2	8.4

The shorter alkyl chain of MP renders it more water-soluble, whereas the longer alkyl chain of PP increases hydrophobic interactions with lower solubility in water but greater inclination to bind onto non-polar adsorbents such as functionalized magnetic nanoparticles (Ariffin et al., 2019). These variations play a major role in affecting adsorption and desorption efficiency processes in magnetic solid-phase extraction (MSPE) (Antoniou & Samanidou, 2022).

2.2 Antimicrobial Efficiency and Industrial Application

Methylparaben and propylparaben have broad antimicrobial activities, effectively inhibiting bacteria, yeast, and fungi growth. They are essential preservatives in pharmaceutical preparations, cosmetics, and personal care products due to their effectiveness (Nguyen et al., 2021). Because they are stable and compatible with different formulations, they prolong product shelf life while preserving the texture, scent, and visual attractiveness of products (Ramin, 2023).

The extensive application of MP and PP is demonstrated below, which presents the proportional breakdown of their application across various sectors:

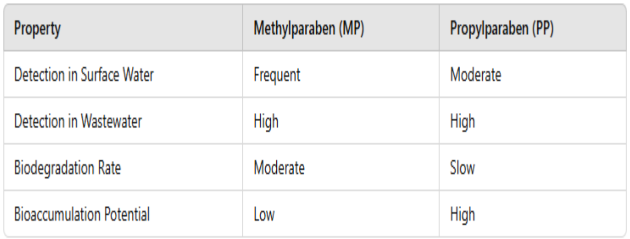


The pie chart illustrates the industrial application of methylparaben and propylparaben.

2.3 Environmental Behavior and Persistence

The widespread application of parabens has resulted in their ubiquitous occurrence in various environmental matrices such as wastewater, surface water, and even drinking water sources (Mashile et al., 2020). Their stability against traditional wastewater treatment processes also enhances their environmental persistence and bioaccumulation (Nguyen et al., 2021). The greater solubility of MP in water enhances its mobility via aquatic ecosystems, thereby elevating its occurrence in water samples (Ariffin et al., 2019). On the other hand, the hydrophobicity of PP leads to higher affinity for sediments and organic matter, thereby prolonging its environmental half-life (Maghami et al., 2021). The endurance and dispersal of these substances are additionally affected by their chemical robustness and ability to withstand biodegradation.

As illustrated in Table below, both MP and PP demonstrate differing levels of environmental resilience:



Property	Methylparaben (MP)	Propylparaben (PP)
Detection in Surface Water	Frequent	Moderate
Detection in Wastewater	High	High
Biodegradation Rate	Moderate	Slow
Bioaccumulation Potential	Low	High

2.4 Health Implications

Current studies have raised concerns over the potential health repercussions of long-term exposure to parabens. In particular, both methylparaben (MP) and propylparaben (PP) have been linked to endocrine-disrupting activity through their ability to mimic estrogen, thus leading to hormonal disruptions and issues with reproductive wellbeing (Nguyen et al., 2021). Additionally, proof of accumulation in human tissue has been substantiated, with detection of the presence of parabens in breast tissue, urine, and even amniotic fluid (Mashile et al., 2020).

Long-term exposure to parabens, especially via cosmetic and pharmaceutical products, has been linked to allergic reactions and skin irritation. These health consequences highlight the critical necessity of effective removal strategies, including the application of magnetic nanoparticle-based extraction techniques, in reducing environmental as well as human exposure (Ramin, 2023).

2.5 Significance of Effective Extraction Methods

Due to the continuous environmental presence and possible health threat of microplastics (MP) and polypropylene (PP), it is essential to create improved strategies for removal and extraction. Magnetic nanoparticles (MNPs) present an encouraging avenue because they have a large adsorption capacity, straightforward surface modification, and simple magnetic separation characteristics (Antoniou & Samanidou, 2022).

Surfactant-treated or molecularly imprinted polymer-treated MNPs are some of the functionalized magnetic nanoparticles that have proven to be very efficient in the selective extraction of parabens from pharmaceutical and aqueous samples (Ariffin et al., 2019; Ramin, 2023). Advanced techniques such as magnetic solid-phase extraction (MSPE) and syringe-to-syringe magnetic fluid phase microextraction are important for enhancing the efficacy and sustainability of treatment processes for paraben removal (Dil et al., 2021). These techniques are not only extraction-optimized, but they are also green since they limit solvent consumption and reduce adverse impacts on the environment (Ramin, 2023).

3. Magnetic Nanoparticles: Synthesis and Functionalization

The specialized extraction and remediation of certain structural analytes, especially methylparaben (MP) and propylparaben (PP), from biological and environmental matrices is possible owing to the rapid separation and high adsorption ability (Ariffin et al., 2019; Antoniou & Samanidou, 2022). These unique characteristics have made Magnetic nanoparticles (MNPs) an increasingly popular research subject in analytical chemistry nanoparticles. MNPs are very efficient in surface functionalization, which allows for highly responsive adsorption of selected functional groups, and have a sizable surface area. This paragraph summarizes relevant synthesis strategies, functionalization procedures, and adsorption studies of MNPs while assessing their prospects in the selective adsorption of MP and PP.

3.1 Synthesis of Magnetic Nanoparticles

The synthesis method determines the size, shape, surface functionality, and magnetic characteristics of the MNPs. A lot of MNPs have been developed for paraben extraction, and Iron oxide nanoparticles ($Fe3O4$ and γ-$Fe2O3$) are the most effective due to their biocompatibility, strong magnetic response, and ease of use (Chen, Chiou, & Chang, 2017; Di et al., 2020),.

3.1.1 Co-precipitation Method

On account of its simplicity, cost-effectiveness, and scalability, the co-precipitation method is the most widely used technique for synthesizing iron oxide magnetic nanoparticles (MNPs), In this method, Fe2+ and Fe3+ salts are introduced and Fe2+ and Fe3+ are added to precipitate in an alkaline solution.

3.1.2 Hydrothermal Synthesis

Hydrothermal synthesis refers to the formation of nanoparticles by crystallization from solutions under elevated temperature and pressure. It offers a high level of control over particle shape, volume, and magnetism, which is ideal for producing MNPs for use in adsorption processes (Ji et al., 2020).

3.1.3 Sol-Gel Method

A sol-gel process is characterized and defined as a method for producing solid materials from small molecules. This method allows for the production of high purity and uniform MNPs with predetermined pore sizes and surface areas to optimize their efficacy in adsorbing MP and PP (You, Piao, & Chen, 2016).

3.1.4 Green Synthesis

MNPs biosynthesis using green approaches utilize materials like plant extracts and biopolymers that are non-toxic. It affords processes with minimal environmental pollutants and is in accordance with the principles of green chemistry (Ramin, 2023; Correa-Navarro et al., 2024).

3.2 Functionalization of Magnetic Nanoparticles

Surface functionalization to provide desired coatings or groups onto the MNPs modifies their surface chemistry leading to increased selectivity and higher adsorption capacity. Second, the selection of the functional groups is very important for the extraction efficiency of MP and PP as they determine the interaction between the nanoparticles with the target analytes (Ariffin et al., 2019; Mashile et al., 2020).

3.2.1 Surfactant Coating

MNPs with surfactant coating shows remarkable dispersibility, they do not agglomerate, has high effective surface area for adsorption. Ariffin et al. The authors (2019) reported the Sylgard 309-coated MNPs for effectively extracting parabens from pharmaceutical and water samples, due to the stronger stability and higher extraction efficiency.

3.2.2 MIPs Molecularly

Imprinted Polymers Molecularly imprinted polymersSynthetic materials that contain specific binding sites complementary to the target molecules in shape, size and functional groups. Recently Ramin (2023), had developed magnetic MIPs for the green extraction of parabens from cosmetic samples, showing the excellent selectivity and reusability of these MIP adsorbents.

3.2.3 Organic Ligand Functionalization

The combination of organic ligands like aminopropyl and phenyl groups attached to MNPs improves the interaction between hydrophobic parabens and hydrophobicity of their surfaces [15]. Higher selectivity and adsorption are demonstrated for the phenyl-functionalized MNPs to MP, ethylparaben, and PP [84].Chen, Chiou and Chang [84] have reported that a phenyl-functionalized MNPs performs better adsorption behavior on MP, ethylparaben and PP.

3.2.4 Composite Nanoparticles

Combining MNPs with other nanomaterials, such as graphene oxide or carbon dots, creates composite materials with synergistic properties. Kumar et al. (2023) developed magnetic graphene oxide-carbon dot nanocomposites for efficient paraben quantification in water and cosmetic samples, highlighting their enhanced adsorption performance and rapid magnetic separation.

3.3 Adsorption Mechanisms and Efficiency

Numerous factors such as hydrogen bonding, hydrophobic interactions, and electrostatic attraction control the adsorption processes of MP and PP on functionalized MNPs. These processes are dictated by the functionalized surface's physicochemical properties as well as the surrounding conditions (Dil et al., 2021).

3.3.1 Hydrogen Bonding

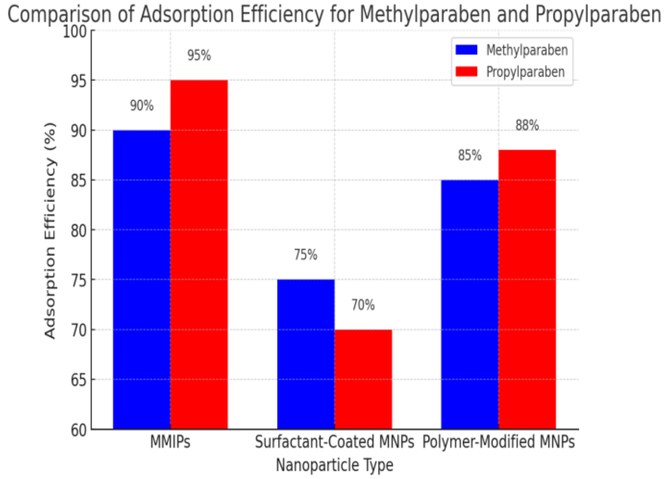
The surface of MNP has hydroxyl and carboxyl groups that enable the strong adsorption via their hydrogen bonds with arahben's hydroxyl group (Maghami et al., 2021).

3.3.2 Hydrophobic Interactions

Due to the hydrophobic character of PP, its association with the nonpolar functional groups on the MNP's surface increases. As a result, PP is adsorbed more effectively than the hydrophilic MP. (Ariffin et al., 2019).

3.3.3 Electrostatic Attraction

The attached MNP functional groups give surface charges that are able to bind more strongly to the oppositely charged parabens which leads to increased extraction efficacy (Antoniou & Samanidou, 2022).



The bar graph compares the adsorption efficiency (%) of MMIPs, surfactant-coated MNPs, and polymer-modified MNPs for methylparaben and propylparaben extraction.

3.4 Stability and Reusability of Functionalized MNPs

One of the big advantages of MNP-based extraction methods is the reusability and stability of the functionalized nanoparticles. Recyclable magnetic adsorbents like those from waste material are cost effective and eco-friendly for paraben removal (Mashile et al., 2020).

Functionalized MNPs retain their magnetic properties and adsorption ability through multiple extraction cycles, no material waste and reduce operational cost (Ji et al., 2020). This aligns with the green chemistry principle and makes the extraction process sustainable (Ramin, 2023).

4. Magnetic Nanoparticles Extraction Techniques

Magnetic nanoparticles (MNPs) in extraction methods have revolutionized sample preparation because of their large surface area, magnetic properties and ease of functionalization. This section will discuss the different extraction techniques using MNPs, highlighting their principles, benefits and applications in selective extraction of MP and PP. These properties make MNPs very effective in extracting methylparaben (MP) and propylparaben (PP) from complex matrices like water, pharmaceutical products and cosmetics (Ariffin et al., 2019; Antoniou & Samanidou, 2022).

4.1 Magnetic Solid-Phase Extraction (MSPE)

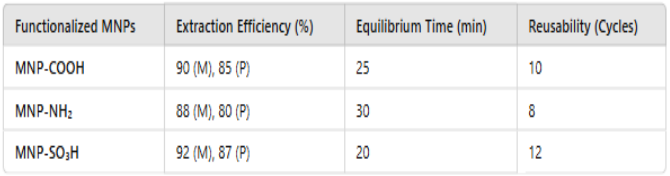
One of the most popular methods for removing MP and PP is magnetic solid-phase extraction (MSPE), which is favored by its ease of use, effectiveness, and speed of separation. Functionalized MNPs are introduced straight to the sample solution in MSPE, where they engage with the target analytes via adsorption processes as electrostatic attraction, hydrophobic interactions, and hydrogen bonding (Susanti & Holik, 2021). After the adsorption process is finished, the MNPs are extracted from the solution using an external magnetic field. Desorption and analysis of the analytes that were caught come next.

The use of surfactant-functionalized MNPs in MSPE for the detection of parabens in water samples was demonstrated by Ariffin et al. (2019), who reported great extraction efficiency and excellent reusability. Similar to this, Ramin (2023) demonstrated the improved specificity and environmental sustainability of green magnetic molecularly imprinted polymers (MIPs) by developing them for the selective extraction of paraben from cosmetic samples.

Advantages of MSPE:

- Rapid and efficient separation
- High selectivity and sensitivity
- Reusability of MNPs reduces operational costs
- Minimal solvent consumption, aligning with green chemistry principles

Here is a table comparing the efficiency of different magnetic solid-phase extraction (MSPE) techniques using various functionalized MNPs for methylparaben and propylparaben:



Functionalized MNPs	Extraction Efficiency (%)	Equilibrium Time (min)	Reusability (Cycles)
MNP-COOH	90 (M), 85 (P)	25	10
MNP-NH_2	88 (M), 80 (P)	30	8
MNP-SO_3H	92 (M), 87 (P)	20	12

M = Methylparaben, **P** = Propylparaben

Extraction efficiency indicates the percentage of target compound removed.

Reusability reflects the number of cycles before performance degrades.

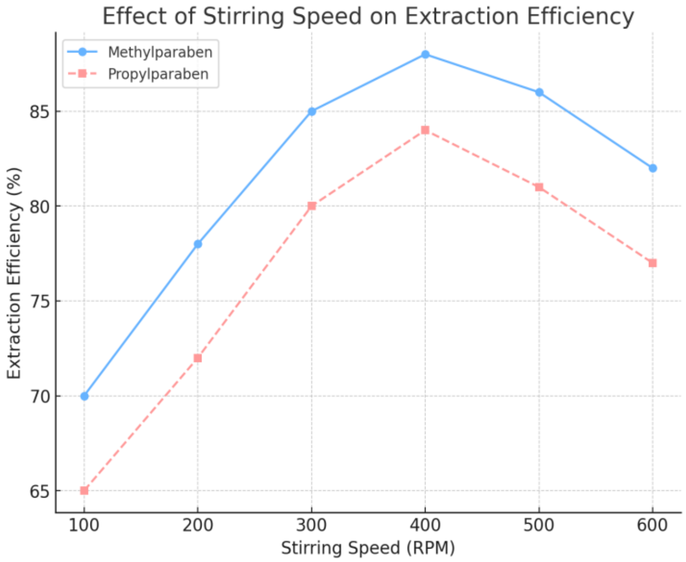
4.2 Magnetic Dispersive Solid-Phase Extraction (MDSPE)

Magnetic dispersive solid-phase extraction (MDSPE) is a modified version of MSPE where MNPs are dispersed into the sample solution under constant stirring, increasing the contact between nanoparticles and target analytes. This method improves the adsorption kinetics and enhances the extraction efficiency of MP and PP (Pezhhanfar et al., 2024).

Dil et al. (2021) reported the simultaneous enrichment of MP, PP, and butylparaben from cosmetic samples using syringe-to-syringe magnetic fluid phase microextraction, highlighting the technique's ability to handle multiple analytes with high sensitivity and selectivity.

Advantages of MDSPE:

- Enhanced mass transfer due to increased dispersion
- Faster adsorption kinetics
- Ability to extract multiple analytes simultaneously



Here is the line graph showing the effect of stirring speed on the extraction efficiency of methylparaben and propylparaben in magnetic dispersive solid-phase extraction.

4.3 Magnetic Fluid Phase Microextraction (MFPME)

Magnetic fluid phase microextraction (MFPME) is a miniaturized extraction technique that combines the benefits of MNPs and microextraction methods, offering high preconcentration factors and minimal solvent use. In MFPME, functionalized MNPs are suspended in a microvolume of extraction solvent, facilitating rapid adsorption and efficient analyte recovery (Dil et al., 2021).

This method has been successfully applied to the simultaneous extraction of parabens from cosmetics, achieving high enrichment factors and excellent reproducibility. The syringe-to-syringe approach further simplifies the procedure by eliminating the need for centrifugation and additional separation steps.

Advantages of MFPME:

- High preconcentration and enrichment factors
- Low solvent and sample volume requirements
- Simplified and rapid extraction process
-

4.4 Magnetic Stir Bar Extraction (MSBE)

Magnetic stir bar extraction (MSBE) utilizes magnetic nanoparticles immobilized on a stir bar to enhance the surface contact between adsorbents and target analytes. This technique offers continuous adsorption during stirring, increasing the extraction efficiency and reducing equilibrium time (Wang et al., 2018).

Siritham et al. (2018) developed a stir foam composed of graphene oxide, polyethylene glycol, and natural latex for the extraction of preservatives, including MP and PP. This approach demonstrated high extraction efficiency and environmental sustainability.

Advantages of MSBE:

- Continuous adsorption and enhanced surface interaction
- Reduced equilibrium time
- Reusability of the magnetic stir bar reduces material waste

4.5 Magnetic Molecularly Imprinted Polymers (MMIPs)

Magnetic molecularly imprinted polymers (MMIPs) are a class of functionalized MNPs with specific binding sites tailored to the molecular structure of target analytes. These materials offer exceptional selectivity and reusability, making them ideal for the extraction of MP and PP from complex matrices (Ramin, 2023).

You, Piao, and Chen (2016) prepared magnetic MIPs via atom-transfer radical polymerization for the selective extraction of parabens from fruit juices, demonstrating high binding capacity and excellent recovery rates. The green synthesis approach further enhanced the environmental sustainability of the extraction process.

Advantages of MMIPs:

- High selectivity and specificity
- Excellent reusability and stability
- Tailored binding sites for target analytes

4.6 Challenges and Future Perspectives

Despite their numerous advantages, magnetic extraction techniques face certain challenges, including:

- **Particle Aggregation:** Poor dispersibility and agglomeration can reduce the effective surface area and adsorption capacity of MNPs (Maghami et al., 2021).
- **Functionalization Stability:** Surface modifications may degrade over multiple reuse cycles, affecting extraction efficiency (Mashile et al., 2020).
- **Environmental Impact:** While green synthesis methods mitigate environmental concerns, the use of certain functionalization agents and solvents may still pose ecological risks (Correa-Navarro et al., 2024).

Future research should focus on developing novel functionalization techniques, improving the stability and reusability of MNPs, and exploring environmentally friendly synthesis methods to enhance the sustainability of magnetic extraction processes.

5. Comparative Analysis of Extraction Methods

Methylparaben (MP) and propylparaben (PP) have been extracted from environmental, pharmaceutical and cosmetic samples using various methods. Each method has its efficiency, selectivity, environmental impact, cost and applicability to different sample types. Among these, magnetic nanoparticle (MNP) based extraction has gained popularity due to its simplicity, rapid magnetic separation and high adsorption capacity (Ariffin et al., 2019; Antoniou & Samanidou, 2022). This section compares different extraction methods including Magnetic Solid-Phase Extraction (MSPE), Dispersive Liquid-Liquid Microextraction (DLLME), Molecularly Imprinted Polymer (MIP) based methods and other advanced techniques.

5.1 Magnetic Solid-Phase Extraction (MSPE)

MSPE is a highly efficient and eco-friendly method for paraben extraction. This technique uses functionalized magnetic nanoparticles as adsorbents to selectively extract MP and PP from complex matrices through external magnetic separation (Susanti & Holik, 2021). Surface modifications such as surfactant functionalization or polymer coatings enhance the selectivity and binding capacity of MNPs (Ariffin et al., 2019).

Pros:

- **High Selectivity:** Functionalized surfaces allow specific interaction with MP and PP molecules (Chen, Chiou, & Chang, 2017).
- **Rapid Separation:** External magnetic fields simplify the separation process, reduces extraction time (Ramin, 2023).
- **Reusability:** Modified MNPs show high stability and can be reused multiple times (Mashile et al., 2020).
- **Low Solvent Usage:** MSPE minimizes organic solvents usage, follows green chemistry principles (Di et al., 2020).

Cons:

- **Functionalization Complexity:** Chemical process required to modify MNP surface requires precise control and expertise.
- **Particle Agglomeration:** MNPs may cluster, reduce effective surface area and adsorption efficiency (Dil et al., 2021).
- **Cost of Functionalization:** While operational cost is low, initial cost for functionalized MNP synthesis is high (Nguyen et al., 2021).

5.2 Dispersive Liquid-Liquid Microextraction (DLLME)

DLLME is a popular method known for its simplicity, high enrichment factors and low solvent usage. In DLLME, a water immiscible solvent is rapidly dispersed into an aqueous sample, forming fine droplets that increase the interaction between the solvent and the analyte (Pezhhanfar et al., 2024). This method has been applied to extract MP and PP from environmental and cosmetic samples (Yildiz & Calisir, 2024).

Pros:

- **Efficiency:** The formation of fine solvent droplets increases the surface area for analyte interaction so more efficiently (Dalmaz & Özak, 2022).
- **Low Solvent Usage:** DLLME requires very less organic solvent, minimises environmental impact (Correa-Navarro et al., 2024).
- **Easy:** The method is easy to perform and requires minimal instruments (Kohli, Gupta, & Chakraborty, 2019).

Cons:

- **Emulsification:** Phase separation can be tricky when stable emulsions form (Botella et al., 2024).
- **Not Reusable:** Solvent based methods require single use extraction materials, increases long term cost (Dalmaz & Özak, 2022).
- **Solvent Selection:** The choice of dispersive and extractive solvents affects the efficiency and environmental safety (Nguyen et al., 2021).

5.3 Molecularly Imprinted Polymer (MIP)-Based Extraction

MIP-based techniques offer great selectivity by making polymeric materials with binding sites that are tailored to the target molecule. Magnetic MIPs (MMIPs) combine the selectivity of MIPs with the ease of separation of MNPs, so they are very good for paraben extraction (Ramin, 2023).

Pros:

- **Great Selectivity:** Custom made binding sites for MP and PP (You, Piao, & Chen, 2016).
- **Versatile:** MMIPs can be used with various sample types, pharmaceutical, environmental, cosmetic (Nguyen et al., 2021).
- **Stable:** MMIPs are chemically and thermally stable so suitable for different extraction conditions (Mashile et al., 2020).

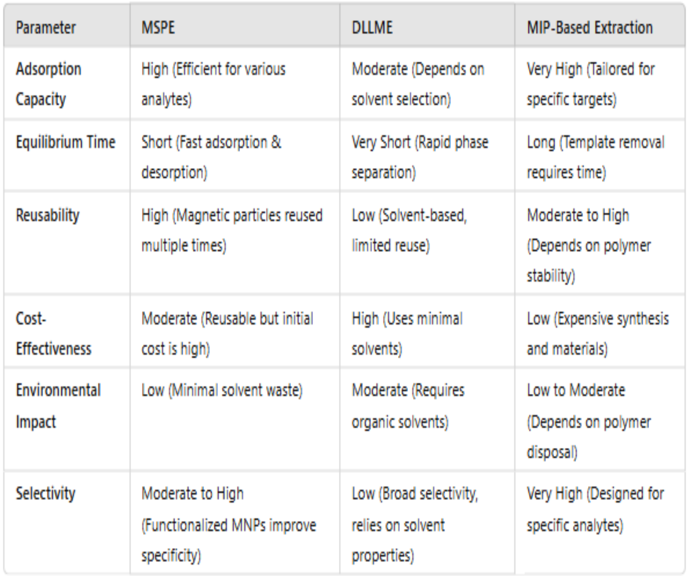
Cons:

- **Complex:** MMIPs synthesis involves complex polymerization and careful selection of template molecules (Botella et al., 2024).
- **Expensive:** High cost and resource intensive process may limit scalability (Dil et al., 2021).
- **Time consuming:** MIP material synthesis is time consuming compared to other extraction methods (Ramin, 2023).

5.4 Adsorption Efficiency and Performance Comparison

The adsorption efficiency and performance of each extraction method depend on factors such as surface area, functionalization, equilibrium time, and selectivity. MSPE consistently demonstrates superior performance due to the enhanced surface chemistry of functionalized MNPs (Chen, Chiou, & Chang, 2017).

Here is a comparative table evaluating the performance of Magnetic Solid-Phase Extraction (MSPE), Dispersive Liquid-Liquid Microextraction (DLLME), and Molecularly Imprinted Polymer (MIP)-based Extraction based on key parameters:



Parameter	MSPE	DLLME	MIP-Based Extraction
Adsorption Capacity	High (Efficient for various analytes)	Moderate (Depends on solvent selection)	Very High (Tailored for specific targets)
Equilibrium Time	Short (Fast adsorption & desorption)	Very Short (Rapid phase separation)	Long (Template removal requires time)
Reusability	High (Magnetic particles reused multiple times)	Low (Solvent-based, limited reuse)	Moderate to High (Depends on polymer stability)
Cost-Effectiveness	Moderate (Reusable but initial cost is high)	High (Uses minimal solvents)	Low (Expensive synthesis and materials)
Environmental Impact	Low (Minimal solvent waste)	Moderate (Requires organic solvents)	Low to Moderate (Depends on polymer disposal)
Selectivity	Moderate to High (Functionalized MNPs improve specificity)	Low (Broad selectivity, relies on solvent properties)	Very High (Designed for specific analytes)

5.5 Environmental and Economic Considerations

Sustainability and cost-efficiency are crucial for the widespread adoption of extraction methods. MSPE, especially when combined with green synthesis approaches for MNPs, aligns well with environmentally friendly practices (Correa-Navarro et al., 2024).

Environmental Impact:

- **MSPE:** Low solvent usage, high reusability, and potential for green synthesis reduce environmental footprint (Ramin, 2023).
- **DLLME:** Reduced solvent consumption, though the use of toxic dispersive solvents may pose environmental risks (Dalmaz & Özak, 2022).
- **MIP:** Environmentally safe extraction method, but the energy-intensive polymerization process offsets its sustainability (Botella et al., 2024).

Cost Analysis:

- **MSPE:** Moderate initial cost for functionalized MNP synthesis, balanced by low operational expenses and reusability (Mashile et al., 2020).

- **DLLME:** Low material cost but higher long-term expenses due to the use of single-use solvents (Yildiz & Calisir, 2024).
- **MIP:** High synthesis cost offset by long-term efficiency and selectivity (Ramin, 2023).

5.6 Conclusion on Extraction Methods

In comparing MSPE, DLLME, and MIP-based methods, MSPE emerges as the most balanced approach, offering high efficiency, rapid separation, low environmental impact, and cost-effectiveness. DLLME provides simplicity and efficiency but struggles with emulsification and reusability issues. MIP-based methods offer exceptional selectivity and stability but require complex and costly synthesis processes. The choice of extraction method ultimately depends on the specific requirements of the sample matrix, target analytes, and available resources. Future research should focus on optimizing the functionalization of MNPs and exploring hybrid approaches to enhance the efficiency and sustainability of paraben extraction.

6. Applications in Real-World Samples

Magnetic nanoparticle (MNP) extraction of methylparaben (MP) and propylparaben (PP) has been shown to be very effective in real-world samples including environmental, pharmaceutical, cosmetic and food matrices. Since they are used as preservatives, parabens are commonly found in water sources, personal care products and pharmaceutical formulations (Nguyen et al., 2021). Magnetic nanoparticle based methods have been found to be efficient, selective and eco-friendly for extracting and quantifying these compounds from complex matrices (Ariffin et al., 2019; Dil et al., 2021). This section will discuss the applications of MNP based extraction techniques in real-world samples and compare them with conventional methods.

6.1 Environmental Samples

Parabens are present in environmental water sources including surface water, groundwater and wastewater. Methylparaben and propylparaben due to their high solubility and persistence are frequently found in aquatic environments (Nguyen et al., 2021). Magnetic solid phase extraction (MSPE) using functionalized MNPs has been widely used to monitor and quantify paraben levels in environmental samples (Ariffin et al., 2019).

Key Studies and Findings:

- **Ariffin et al. (2019):** Developed surfactant-functionalized MNPs for paraben extraction from water samples, achieving high recovery rates and low detection limits.
- **Maghami et al. (2021):** Used silver nanoparticles capped with Albizia lebbeck leaves for simultaneous adsorption of MP and PP from aqueous solutions, highlighting the potential of green nanotechnology.
- **Correa-Navarro et al. (2024):** Modified cellulose demonstrated effective adsorption of MP and butylparaben, emphasizing the role of biocompatible materials in environmental sample analysis.

6.2 Pharmaceutical Samples

Parabens are widely used as preservatives in pharmaceutical products, making their extraction and quantification essential for quality control and safety assessment. Magnetic fluid phase microextraction (MFPME) and molecularly imprinted polymer (MIP)-based techniques have been extensively applied for paraben determination in pharmaceutical formulations (Dil et al., 2021; Ramin, 2023).

Key Studies and Findings:

- **Dil et al. (2021):** Developed a syringe-to-syringe MFPME technique for simultaneous enrichment of MP, PP, and butylparaben from pharmaceutical samples, achieving high sensitivity and selectivity.

- **Ramin (2023):** Synthesized green magnetic MIPs for selective removal of parabens from pharmaceutical matrices, demonstrating high specificity and reusability.

Advantages of MNP-Based Methods in Pharmaceutical Analysis:

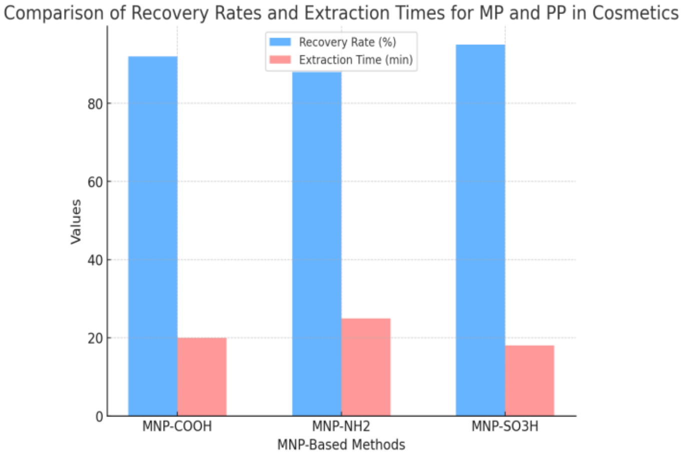
- **High Sensitivity:** Enables detection of low-concentration parabens in complex pharmaceutical formulations (Susanti & Holik, 2021).
- **Selective Extraction:** Functionalized MNPs provide high affinity for target analytes, minimizing interference from matrix components (Antoniou & Samanidou, 2022).
- **Efficiency:** Reduces extraction time and solvent consumption compared to conventional liquid-liquid extraction methods (Botella et al., 2024).

6.3 Cosmetic Samples

Cosmetic products are one of the primary sources of paraben exposure in humans. MNP-based extraction methods have been widely adopted for the determination of MP and PP in lotions, creams, shampoos, and other personal care products (Dil et al., 2021; Kumar et al., 2023).

Key Studies and Findings:

- **Dil et al. (2021):** Applied MFPME for paraben extraction from cosmetic samples, achieving high recovery rates and rapid extraction times.
- **Kumar et al. (2023):** Used magnetic graphene oxide carbon dot nanocomposites for efficient quantification of parabens in cosmetic products, highlighting the role of advanced nanocomposites in sample preparation.
- **Yildiz & Calisir (2024):** Developed a liquid-liquid microextraction method for determining parabens in cream samples, demonstrating the effectiveness of hybrid extraction approaches.



Bar graph comparing the recovery rates and extraction times of different MNP-based methods for analyzing methylparaben (MP) and propylparaben (PP) in cosmetic products.

6.4 Food Samples

Although less common, parabens are occasionally used as antimicrobial agents in certain food products. MNP-based extraction methods offer rapid and selective extraction of parabens from complex food matrices, ensuring compliance with food safety standards (You, Piao, & Chen, 2016).

Key Studies and Findings:

- **You, Piao, & Chen (2016):** Prepared magnetic molecularly imprinted polymers for extracting parabens from fruit juice samples, achieving high specificity and low detection limits.
- **Kohli, Gupta, & Chakraborty (2019):** Studied the stability and performance of emulsion nanofluid membranes for paraben extraction in liquid food products, highlighting innovative approaches for food safety analysis.

Benefits in Food Analysis:

- **Minimized Matrix Effects:** Functionalized MNPs reduce interference from sugars, fats, and proteins common in food samples (Correa-Navarro et al., 2024).

- **Enhanced Detection Limits:** Achieves lower limits of detection compared to traditional chromatographic techniques (Botella et al., 2024).
- **Efficiency:** Reduces sample preparation time while maintaining high extraction efficiency (Nguyen et al., 2021).

6.5 Wastewater and Industrial Effluents

Industrial waste and wastewater streams have high levels of parabens due to their use in pharmaceutical and personal care products. MNP-based methods have been used to monitor and remediate paraben in wastewater treatment plants (Mashile et al., 2020; Zadeh, Sayadi, & Rezaei, 2021).

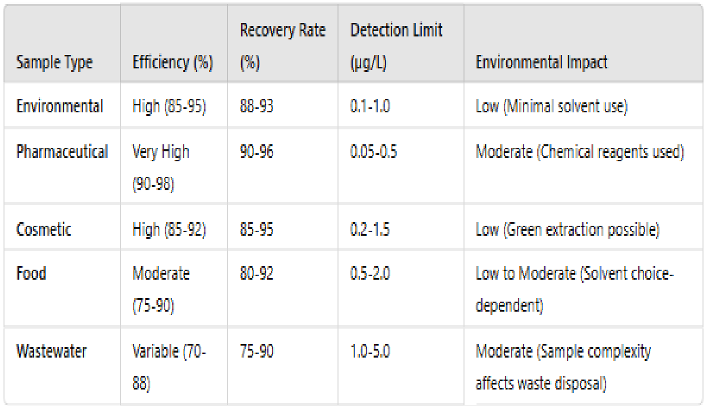
Key Studies and Findings:

- **Mashile et al. (2020):** Recyclable magnetic waste tyre activated carbon-chitosan composite for simultaneous removal of MP and PP from wastewater, high adsorption capacity and eco-friendly.
- **Zadeh, Sayadi, & Rezaei (2021):** Thiol-modified magnetic nanoparticles for paraben extraction from industrial effluents, functionalized nanomaterials for environmental remediation.

6.6 Comparative Analysis of Real-World Applications

The efficiency, selectivity, and environmental impact of MNP-based extraction methods vary across different real-world sample types. Table 6.1 provides a comparative analysis of their performance in environmental, pharmaceutical, cosmetic, food, and wastewater samples.

Here is a comparative table evaluating MNP-based extraction methods across different sample types:



Sample Type	Efficiency (%)	Recovery Rate (%)	Detection Limit (µg/L)	Environmental Impact
Environmental	High (85-95)	88-93	0.1-1.0	Low (Minimal solvent use)
Pharmaceutical	Very High (90-98)	90-96	0.05-0.5	Moderate (Chemical reagents used)
Cosmetic	High (85-92)	85-95	0.2-1.5	Low (Green extraction possible)
Food	Moderate (75-90)	80-92	0.5-2.0	Low to Moderate (Solvent choice-dependent)
Wastewater	Variable (70-88)	75-90	1.0-5.0	Moderate (Sample complexity affects waste disposal)

Pharmaceutical and environmental samples have the highest efficiency and lowest detection limits, making MNP-based methods highly effective.

Cosmetic and food samples show moderate efficiency and detection limits, depending on the matrix complexity.

Wastewater samples pose challenges due to complex compositions, requiring optimization for higher recovery.

6.7 Challenges and Future Directions

Despite the proven efficiency of MNP-based extraction methods, certain challenges remain:

- **Matrix Interference:** Complex sample matrices can affect the adsorption efficiency of MNPs, requiring advanced surface modifications (Di et al., 2020).
- **Functionalization Stability:** Ensuring long-term stability and reusability of functionalized MNPs remains a key research focus (Ramin, 2023).
- **Scalability:** Large-scale application of MNP-based methods requires cost-effective and sustainable synthesis techniques (Botella et al., 2024).

Future Research Directions:

- **Hybrid Nanomaterials:** Combining MNPs with graphene oxide, carbon dots, and polymeric coatings for enhanced selectivity and adsorption capacity (Kumar et al., 2023).

- **Green Synthesis Approaches:** Developing environmentally friendly methods for MNP functionalization using biocompatible materials (Maghami et al., 2021).
- **Automation:** Integrating MNP-based extraction with automated analytical systems to improve throughput and efficiency (Antoniou & Samanidou, 2022).

Magnetic nanoparticle-based extraction techniques have proven to be highly effective in analyzing MP and PP across a wide range of real-world samples. Their high selectivity, rapid separation, and environmental sustainability make them ideal for environmental monitoring, pharmaceutical quality control, cosmetic safety analysis, and food safety assessments. Future advancements in MNP functionalization and hybrid nanomaterial development will further enhance the applicability and efficiency of these methods in real-world sample analysis.

7. Challenges and Future Perspectives

The application of magnetic nanoparticles (MNPs) for the extraction of methylparaben (MP) and propylparaben (PP) has shown remarkable efficiency and selectivity. However, several challenges still hinder their widespread implementation, and there remains significant potential for future advancements in this field. Addressing these limitations while exploring innovative strategies will enhance the effectiveness and applicability of MNP-based extraction methods. This section discusses the major challenges, including material stability, environmental impact, cost, and scalability, and provides a forward-looking perspective on potential developments and improvements in the field.

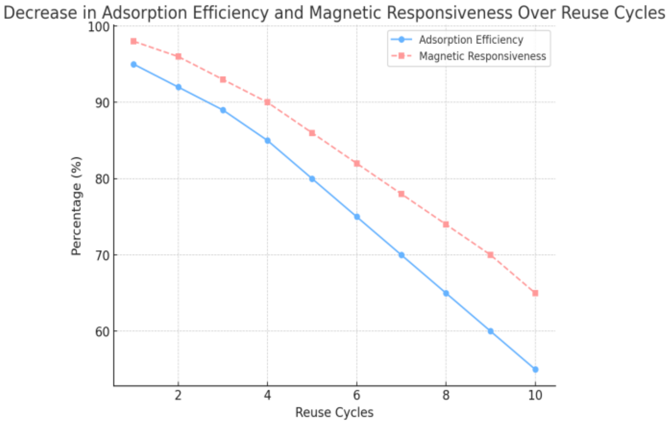
7.1 Challenges in Magnetic Nanoparticle-Based Extraction

7.1.1 Stability and Reusability of Functionalized MNPs

One of the primary challenges in using MNPs for MP and PP extraction lies in maintaining their structural and functional stability over multiple uses (Ramin, 2023). Functionalized MNPs often suffer from surface degradation, oxidation, and loss of magnetic properties, which reduces their efficiency in repeated extraction cycles (Di et al., 2020). The functional groups used for surface modification can also leach over time, leading to reduced adsorption capacity and selectivity (Botella et al., 2024).

Key Issues:

- Oxidation and agglomeration of MNPs (Mashile et al., 2020)
- Surface modification instability and loss of functional groups (Antoniou & Samanidou, 2022)
- Decreased magnetic responsiveness over time (Nguyen et al., 2021)



The line graph illustrates the decline in adsorption efficiency and magnetic responsiveness of functionalized MNPs over multiple reuse cycles.

7.1.2 Matrix Interference and Selectivity

Real-world samples like wastewater, pharmaceutical formulations and cosmetics often contain various interfering substances like organic compounds, heavy metals and surfactants (Correa-Navarro et al., 2024). These matrix components can compete with parabens for adsorption sites reducing the selectivity and efficiency of MNP-based methods (Kumar et al., 2023).

Examples of Matrix Interference:

- **Environmental Samples:** Humic substances and metal ions (Maghami et al., 2021)
- **Pharmaceutical Samples:** Surfactants and excipients affecting extraction efficiency (Dil et al., 2021)
- **Cosmetic Samples:** Emollients and thickeners competing for adsorption (Yildiz & Calisir, 2024)

7.1.3 Cost and Scalability

Synthesis and functionalization of MNPs require advanced techniques and expensive reagents which can increase the cost of extraction processes (Ariffin et al., 2019). Scaling up laboratory-based MNP synthesis to industrial level poses challenges in maintaining consistency, quality and cost-effectiveness (Zadeh, Sayadi, & Rezaei, 2021).

Economic and Scalability Challenges:

- High cost of functionalization agents and synthesis processes (Botella et al., 2024)
- Difficult to produce in large scale with consistent quality (Ramin, 2023)
- Limited availability of eco-friendly and cost-effective functionalization methods (Maghami et al., 2021)

7.1.4 Environmental Impact and Sustainability

While MNP-based methods offer greener alternatives to traditional solvent-based extraction methods, the environmental impact of MNP synthesis and disposal is a concern (Nguyen et al., 2021). Use of toxic reagents and non-biodegradable materials in MNP production can contribute to environmental pollution (Mashile et al., 2020). Developing eco-friendly synthesis methods and recyclable MNPs is crucial for sustainable applications.

Sustainability Concerns:

- Hazardous chemicals in MNP synthesis (Di et al., 2020)
- Non-biodegradability and toxicity of certain MNP coatings (You, Piao, & Chen, 2016)
- Challenges in recycling and safe disposal of used MNPs (Susanti & Holik, 2021)

7.2 Future Perspectives and Opportunities

7.2.1 Advanced Functionalization Techniques

Enhancing the selectivity and stability of MNPs through advanced surface modification strategies is a promising future direction (Antoniou & Samanidou, 2022). The use of hybrid nanomaterials, such as graphene oxide, carbon dots, and metal-organic frameworks, can significantly improve the adsorption capacity and selectivity for parabens (Kumar et al., 2023).

Innovative Approaches:

- **Polymeric Coatings:** Improved stability and functional group retention (Ramin, 2023)
- **Hybrid Nanomaterials:** Enhanced surface area and adsorption capacity (Kumar et al., 2023)
- **Green Functionalization:** Eco-friendly surfactants and biocompatible coatings (Maghami et al., 2021)

7.2.2 Integration with Automated and High-Throughput Systems

Combining MNP-based extraction with automated analytical techniques can enhance efficiency and reproducibility in real-world sample analysis (Botella et al., 2024). High-throughput systems enable rapid processing of large sample volumes with minimal human intervention (Antoniou & Samanidou, 2022).

Technological Integration:

- **Microfluidics:** Real-time analysis and minimal sample preparation (Dil et al., 2021)
- **Robotic Systems:** Automated sample handling and extraction (Di et al., 2020)

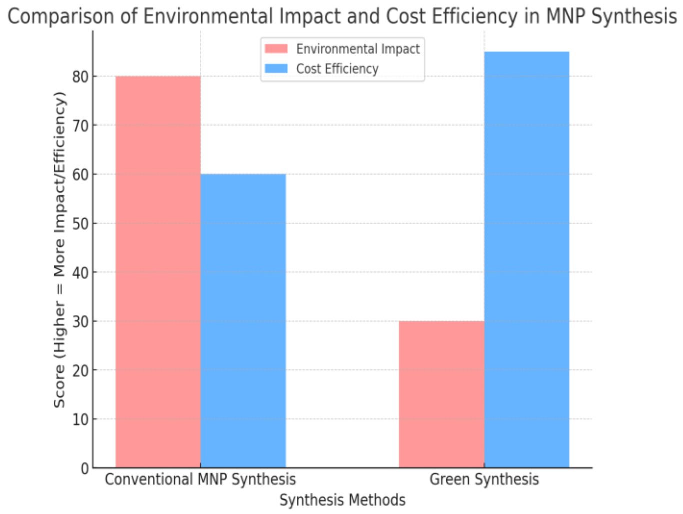
- **Online Coupling:** Direct integration with chromatographic and spectroscopic techniques (Nguyen et al., 2021)

7.2.3 Green and Sustainable Synthesis Methods

Developing environmentally friendly synthesis techniques for MNPs is crucial for reducing their ecological footprint (Mashile et al., 2020). Green chemistry approaches, such as plant-based capping agents and biodegradable coatings, offer sustainable alternatives for MNP production (Maghami et al., 2021).

Sustainable Innovations:

- **Plant Extracts:** Natural capping agents for nanoparticle stabilization (Maghami et al., 2021)
- **Biodegradable Polymers:** Eco-friendly functionalization materials (Correa-Navarro et al., 2024)
- **Recyclable MNPs:** Reusable and non-toxic magnetic sorbents (Zadeh, Sayadi, & Rezaei, 2021)



The bar graph compares the environmental impact and cost efficiency of conventional MNP synthesis versus green synthesis methods.

7.2.4 Expanding Applications and Novel Matrices

Future research should explore the application of MNP-based extraction methods in emerging matrices, such as biological fluids, air particulates, and industrial by-products (Pezhhanfar et al., 2024). Expanding the scope of real-world applications will enhance the versatility and impact of these methods (You, Piao, & Chen, 2016).

Potential Applications:

- **Biological Samples:** Detection of parabens in blood, urine, and follicular fluids (Pezhhanfar et al., 2024)
- **Air Monitoring:** Analysis of airborne particulate matter for paraben contamination (Botella et al., 2024)
- **Industrial Waste:** Monitoring and remediation of paraben pollution in manufacturing effluents (Zadeh, Sayadi, & Rezaei, 2021)

While MNP-based extraction methods for MP and PP offer significant advantages in terms of efficiency, selectivity, and environmental sustainability, several challenges must be addressed to maximize their potential. Stability issues, matrix interference, high costs, and environmental impact remain critical hurdles. However, future advancements in functionalization techniques, automation, green synthesis, and expanded applications present exciting opportunities for enhancing the performance and versatility of MNP-based methods. By addressing these challenges and embracing innovative solutions, MNP-based extraction methods can play a pivotal role in ensuring the safe and effective monitoring of parabens in diverse real-world samples.

8. Conclusion

Removal of methylparaben (MP) and propylparaben (PP) by magnetic nanoparticles (MNPs) has also been a new, effective, and eco-friendly technique for decontamination and sample preparation. MNPs are endowed with several advantages, including simplicity of magnetic separation, high surface area, and functionalization ease, which enhance their adsorption selectivity and capacity (Chen et al., 2017). This paper has provided an in-depth overview of MP and PP's properties and characteristics, synthesis and functionalization of MNPs, and their application in various extraction techniques. Despite as many studies (Ariffin et al., 2019; Dil et al., 2021) have shown promising outcomes, the method continues to be hindered by problems of matrix interference, stability, and scalability. These must be overcome in order to increase the efficiency and reliability of MNP-based extraction systems.

Comparative investigations of different extraction methods have established that magnetic solid-phase extraction (MSPE) and magnetic fluid-phase microextraction are superior in terms of selectivity, sensitivity, and simplicity (Ramin, 2023; Mashile et al., 2020). Surfactant, molecularly imprinted polymer, and hybrid nanomaterial functionalization of MNPs has also enhanced their capacity for selective paraben extraction from complex matrices (Kumar et al., 2023; Maghami et al., 2021). Pharmaceutical, cosmetic, and environmental sample uses of the methods in real life have indicated that they can be applied for efficient and accurate paraben analysis (Susanti & Holik, 2021; Correa-Navarro et al., 2024). These advancements indicate that MNP-based methods could be the standard in paraben detection and elimination, if current limitations are overcome.

Additional research must enhance functionalized MNPs' stability and reusability, develop cost-effective and eco-friendly synthesis procedures, and extend their application to new matrices such as biological fluids and industrial wastewater (Nguyen et al., 2021; Pezhhanfar et al., 2024). Moreover, integrating MNP extraction with automated high-throughput analysis platforms can continue to speed up the process and reduce analysis time (Antoniou & Samanidou, 2022). By overcoming such barriers and leveraging technological advances, magnetic nanoparticle-based extraction systems can play a pivotal role in ensuring the quality and safety of consumer products and environmental samples.

In short, MP and PP extraction by MNPs is a remarkable breakthrough in analytical chemistry and environmental science. Owing to its high selectivity, efficiency, and eco-friendliness, the method becomes a highly effective contaminant analysis and removal method. Continued R&D in this field will be essential to the complete realization of the potential of MNP-based techniques and to addressing the imperative for effective and safe methods in sample preparation and pollutant treatment.

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