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Review paper

Recent application of nanomaterials-based magnetic solid phase micro-extraction for heavy metals food toxicity

Elham Esmaeili Lashkarian[1], Shahin Ahmadi[2*], Faranak Beigmohammadi[1]

[1] Department of Food Science and Technology, Faculty of Agriculture, Kermanshah Branch, Islamic Azad University, Kermanshah, Iran.

[2*] Department of Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran.

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ABSTRACT

Nanoparticle-based magnetic solid phase microextraction (MSPME) has advanced in heavy metal ion concentration and speciation in recent years. This comprehensive review covers the latest developments in this field and their application to complex food samples. The review begins with conventional MSPE methods' challenges and constraints, then examines off-line and online MSPE formats. Later sections of the review examine solid phase extraction's (SPE) use of magnetized inorganic nanomaterials. These include magnetic silica, alumina, titania, and layered double oxides. Magnetized carbonaceous nanomaterials, such as magnetic graphene and/or graphene oxides, carbon nanotubes, and carbon nitrides, also belong to this study. The study describes how magnetized organic polymers-non-imprinted and ion-imprinted improved SPE. Magnetized metal-organic frameworks (MOF), ionic liquids, and biosorbents are also covered briefly. Each section carefully examines nanomaterials' selectivity, sorption capacity, mechanisms of sorption, and synthesis routes. Nanomaterials are becoming key sorbents for toxic heavy metal extraction from food samples. Carbon nanomaterials (CNMs), magnetic nanoparticles (MNPs), nano-imprinted polymers (NIPs), nano-based metal-organic frameworks (N-MOFs), and silica nanoparticles (SiNPs) are leading preconcentration methods due to their high surface area, selectivity, rapid adsorption kinetics, and food contamination capture efficiency. The review emphasizes the importance of SPE and SPME, enhanced by nanomaterial sorbents and summarizes nanomaterial-infused solid phase extraction strategies and their impact on heavy metal extraction from food matrices. The review examines a variety of nanomaterials and their complex use to improve selectivity, extraction efficiency, and future research in this crucial area.

Keywords: MSPME, SPE, SPME, Heavy metal ions, Magnetic nanomaterials, Magnetized metal organic framework, Ionic liquids, Food sample

*Corresponding author email address: ahmadi.chemometrics@gmail.com

Introduction

The presence of heavy metals in food has become a significant concern due to its potential health risks to consumers. Traditional analytical methods for heavy metal detection in food samples often involve time-consuming and labor-intensive procedures. However, recent advancements in nanotechnology have paved the way for innovative and efficient techniques such as nanomaterials-based magnetic solid phase microextraction (MSPME). This article review delves into the recent applications of nanomaterials-based MSPME in addressing heavy metal food toxicity concerns. Solid phase extraction (SPE) has long been a cornerstone in the realm of heavy metals analysis within food samples [1]. Its widespread adoption owes much to its exceptional cleaning capabilities, operational simplicity, cost-effectiveness, rapid phase separation, and swift kinetics [2, 3]. Within this context, solid phase microextraction (SPME) emerged as a refined iteration of SPE, marking a significant milestone in the field of sample preparation.

The inception of SPME dates back to the 1990s, attributed to the pioneering work of Pawliszyn et al. [4]. This innovation was underpinned by the compelling advantages it offered, including ease of operation, rapid extraction, solvent-free methodology, and a high preconcentration factor [5]. Yet, it is essential to recognize that the selection of the adsorbent material in both SPE and SPME techniques plays a pivotal role in their efficacy for heavy metals extraction. While the advances made through SPE and SPME have significantly elevated analytical capabilities, recent strides have brought forth nanoparticle-based MSPME as a groundbreaking evolution in this field. The fusion of nanotechnology and magnetic principles into the microextraction process introduces an array of benefits that push the boundaries of heavy metals analysis in food samples. MSPME stands as a classical yet crucial technique extensively employed in sample preparation for analytical purposes. Its fundamental principle relies on the partition equilibrium established between the analytes in a mobile/aqueous phase and an adsorbent solid.

Over time, numerous innovative adaptations of MSPME have emerged. These encompass column-based SPME, pipette tip SPME (PT-SPE), magnetic solid phase extraction (MSPE), and dispersive solid phase extraction (DSPE), each serving as prevalent branches of the technique [6].

However, this discourse exclusively centers on the exceptional realm of MSPME harnessing the capabilities of nanomaterials. This innovative approach leverages nanomaterials to enhance the efficacy and selectivity of the extraction process, particularly in the context of heavy metal analysis within food matrices.

Magnetized inorganic nanomaterials

Recent advancements in the utilization of nanomaterials-based MSPME have significantly enhanced the extraction of heavy metals, thereby addressing food toxicity concerns. Within the family of magnetic nanomaterials, diverse inorganic nanoparticles take the spotlight. Among these, magnetic nanoparticles (MNPs) exhibit a remarkable combination of traits, showcasing nanoscale dimensions coupled with intense magnetic properties, heightened surface reactivity, expansive surface area, substantial adsorption proficiency, and adaptable temperature responsiveness. These distinctive attributes position MNPs as a preferred choice for adsorbent materials in the domain of sample preparation methodologies.

The efficacy of MNPs' adsorption capacity can be elevated through physical or chemical modifications involving complexing agents or organic compounds. The mechanism underpinning analyte extraction using magnetic nanoparticles predominantly relies on hydrophobic interactions, electrostatic attractions, and/or the formation of covalent bonds [7].

The inherent super-magnetic quality of these nanoparticles readily draws them towards magnetic fields. This innate propensity facilitates the effortless separation of magnetic nanoparticles from intricate sample matrices subsequent to the interaction between analytes and MNPs. Notably, this separation can be achieved without resorting to centrifugation, as highlighted by studies [8-11].

Prominent candidates among the magnetic nanoparticles commonly employed as sorbents in techniques for heavy metal extraction from food samples encompass Fe_3O_4, TiO_2, Al_2O_3, ZrO_2, and their various modified iterations [12, 13]. As a promising alternative, inorganic materials, particularly metal oxides, have emerged as effective coating options for encapsulating MNPs. Their notable attributes include exceptional tolerance to extreme conditions such as varying pH levels and temperatures. Additionally, their diverse structural compositions facilitate a wide array of surface reactivity through the anchoring of hydroxyl groups. Among these inorganic coatings, silica, alumina, titania, and the newer category known as layered double hydroxides

(LDHs) have gained substantial prominence. The subsequent sections delve into the pivotal role of these coatings in the extraction of metal ions, contributing significantly to the field.

Magnetic silica

Silica nanoparticles are widely used as a stationary phase in chromatographic techniques because they have a large surface area, come in various particle sizes, and can be modified with silanes. The primary benefit resides in their ability to be manipulated in terms of size, a critical factor for achieving efficient separation and mass transfer in liquid environments. Nanoparticles with sizes exceeding 7 nm are considered more favorable for achieving effective separation, whereas those larger than 100 nm are deemed appropriate for macromolecules. Nevertheless, silica nanoparticles possess certain limitations, such as a restricted pH range (pH 2–8), alongside chemical and thermal instability. Applying a layer of different materials can help alleviate these limitations.

The sol-gel technique is frequently utilized in the synthesis of nano silica. This approach entails the catalyzed hydrolysis and condensation of metal alkoxides, such as tetraethyl orthosilicate, resulting in the formation of silanol groups. The silanol groups undergo self-polymerization, leading to the formation of siloxane linkages and ultimately resulting in the creation of a silica structure.

According to previous research, the magnetite phase, widely favored for its magnetic properties, can be enveloped with a silica shell using an efficient and uncomplicated sol-gel technique. This method involves hydrolysis and condensation reactions utilizing alkoxysilane precursors, primarily tetraethyl orthosilicate (TEOS). The outcome is a homogeneously coated MNP with adjustable dimensions and configurations. Silica serves as a versatile coating agent due to its abundant availability, low toxicity, cost-effectiveness, resilience to high temperatures, chemical inertness, ease of integration with the magnetic core, and straightforward surface customization [14]. Enhancing the discriminative capabilities of these hybrid MNPs can be readily achieved through a silanation process. This involves the utilization of silane coupling agents that bear diverse functional groups, including amine, thiol, carboxylic, and more (Fig. 1).

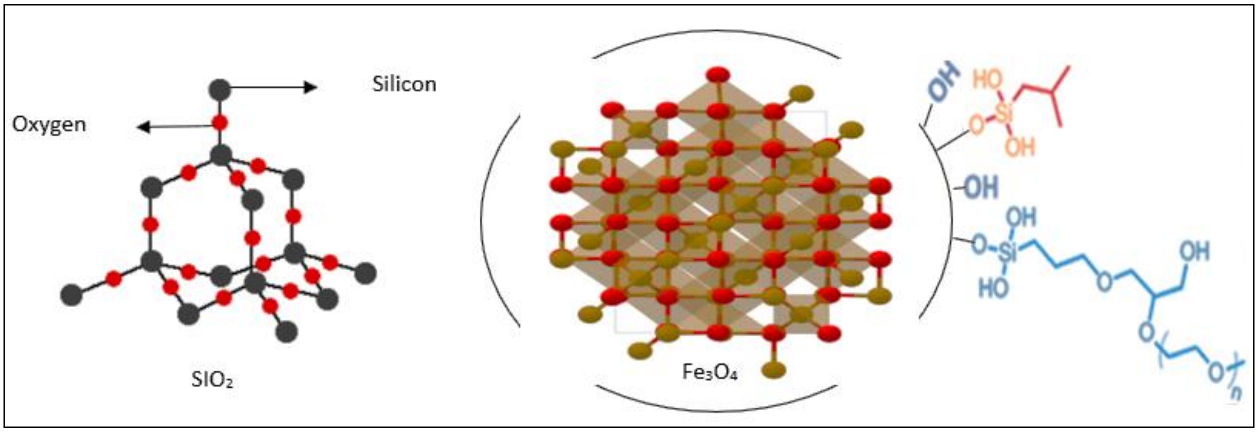

Figure 1. Silica NP structure and magnetic silica superficial modification.

The use of silica-coated magnetic nanoparticles (MNP) as hydrophilic and responsive sorbents for different metal ions' uptake or speciation has been well-established [15-18]. Incorporating schiff base or organic dye compounds with electron-rich groups onto the silica-coated MNP can result in selective and intriguing sorbents. Effective alternatives include grafting salicylic acid (SA) [19], iminodiacetic acid (IDA) [20], or bismuthiol II [21] onto iron oxide–silica hybrids, offering efficiency and reusability. Numerous applications involving the pre-concentration/speciation of metallic compounds have been reviewed, utilizing silica@MNP or other modified formats with organic/inorganic re-coatings of SiO_2 shells [22-27]. Also, Molaei et al. [28] introduced a magnetic solid-phase extraction technique for the purpose of preconcentration and detection of copper, lead, chromium, zinc, and cadmium. In this research, a new type of adsorbent called mGO/SiO_2@coPPy-Th, which is a SiO2-coated magnetic graphene oxide modified with a pyrrole-thiophene, was synthesized (Fig. 2).

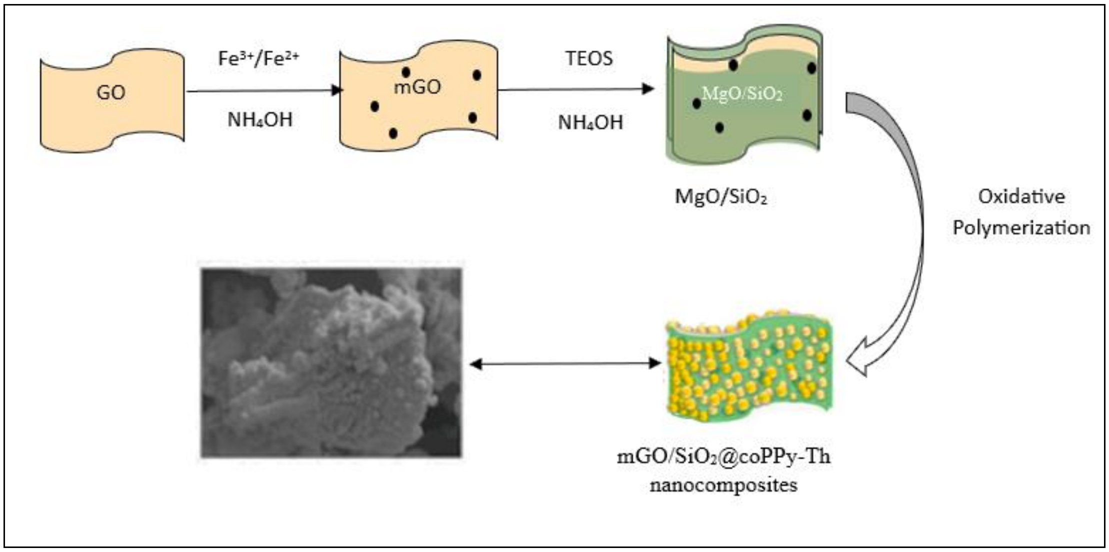

Figure 2. Schematic of mGO/SiO2@coPPy-Th nanocomposites synthesis.

Magnetic alumina and/or titania

Metal oxide nanoparticles such as alumina and titania are commonly utilized in various applications. These coatings are not only effective when applied to individual magnetic nanoparticles (MNPs) or MNPs that are enveloped by SiO_2 nanoparticles, but they also show promise for various other organic or inorganic functionalization. The study conducted by Wang et al. [29] investigated the extraction of cobalt traces using Fe_3O_4@Al_2O_3 nanoparticles in a sequential injection lab-on-valve (SI-LOV) system. The detection method employed was electrothermal atomic absorption spectrometry (ET-AAS). The nano adsorbent was synthesized using a method called alkoxide hydrolysis precipitation. This involved obtaining aluminum isopropoxide and Fe_3O_4 NP core through a chemical co-precipitation route. In the field of metal ion extraction and speciation, various innovative methodologies utilizing magnetic nanocomposites have been explored. Alumina-coated magnetite nanoparticles, modified by the surfactant Triton X114 and 1-(2-pyridilazo)-2-naphthol (Fe_3O_4@Al_2O_3@TX-114@PAN), were employed for magnetic mixed hemimicelles solid-phase extraction (MMHSPE) of chromium species in water and soil samples. By adjusting acidity and temperature at pH 3 and 0-10 °C, respectively, Triton X-114 was incorporated to facilitate the formation of hemimicelles onto Fe_3O_4@Al_2O_3. After reducing Cr(VI) to Cr(III), total chromium analysis was conducted. This approach demonstrated exceptional cleanup within complex matrices, eliminating the need for extensive pretreatments. Optimal conditions yielded an enhancement factor of 120, detection limits ranging from 1.4 to 3.6 ng mL^{-1} for water samples, and 5.6 ng mg^{-1} for soil samples, with notable reusability for up to 20 cycles and recoveries exceeding 97% [30].

Ligandless ultrasound-assisted magnetic solid-phase extraction (UAMSPE) using $Fe_3O_4@Al_2O_3$ nanoparticles, followed by ICP-OES, was introduced by Nyaba et al. This nanocomposite, synthesized through sol-gel reactions, demonstrated efficient extraction due to electrostatic interactions, resulting in detection limits between 0.16-0.18 ng L^{-1} and pre-concentration factors of 215-270. The method's accuracy was substantiated through certified reference materials (CRM) and standard reference materials (SRM) [31].

Another study employed $Fe_3O_4@MnO_2$, $Al_2O_3@NH_2$ nanocomposite for ultrasound-assisted pre-concentration and speciation of chromium species, achieving low detection limits of 20 ng L^{-1} and a pre-concentration factor of 94. The nanocomposite's diverse components, including Fe_3O_4 NP for magnetic decantation, Al_2O_3 shell for sorptive capacity, MnO_2 for oxidation, and active amino groups for selectivity, synergistically contributed to its effectiveness [32].

$Fe_3O_4@SiO_2@TiO_2$ nanoparticles combined with light-induced malachite green carbinol base (MGCB) were employed for the trace enrichment of Cd(II), Cr(III), Mn(II), and Cu(II) ions from environmental water samples before ICP-MS quantification. The unique properties of titania facilitated efficient adsorption due to electrostatic interactions, while the doubly-coated core shell structure enhanced reusability. Fe_3O_4/TiO_2/PPy nanocomposite, decorated with TiO_2 NP and a polymeric shell via sol-gel reactions and in situ electro polymerization, was utilized for the trace extraction of lead (II) ions. The composite exhibited adsorption capacity of 126 mg g^{-1}, a pre-concentration factor of 185, and a detection limit of 0.21 ng L^{-1} [33].

Magnetic layered double oxides

Layered double hydroxides (LDHs) are considered to be highly promising inorganic sorbents because of their distinctive structural characteristics [34]. LDHs consist of a combination of di- and trivalent metal cations that are organized in octahedral units. These units form positively-charged shells that are connected to basal layer anions or water molecules through electrostatic forces. LDHs have the advantage of having adjustable lamellar structures, which provide them with high porosity, significant surface area, resistance, and the ability to exchange anions.

Different synthesis methods, such as anion exchange, sol-gel, hydrothermal, and co-precipitation, are commonly utilized to produce well-defined lamellar structures that exhibit remarkable properties. LDHs exhibit notable anion-exchange properties, rendering them highly suitable for the preferential absorption of metal ions. This is particularly advantageous when LDHs are combined with chelating agents within the interlayer regions. Elution can be conveniently accomplished by dissolving the substance in media that can be adjusted for pH. The aforementioned characteristics render LDHs highly suitable for the application of MSPE in the context of heavy metal ion removal. The integration of MNPs with LDHs using cost-effective co-precipitation methods yields highly effective hybrid structures. These structures exhibit core/shell configurations with exceptional properties, such as increased contact surface area for efficient analyte trapping. This integration also improves the overall extraction process, especially in automated procedures (Fig. 3).

Abdolmohammad-Zadeh and Talleb conducted a study where they utilized Fe_3O_4/Mg-Al layered double hydroxide (Fe_3O_4/Mg-AlLDH) nano-hybrids to determine the speciation of As(III)/As(V) in water samples [35]. Subsequently, they employed a chemiluminescence (CL) technique to sensitively detect As(V). The present technique employed the process of oxidizing luminol using vanadomolybdoarsenate heteropoly acid (VMoAs-HPA) in an alkaline environment. The nano-hybrid material was synthesized using ultrasound-assisted precipitation, by combining suspensions of Fe_3O_4 nanoparticles and Mg-Al layered double hydroxides. The hybrid material's distinct sorption sites enabled the successful and precise speciation and quantification of As(III)/As(V) in water samples.

In their study, Kardar et al. [36] presented a novel magnetic synthetic clay known as akovite-aluminosilicate@$MnFe_2O_4$ nanocomposite. This composite was developed with the aim of effectively extracting lead ions from food samples before conducting FAAS analyses. The composite was synthesized by co-precipitation, with the inclusion of $MnFe_2O_4$ nanoparticles. This composite demonstrated effective extraction mechanisms, which were facilitated by complexation and hydrogen bonding. These extraction mechanisms were further enhanced by the composite's superior structural properties, including its magnetism capability, penetration paths, and contact area. The method exhibited a detection limit of 0.67 $\mu g\ L^{-1}$ and an enrichment factor of 70.0.

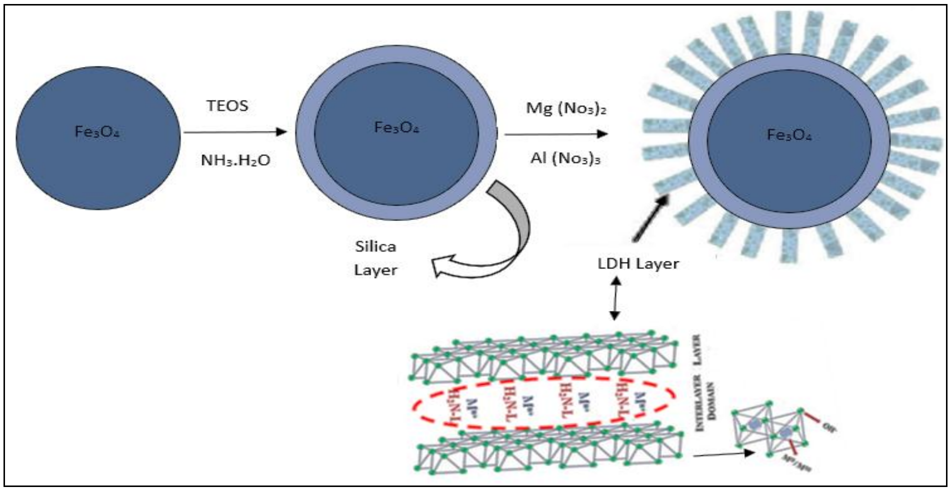

Figure 3. Regular brush-like LDH attachment to magnetite core and effective electrostatic/coordinative ion species uptake spots.

The aforementioned examples highlight the wide-ranging capabilities of LDH-based magnetic nanocomposites in improving metal ion extraction techniques. These nanocomposites provide effective, specific, and precise methods for isolating and quantifying analytes in different sample matrices.

Magnetized carbonaceous nanomaterials

MSPME is a technique used in analytical chemistry for the extraction, separation, and preconcentration of various compounds, particularly heavy metals, from complex matrices such as food samples. In this context, carbon nanomaterials (CNs) have emerged as highly effective adsorbents within the realm of MSPME for the determination of heavy metals in food samples [37-40]. CNs encompass a diverse range of materials including fullerene, graphene, graphene oxide, carbon nanocones, carbon nanodisks, carbon nanofibers, diamond, nanotube rings, single-walled carbon nanotubes (SWCNTs), and multi-wall carbon nanotubes (MWCNTs) [41, 42].

CNTs, fullerene, graphene, and graphene oxide are among the most commonly employed carbon nanomaterials due to their distinctive properties. CNTs, for instance, offer advantages such as high chemical stability, a large surface area, small pore size, hollow structure, and ease of modification, setting them apart from conventional adsorbent materials. The efficiency of CNTs in adsorption is influenced by factors including purity, surface area, surface functional groups, available adsorption sites, and experimental conditions [43, 44].

Graphene, another notable carbon nanomaterial, boasts characteristics like a high surface area, cost-effectiveness, delocalized pi-electrons, and facile modification. Its nanosheet morphology lends it greater effectiveness as an adsorbent compared to CNTs and fullerenes. Graphene oxide (GO), derived from graphene through oxidation, provides active sites that simplify the synthesis of composite materials. This enables the combination of GO with MNPs to enhance efficiency and minimize adsorbent wastage [45, 46].

The synthesis of carbon nanomaterials involves various techniques. For CNTs, methods like chemical vapor deposition (CVD), laser ablation, and arc discharge are employed, while graphene can be synthesized through techniques such as mechanical exfoliation, chemical reduction of GO, epitaxial growth on silicon carbide, liquid-phase exfoliation, and CNT unzipping. CVD stands out as a highly effective technique for both CNT and graphene synthesis, offering simplicity, cost-efficiency, and scalability [47-49]. It allows for the production of a wide range of morphologies by adjusting relevant parameters (Fig. 4).

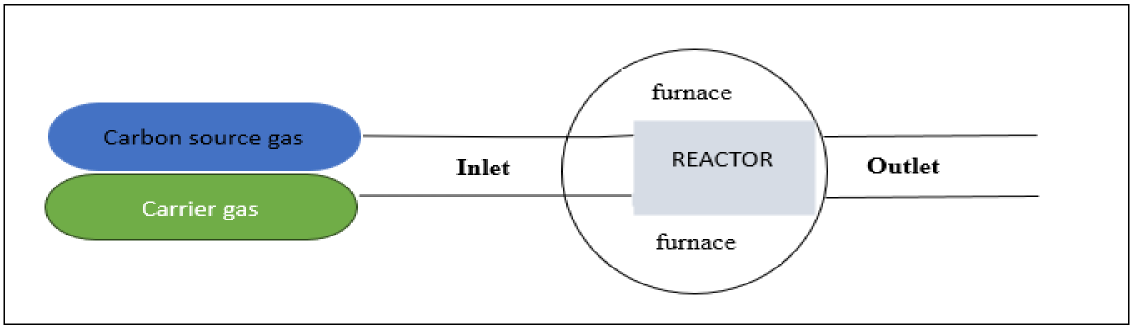

Figure 4. The typical CVD reactor schematic [47]

Magnetic carbon nanomaterials, possessing unique physicochemical properties, high surface-to-volume ratios, substantial sorption capacities, and exceptional thermal and chemical stability, have gained prominence in modern sample preparation methods. Figure 5 illustrates magnetic carbonaceous nanocomposites and their roles in metal ion extraction. This overview aims to provide an updated insight into magnetized carbon materials based on CNTs, as well as more recent materials like graphene (G) or graphitic carbon nitride (g-C_3N_4), focusing on their applications in the separation and preconcentration of cationic species.

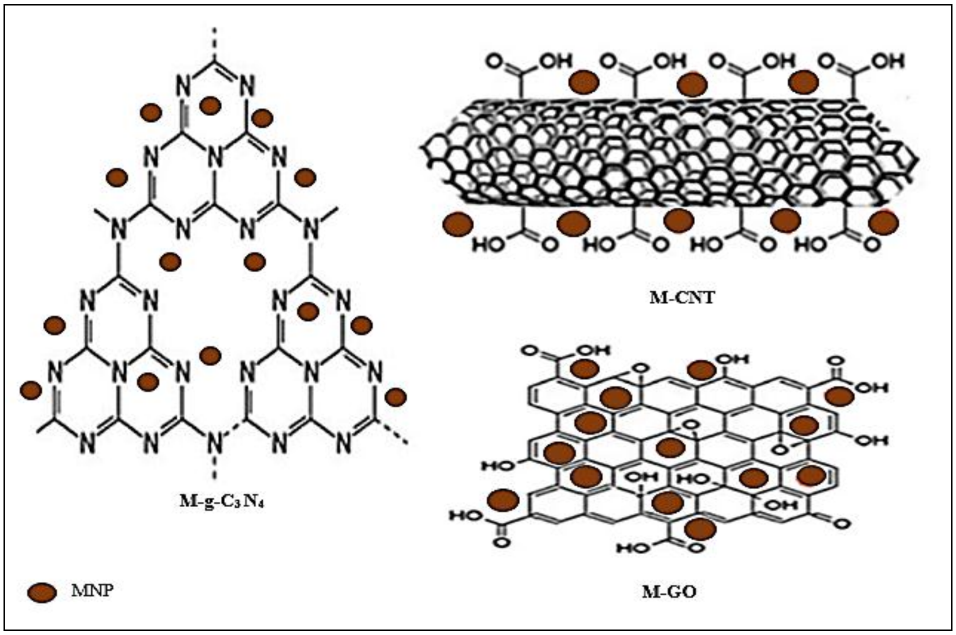

Figure 5. Famous magnetized carbonaceous nanomaterials sensitive to metal ions.

Magnetic graphene and/or graphene oxide

Graphene, a carbon-based material, possesses remarkable properties for adsorption owing to its two-dimensional structure consisting of well-arranged hexagonal sp2 hybridized carbon atoms. The structural flexibility of this material enables efficient adsorption of a diverse array of organic and inorganic substances, including metal ions, dyes, and pharmaceuticals, through a variety of interactions such as π-π, van der Waals, hydrophobic, hydrogen bonding, and electrostatic forces. Cation-π interactions are noteworthy for their involvement in metal ion interactions, which are frequently intensified by the presence of chelating agents that facilitate the formation of complex compounds. Graphene can be synthesized from inexpensive graphite via oxidation, ultrasonic exfoliation, and reduction methodologies. The utilization of GO presents several benefits, including facile large-scale synthesis, exceptional purity, and the potential for modification [46, 50, 51].

GO, an intermediate derivative of graphene, exhibits a high level of reactivity owing to the presence of epoxy, hydroxyl, and carboxyl functional groups. This process enables the modification of graphene, leading to the creation of diverse functionalized derivatives. GO can also function as a highly efficient adsorbent for a wide range of cations by utilizing electrostatic forces and complexation interactions. The advantages of this material lie in its low production costs, expansive surface area, stability, and amphiphilic characteristics. Nevertheless, the inherent softness of graphene and GO may impede their practical application in MSPME as it can lead to undesired losses caused by pressure. The problem at hand is effectively addressed through the covalent bonding of graphene to silica, which serves to improve efficiency and reduce the loss of sorbent material.

While the use of graphene-based dispersive Solid Phase Extraction (d-SPE) has proven effective in overcoming common limitations associated with SPE, there are still challenges that need to be addressed regarding the retrieval and reusability of the material. The issues mentioned can be effectively addressed by immobilizing magnetic nanoparticles (MNPs) onto graphene sheets using the co-precipitation method. The present study investigates the utilization of composites consisting of thiol-functionalized graphene oxide/magnetic chitosan (SH/GO-MC) and magnetic bucky gel incorporating Fe_3O_4 nanoparticles and graphene oxide [52-54]. These composites are examined for their effectiveness in pre-concentrating metal ions. These materials leverage the functional groups and contact surface of graphene to enhance chelating mechanisms effectively. The utilization of MNPs in conjunction with graphene oxide and ionic liquid has been found to effectively facilitate the swift separation and achieve a notable extraction efficiency for heavy metal ions.

Magnetic carbon nanotube

CNTs are a distinct form of carbon, characterized by their tubular structures. They can exist as either SWCNT or MWCNT configurations. The multi-wall form is particularly advantageous in terms of its wider range of applications. This is primarily due to its simpler synthesis process, greater potential for modification, and impressive mechanical and thermal properties. The crucial aspects of MSPME processes, which include both column and magnetic variants, are their high surface area and strong sorption capacity. These properties are attained through electrostatic, covalent, and hydrophobic interactions [55-57].

Within the field of metal ion SPE, functionalized CNTs, which are commonly oxidized or chemically modified, interact with metal cations through electrostatic or covalent bonding. On the other hand, unmodified CNTs participate in hydrophobic interactions with the complexes that are formed [58, 59]. The remarkable physical and chemical characteristics of CNTs, including their stability, ability to undergo surface functionalization, and possession of a porous structure, render them well-suited for integration with MNPs. This enables the achievement of efficient recycling through the utilization of suspensions, resulting in high adsorption capacity, rapid kinetics, and enhanced reusability.

The fabrication of magnetic carbon nanotube (MCNT) composites can be accomplished using either a two-step or an in-situ one-step functionalization process, which rely on chemical or physical interactions [60]. The two-step methodology involves the covalent functionalization of MNPs to oxidized CNTs using a linker such as silane-modified silica. This linker is coated onto the magnetite core. In a different approach, noncovalent interactions, such as π-π stacking and electrostatic forces, can prompt hybridization onto CNTs that are either bare or oxidized. This is frequently achieved by employing auxiliary additives, such as polyaromatic compounds that possess active groups. The in-situ synthesis method is widely employed owing to its inherent simplicity and rapidity. This approach entails the interaction between oxygen-functionalized CNTs and iron salts on the surface, which is then followed by the in-situ deposition of Fe_3O_4 nanoparticles using co-precipitation techniques.

The synthesis rout and the interactions between the adsorbent and adsorbates are largely consistent with the information provided in the preceding sections.

Wang et al. [29] presented the initial study on the online pre-concentration of cadmium using the MSPE technique, employing MMWCNT nanocomposites (Fig. 6).

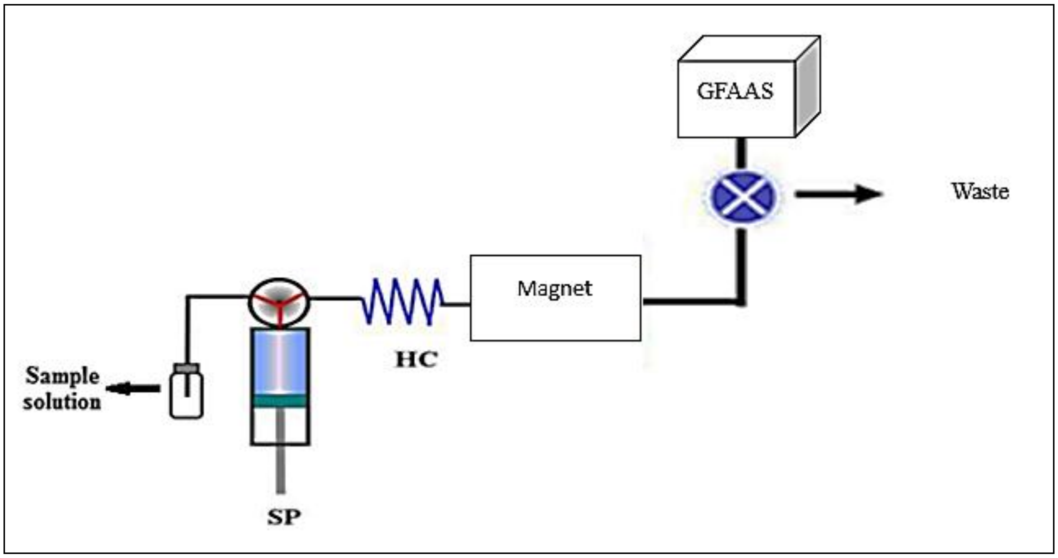

Figure 6. Cadmium determination using magnetic multiwalled carbon nanotube FI-pre-concentration and GFAAS (SP: syringe pump, HC: holding coil).

The quantification of analytes was carried out using a flow injection analysis (FIA) technique combined with graphite furnace atomic absorption spectrometry (GFAAS). The method demonstrated a linear dynamic range from 0.01 to 10 μg L^{-1}, with a relative standard deviation of 2.3% at 1.0 μg L^{-1}. The limit of detection was exceptionally low, at 1.2 ng L^{-1}, and a pre-concentration factor of approximately 160 was achieved. The on-line extraction and detection system consisted of a custom glass microcolumn (5 × 20 mm) integrated with the GFAAS instrument. In the experimental setup, a magnetic multi-wall carbon nanotube (MMWCNT) nanocomposite was introduced into the microcolumn and immobilized using a strong magnetic field. The microcolumn and connecting lines were subsequently rinsed with nitric acid and water to prepare the extraction cell. Following this, the sample was passed through the extraction cell at an appropriate flow rate to ensure effective interactions between the analytes and the sorbent material.

Magnetic carbon nitride

One of the most recent advancements in the field of two-dimensional carbon sheets is the introduction of g-C_3N_4 [61]. This material is comprised of aromatic tri-s-triazine units that are organized into layers through interlayer van der Waals forces. The material contains nitrogen-rich functional groups (-NH2/-NH-/=N-) that are integrated into its π-delocalized systems, distinguishing it from other carbon analogues such as GO and CNT. The distinctive architecture of this structure facilitates enhanced dispersion in solutions containing water and enables more efficient engagement in diverse sorption mechanisms. The efficient Lewis base properties of this substance allow for remarkable metal-sorption mechanisms. Both secondary/tertiary amines present within the network, as well as terminal ones, participate in metal chelation and acid-base reactions. The interaction between aromatic tri-s-triazine rings occurs via π–π conjugation, hydrophobic interactions, and hydrogen bonding, which aids in the binding process with neutrally-charged metal-ligand compounds. Ionic compounds, whether in the form of cationic or anionic complexes, are effectively immobilized due to the influence of electrostatic forces when the pH level is in the vicinity of the isoelectric point, which is approximately 5 [62, 63].

The sorption behaviors of materials are affected by various structural characteristics, such as topology, surface defects, functionalities, specific surface area (SBET), and isoelectric points (IEP). These properties, in turn, are determined by the methods used for synthesis. Thermal decomposition is widely recognized as the predominant technique employed to produce N-bridged structures with favorable porosity, utilizing environmentally friendly precursors rich in nitrogen such as melamine, thiourea, and urea. The surface modifications of these structural features can be achieved through various methods, including soft or hard templating, protonation, post-atomic doping, in-situ synthesis of modified g-C_3N_4, oxidation, and grafting of macromolecular compounds. These alterations result in hybrid sorbents that exhibit superior efficiency and selectivity. The utilization of metallic oxides, specifically those with magnetic properties, as dopants, is a viable method for the synthesis of magnetically-labeled g-C_3N_4. The synthesis of this hybrid material primarily involves precipitation methods using melamine-derived g-C_3N_4 [64, 65].

Magnetized organic polymers

The limited availability of intrinsically hydrophilic polymer sorbents, which possess influential polar sites (both imprinted and non-imprinted), proper chemical stability, and cost-effective one-pot fabrication methods, has greatly motivated the research and development of advanced polymeric materials [66]. In this context, it is worth considering the use of conductive polymers [67-69] consisting of extensively π-delocalized systems and imprinted polymers featuring selectively recognized sites as suitable choices for the selective extraction of metal ions (Fig.6).

Magnetized metal organic frameworks

Metal-organic frameworks (MOFs) are nanocomposite materials that have gained recognition for their exceptional characteristics, including their remarkable porosity, thermal stability, and expansive surface area. Researchers are highly interested in the numerous benefits provided by these materials, including their low density, well-organized pores, customizable pore sizes, varied morphologies, significant adsorption capacity, and strong mechanical stability [70]. MOFs possess distinct surface pore sizes, porous channels, nanospaces, and versatile properties that range from polarity to hydrophobicity. These characteristics render them highly advantageous as adsorbent materials. The combination of MOFs and MNPs through basic physical mixing can yield a magnetically heterogeneous hybrid material [71]. This hybridization is achieved through the establishment of electrostatic or van der Waals interactions. Another significant approach involves the in-situ synthesis of Fe_3O_4 nanoparticles in the presence of stable MOF crystals, resulting in the production of magnetic MOFs with a high yield [72]. Although there is generally satisfactory aggregation among the main components, it is possible for some magnetite particles to be loosely connected or exist as separate entities, which can be easily separated (Fig. 7). Nonetheless, a possible concern arises regarding the hinderance of MOFs by vulnerable conglomerated uncoated MNPs, which may have an adverse effect on the efficiency of extraction. In order to mitigate this issue, various effective strategies have been proposed. These strategies encompass the straightforward combination of MOF precursors with unadorned MNPs in carefully regulated conditions, such as hydrothermal, solvothermal, and mechanochemical routes. These routes involve various factors, including temperature, pressure, reactant ratios, and conditions for functionalization and coating.

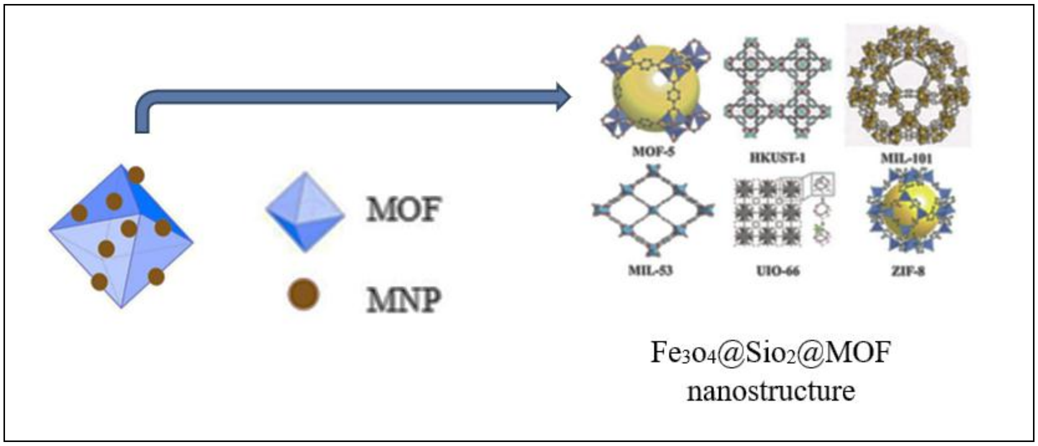

Figure 7. Different MOFs for two magnetic MOF hybrid configurations.

Various coating morphologies can be obtained by manipulating the growth conditions of MOFs. One commonly employed method involves the incorporation of MNPs into the MOF crystals. An alternative approach that proves to be efficient entails the application of a layer of nano-MOFs onto either exposed or protected MNPs. These structures serve the dual purpose of safeguarding highly reactive MNPs against oxidation and aggregation, while also improving the accessibility to specific sorption sites in comparison to conventional coatings such as silica or polymers. The technique of controlled layer-by-layer growth of MOFs onto modified (MNPs is considered to be a highly efficient method.

In a conventional synthesis, the procedure commences by adsorbing metal precursors onto the surface of functionalized NPs that possess electron-donor groups with high reactivity. The subsequent inclusion of organic linkers leads to the formation of core/shell structures that can be adjusted or modified. Automated flow-based techniques can help alleviate the time-consuming nature of this process, thereby enabling more convenient and efficient modification steps.

Magnetized ionic liquids

Ionic liquids (ILs) refer to a class of liquid salts that possess melting points below 100 °C. They are comprised of large organic cations, such as imidazolium, phosphonium, ammonium, or pyridinium, and either organic or inorganic anions, such as PF_4^-, PF_6^-, Cl^-, or Br^-. These materials exhibit customizable structures, low vapor pressure, excellent thermal stability, a wide range of sorptive interactions, non-flammability, and adjustable solubility in different solvents. These characteristics make them highly appealing for a variety of extraction applications. Nevertheless, there are certain challenges that arise due to their elevated viscosity in aqueous environments, sluggish diffusion towards the bulk ionic liquid, and the complexity involved in achieving phase separation [73-79].

In order to tackle these challenges, researchers have investigated the integration of a paramagnetic component into IL structures as a means to enhance the efficiency of collection. However, challenges such as sluggish mass transfer, prolonged equilibrium times, elevated costs resulting from greater IL utilization, and durability considerations continue to persist. Another possible method entails the immobilization of ILs onto supported materials, such as silica, polymers, graphene/graphene oxide (G/GO) [80], and CNTs [81, 82]. The combined IL phases with solid supports facilitate various interactions such as ion-exchange, hydrophobic, electrostatic, and hydrogen bonding, by leveraging the distinctive attributes of ILs along with the benefits offered by solid supports [83].

The use of supported ion exchange materials provides improved stability, thereby reducing the loss of IL during extraction and elution procedures. An exemplary instance is Fe_3O_4@IL, which represents a magnetically supported ionic liquid structure. This hybrid demonstrates synergistic characteristics derived from both components, namely Fe_3O_4 nanoparticles and IL. As a result, it exhibits robust sorption interactions, convenient synthesis through covalent immobilization or physical assembly, and effortless retrieval.

Magnetized bio-sorbent

Researchers have recently focused on the development of MSPME procedures using bio-sorbents that show promise. This approach aligns with the principles of green chemistry and takes into account economic considerations. Biomaterials obtained from microorganisms, including bacteria, yeast, fungi, and algae, as well as bio-polymers such as chitin, chitosan [84-86], and cellulose [13], have become promising choices for sequestration, removal, speciation, and extraction in diverse applications [87].

These biomaterials contain various functional groups (carboxylates, hydroxyls, amines, amides, imidazoles, thiols) [13] that facilitate the effective absorption of metal ions through processes such as ion exchange, adsorption, and complexation. The notable characteristics of these materials include their wide availability, ease of cultivating microorganisms, biocompatibility, degradability, and cost-effectiveness. Nevertheless, the direct application of unmodified bio-sorbents is limited due to their inadequate structural durability in harsh conditions, as evidenced by various batch adsorption studies.

One possible alternative method entails the immobilization of biomaterials onto durable and permeable substrates such as silica gel and polymeric resins. This phenomenon improves the mechanical strength of materials and the ability of metals to remain intact through interactions that are not dependent on metabolic processes. The incorporation of magnetism, particularly in combination with other sophisticated materials such as graphene or ion-imprinted polymers, presents a viable and efficient solution. The altered biomaterials possess the ability to engage various uptake mechanisms, thereby preventing negative effects such as bioaccumulation or degradation. Additionally, they allow for effortless retrieval, operational simplicity, and multiple instances of reuse.

Conclusion and future trends

Magnetic Solid Phase Micro Extraction (MSPME) is a specialized extraction technique that combines the principles of solid phase extraction (SPE) and solid phase microextraction (SPME) with the added benefit of utilizing magnetic materials. This approach involves using magnetic nanoparticles (MNPs) or other magnetic nanomaterials as sorbents to extract and preconcentrate analytes, particularly heavy metal ions, from complex matrices such as food samples. The unique properties of these nanomaterials, including their high surface area, selectivity, adsorption capacity, and stability, make them valuable tools for enhancing the efficiency and sensitivity of extraction processes.

Magnetic nanoparticles, often coated or functionalized with various materials like carbon nanomaterials (CNMs), metal-organic frameworks (MOFs), or silica nanoparticles, are used as sorbents. Their magnetic properties allow for easy separation and manipulation using an external magnetic field.

MSPME involves the preconcentration and extraction of target analytes from a sample matrix. The magnetic sorbents are introduced to the sample, where they interact with the analytes of interest. The sorbents are then separated from the sample matrix using a magnetic field, simplifying the extraction process.

The nanometer-sized sorbents provide a large surface area, enabling efficient adsorption of analytes. This high surface area also contributes to improved selectivity and sensitivity, as the sorbents can selectively adsorb target analytes.

MSPME can be conducted either on-line or off-line. In on-line systems, the magnetic sorbents enriched with analytes are directly eluted and introduced into the analysis system, reducing sample manipulation and enhancing precision. Off-line approaches involve a separate extraction step followed by elution and analysis.

MSPME offers several advantages, including simplicity, rapidity, high efficiency, and cost-effectiveness. The technique holds potential for enhancing the detection of trace heavy metal ions in complex samples like food matrices. Future research might focus on the use of greener desorption solvents, hybrid nanomaterials, and further optimization of on-line systems.

The development of environmental-friendly and selective bio-solid phases based on simple synthesis methods aligns with green chemistry principles and contributes to sustainable analytical practices.

MSPME has found applications in various fields of analytical chemistry, particularly in the analysis of heavy metals in food samples. The method's ability to enhance sensitivity and precision makes it a valuable tool for ensuring food quality and safety.

In summary, Magnetic Solid Phase Micro Extraction (MSPME) is an innovative approach that combines the benefits of solid phase extraction with magnetic nanomaterials to achieve efficient and selective extraction of analytes from complex matrices. The technique holds promise for advancing analytical chemistry and improving the detection of trace analytes in various applications, particularly in the realm of heavy metal analysis in food samples.

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