

REVIEW PAPER

## Recent analytical applications of magnetic nanoparticles

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### ABSTRACT

Analytical chemistry has experienced, as well as other areas of science, a big change due to the needs and opportunities provided by analytical nanoscience and nanotechnology. Now, nanotechnology is increasingly proving to be a powerful ally of analytical chemistry to achieve its objectives, and to simplify analytical processes. Moreover, the information needs arising from the growing nanotechnological activity are opening an exciting new field of action for analytical chemists. Magnetic nanoparticles have been used in various fields owing to their unique properties including large specific surface area and simple separation with magnetic fields. For Analytical applications, they have been used mainly for sample preparation techniques (magnetic solid phase extraction with different advanced functional groups (layered double hydroxide,  $\beta$ -cyclodextrin, carbon nanotube, graphene, polymer, octadecylsilane) and automation of it, microextraction techniques) enantioseparation and chemosensors. This review summarizes the basic principles and achievements of magnetic nanoparticles in sample preparation techniques, enantioseparation and chemosensors. Also, some selected articles recently published (2010-2016) have been reviewed and discussed.

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### INTRODUCTION

Nanoscience has provided new dimensions to research and development in the modern world [1]. In recent years, nanosized materials have attracted much interest in the research community due to their unique size and physical properties. Nanomaterials have begun to revolutionize the world around us; they have been used in various scientific fields such as biotechnology, engineering, biomedical, environmental, catalysis, drug delivery and material science [1-12]. Nanotechnology has become an important technique that made it possible to work at the molecular and cellular levels to produce many recent advances in the field of research and development.

Among different types of nanomaterials (spheres, nanotubes, nanocages and nanohorns),

nanoparticles (NPs) have attracted broad attention due to their potential applications in magnetic resonance imaging, drug delivery, catalysis, hyperthermia treatment, and analytical applications [1-3]. Therefore, during the past decade, great efforts have been devoted to the preparation of MNPs. MNPs have been synthesized with a number of different compositions and phases, including pure metals Fe, Co and Ni; metal oxides, such as  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ ; ferrites, such as  $\text{MFe}_2\text{O}_4$  (M = Cu, Ni, Mn, Mg, etc.); and metal alloys, such as FePt, CoPt [1-3]. During the last few years, a large portion of the published articles about MNPs have described efficient routes to attain shape-controlled, highly stable, and narrow size distribution MNPs. Up to date, several popular methods including co-precipitation, microemulsion,

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thermal decomposition, solvothermal, sonochemical, microwave-assisted, chemical vapour deposition, combustion synthesis, carbon arc, laser pyrolysis synthesis have been reported for the synthesis of MNPs. The details and advantages of each mentioned synthesis method have been previously reviewed by some research groups [1-3].

Analytical chemistry has experienced, as well as other areas of science, a big change due to the needs and opportunities provided by analytical nanoscience and nanotechnology. Now, nanotechnology is increasingly proving to be a powerful ally of analytical chemistry to achieve its objectives, and to simplify analytical processes. Moreover, the information needs arising from the growing nanotechnological activity are opening an exciting new field of action for analytical chemists [13].

The magnetism is nowadays one of the most exciting trends in analytical chemistry. Thus, analytical methodologies have started to take advantage of recent advances in the development of NPs, hybrid magnetic (nano) materials, or magnetic composites, to improve the performance of existing methodologies [13]. Magnetic forces offer great advantages in analytical applications as magnetic interactions are not influenced by chemical variables such as pH, concentration, or surface charges. In addition, they allow controlling fluid motion in microsystems, an important advance for chromatographic separations in microfluidic systems.

Recently, several reviews have summarized the synthesis, functionalization, characterization and application of magnetic nanoparticles in different fields of analytical chemistry, generally of specifically [1-3, 13-23]. In this review, we

have summarized and discussed some selected recent applications of the advanced functionalized magnetic nanoparticles in analytical chemistry in sample preparation, enantioseparation and chemosensors techniques.

## ANALYTICAL APPLICATION OF MAGNETIC NANOPARTICLES

### Sample preparation techniques

#### Magnetic solid-phase extraction (MSPE)

Magnetic separation was first employed by Heden [24] in 1972 and he demonstrated the potential of magnetic separation for biologically active proteins. In 1973, Robinson *et al.* [25] used magnetic supports for the recovery of two enzymes from a stirred reactor. In 1996, Towler *et al.* [26] reported the preconcentration of Ra, Pb and Po from seawater samples by using a magnetic adsorbent (MnO on magnetite) followed by a collection of the adsorbent using a magnet.

However, the first analytical application (and the first use of the term M-SPE) was developed in 1999 by Šafaříková and Šafařík for the separation of a copper phthalocyanine dye using silanized magnetite [27]. M-SPE involves the addition of magnetic sorbent particles to the sample solution. The target compound is adsorbed onto the magnetic material and the magnetic particle (containing the analyte) is then separated from the sample solution by the application of an external magnetic field. Finally, the analyte is recovered from the adsorbent by elution with the appropriate solvent and is subsequently analyzed. A general scheme for the M-SPE procedure is shown in Fig. 1. This approach has several advantages over traditional solid phase

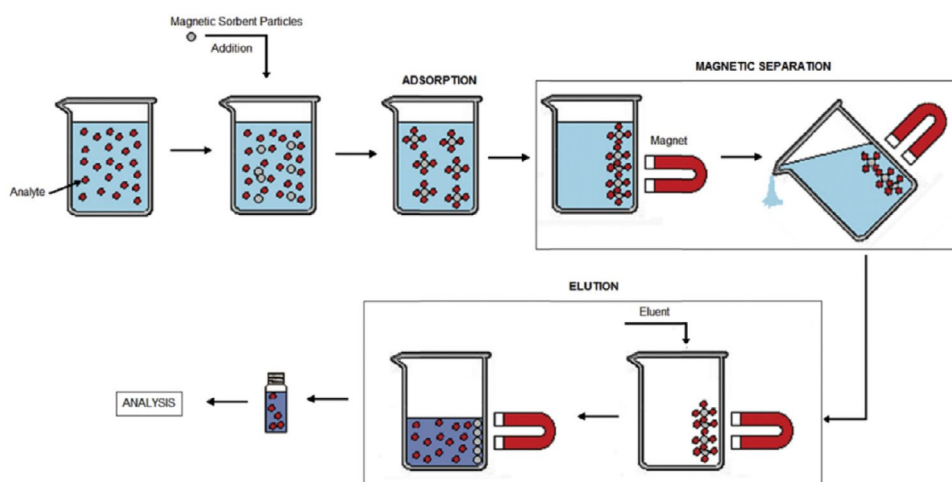


Fig. 1. Schematic presentation of magnetic solid phase extraction (MSPE) [4]

extraction: (i) it avoids time-consuming and tedious on-column SPE procedures, (ii) it provides a rapid and simple analyte separation that avoids the need for centrifugation or filtration steps, (iii) the magnetic sorbents synthesized to date have high selectivity, even when complex matrices from environmental or biological fields were, (iv) since the majority of sample impurities are diamagnetic, they do not interfere with magnetic particles during the magnetic separation step, and (v) automation of the whole process is possible with flow injection analysis and other related techniques, which leads to rapid, selective, sensitive and repeatable methods for routine determinations [16]. These advantages could be achieved as results of unique properties of magnetic nanoparticles including [13]:

1. High extraction efficiency because of the high surface area-to-volume ratio of the extraction phase;
2. Fast separation after extraction compared with conventional SPE methods;
3. Convenience of preparation and surface modification of the extraction phase (e.g., bare  $\text{Fe}_3\text{O}_4$  can be simply and rapidly prepared by coprecipitation or hydrothermal synthesis, and can be conveniently modified with functional groups because of the abundant hydroxyls on the surface of  $\text{Fe}_3\text{O}_4$  NPs);
4. High selectivity of the target analytes and suitability for the complicated matrices (suitable coating not only stabilizes the NPs and prevents their oxidation but also provides specific functionalities that can be selective for analytes);
5. Good reusability (magnetic particles can be reused after appropriate rinsing);
6. Excellent dispersibility in aqueous solution and easy to operate.

#### **MSPE involving layered double hydroxide**

In recent years, layered double hydroxides (LDHs), also known as hydrotalcite-like compounds and/or anionic clays, have attracted considerable attention as extraction sorbents, stabilizers, drug delivery agents, flame retardants and catalysts due to their special structure and unique properties, such as high anion-exchange capacity [28,29].

Due to the ease of the exchangeability of LDH interlayer anions with other anions, they have been applied for the adsorption of many harmful organic and inorganic compounds in aqueous. More recently, Sajid and Basheer reviewed LDH applications as emerging sorbent materials for analytical extractions [30].

LDHs have excellent adsorbing properties because of three major reasons:

- (i) Large interlayer spaces (high porosity)
- (ii) Huge number of exchangeable anions in between the positively charged layers
- (iii) Water resistant structure.

LDHs have shown considerable applications as anion exchangers. Their high anion uptakes can be attributed to large surface area, high anion exchange capacities and highly tunable and flexible interlayer spaces. LDHs can adsorb anions via direct adsorption or anion exchange or by hydration of calcined LDH in an anion containing aqueous solution [31].

Layered, magnetic double hydroxide (MLDH) nanoparticles with large surface area, provide a low cost, three-dimensional structure that has demonstrated potential for use in drug delivery, catalysis, sensing, molecules and biology [32-34]. Orientation and dimensionality hierarchical structure as well as the large expandable inter layer free space make it easier to be further modified. Making MLDH magnetic facilitated an otherwise difficult solid-liquid separation, while the shell-type mesoporous structure shortens the diffusion path and increases the effective area, thus improving the adsorption capacity and extraction efficiency. Therefore, MLDH nanomaterials would be an ideal candidate sorbents for MSPE.  $\text{Fe}_3\text{O}_4$ -LDH has been used as a dissolvable sorbent for extraction of PPCPs [35], phenolic acids [36] and phthalate ester [37]. One of the distinct features of MLDH preparation is its very easy elution step. After adsorption and extraction from water, analytes were eluted from the MLDH by dissolving the double hydroxide layers containing the analytes by changing the pH of the solution.

Recently, Tang *et al.* [35] have reported an approach to d-SPE using dissolvable magnetic  $\text{Fe}_3\text{O}_4$ -layered double hydroxide core-shell microspheres as sorbent to enable automation of the integrative extraction and analytical processes. Through magnetic force, the sorbent, after extraction, was isolated from the sample and then dissolved by acid to release the analytes. Thus, the customary analyte elution step in conventional SPE was unnecessary. The automated d-SPE step was coupled to high-performance liquid chromatography (HPLC) with photodiode array detection for determination of several pharmaceuticals and personal care products (PPCPs) [acetylsalicylic acid (ASA), 2,5-dihydroxybenzoic acid (DBA), 2-phenylphenol

(PP), and fenopfen (FP)] in aqueous samples.

In the other research, Saraji and Chani [36] prepared a magnesium-aluminum layered double hydroxide coated on magnetic nanoparticles and used as a sorbent to extract some phenolic acids including p-hydroxy benzoic acid, caffeic acid, syringic acid, p-coumaric acid and ferulic acid from fruit juices. After extraction, the elution step was performed through dissolving double hydroxide layers containing the analytes by changing the solution pH. The limits of detection were between 0.44 and 1.3  $\mu\text{g L}^{-1}$ .

In other work, Zhao *et al.* [37] synthesized a novel type of layered, flowerlike magnetic double hydroxide (MLDH) nanoparticles modified by surfactants and applied as an effective sorbent for pre-concentration of several phthalate ester pollutants (PAEs) from water prior to quantification. The MLDH was obtained via a simple ultrasound-assisted method by using silica coated  $\text{Fe}_3\text{O}_4$  as the core and anisotropic Mg-Al layered double hydroxide (Mg-Al LDH) nanocrystals as the shell to which analytes were absorbed (Fig. 2). Orientation and dimensionality hierarchical structure as well as the large expandable interlayer free space and positive charge of the Mg-Al LDH shell make it easier to form anionic surfactant micelles on its surface via self-assembly. Due to its high adsorption area, compared with non-mesoporous nano solid-phase extraction agents, mesoporous channel shell and reduction diffusion path, MLDH exhibited high extraction efficiency of organic target residues. Under optimized conditions, the limits of detection were in the range of 12.3-36.5  $\text{ng L}^{-1}$ .

### MSPE involving $\beta$ -cyclodextrin

Recently, CDs have gained significant interest as low-cost adsorbents of choice for wastewater treatment, because of their particular structure, physicochemical characteristics, chemical stability, high reactivity and excellent selectivity towards organic compounds and metals [38]. It is widely known that CDs can form inclusion complexes with a wide variety of organic compounds in its hydrophobic cavity through host-guest interactions [38,39]. This molecular encapsulation ability is widely utilized in many industrial products, technology and analytical methods [40]. More recently, Mohammadzadeh Kakhki [20] reviewed application of magnetic nanoparticles modified with cyclodextrins (Fig. 3) as efficient adsorbents in separation systems. In particular, the CD-based polymers are very efficient in removing acids and dyes from aqueous solutions [41]. However, they have low affinity for basic (cationic) dyes. The high surface area to volume ratio and magnetic properties of the MNPs together with the adsorption capabilities of CD through inclusion complex formation would facilitate the extraction of different compounds [20].

Lia *et al.* [42] prepared  $\beta$ -cyclodextrin ( $\beta$ -CD) functionalized magnetic reduced graphene oxide composite ( $\text{Fe}_3\text{O}_4/\text{RGO}@ \beta\text{-CD}$ ) and its application as a selective adsorbent for the determination of the two naphthalene-derived phytohormones (1-naphthalene acetic acid (NAA) and 2-naphthoxyacetic acid (2-NOA)) investigated. Magnetic reduced graphene oxide composite

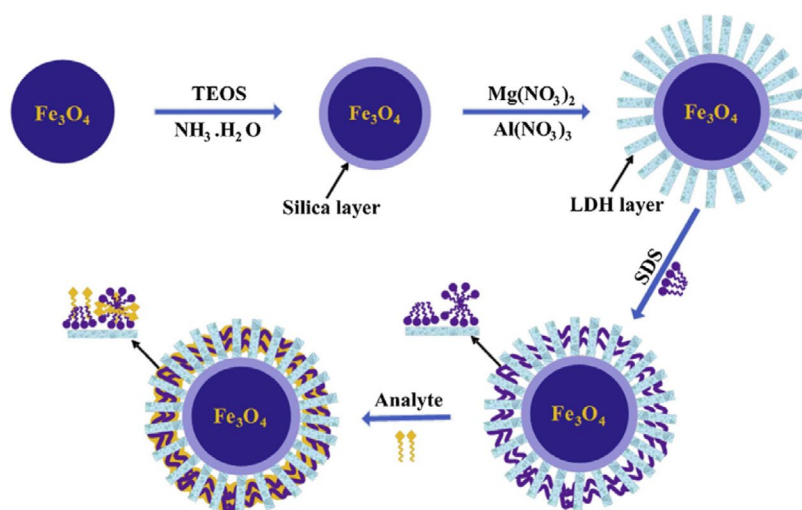


Fig. 2. Schematic illustration of the preparation of surfactants modified  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{Mg-Al}$  MLDH and its application for enrichment of analytes as SPE sorbents [28].

(Fe<sub>3</sub>O<sub>4</sub>/RGO) was first synthesized via in situ chemical precipitation method and then β-CD was applied to further functionalize the resultant Fe<sub>3</sub>O<sub>4</sub>/RGO composite (Fig. 4). Compared with Fe<sub>3</sub>O<sub>4</sub>/RGO, the as-prepared Fe<sub>3</sub>O<sub>4</sub>/RGO@β-CD showed better molecular selectivity and higher extraction efficiency for NAA and 2-NOA by dint of the size complementarity brought by the introduction of β-CD. Under the optimal conditions, the limits of detection (LODs) were 0.67 ng g<sup>-1</sup> for both NAA and 2-NOA.

At the same work, Abdolmohammad-Zadeh and Talleb [43] developed magnetic solid phase extraction method based on β-cyclodextrin (β-CD) grafted graphene oxide (GO)/magnetite (Fe<sub>3</sub>O<sub>4</sub>) nano-hybrid as an innovative adsorbent for the separation and pre-concentration of gemfibrozil prior to its determination by spectrofluorometry. The as-prepared β-CD/GO/Fe<sub>3</sub>O<sub>4</sub> nano-hybrid possesses the magnetism property of Fe<sub>3</sub>O<sub>4</sub> nanoparticles that makes it easily manipulated by an external magnetic field. On the other hand, the

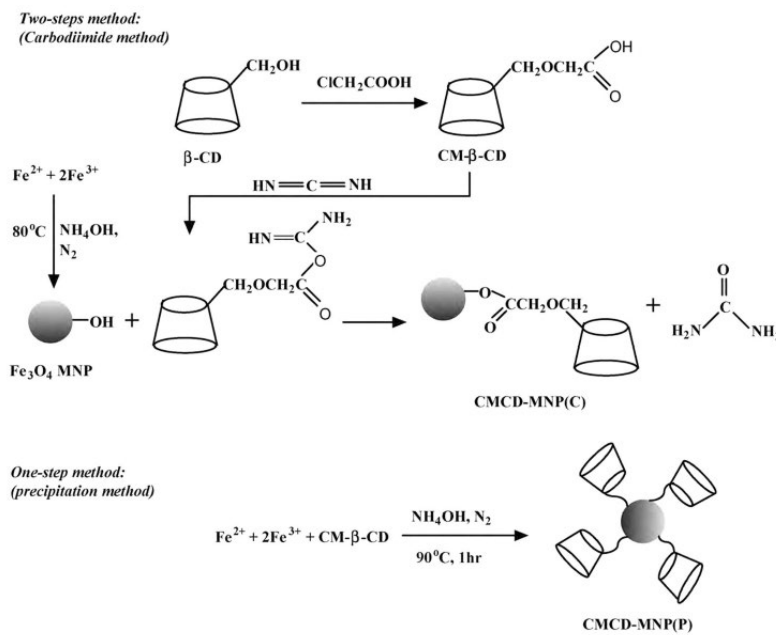


Fig. 3. An illustration for the carboxymethylation and binding of CD onto the Fe<sub>3</sub>O<sub>4</sub> nanoparticles [11]

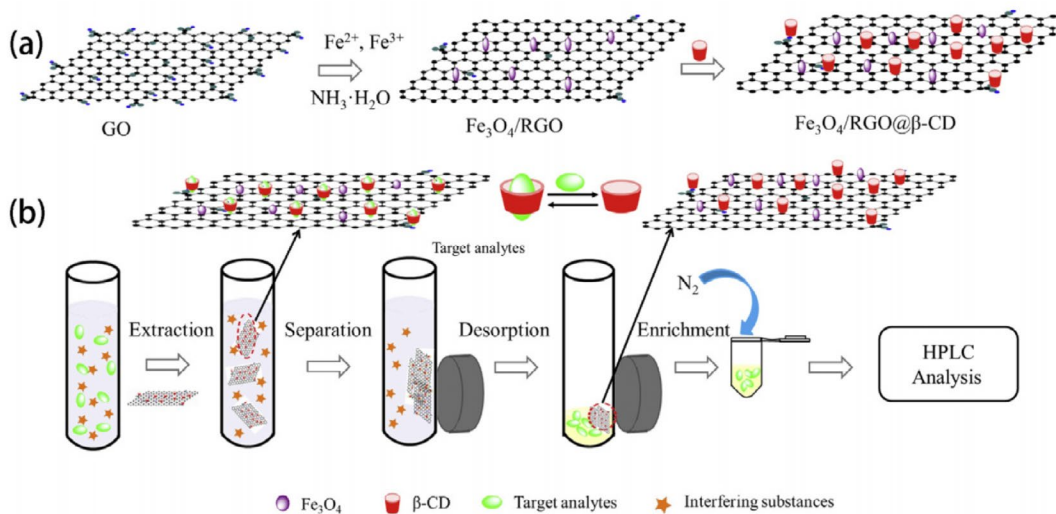


Fig. 4. Scheme of the synthetic route for Fe<sub>3</sub>O<sub>4</sub>/RGO@β-CD and their application for the MSPE [32]

surface modification of GO by  $\beta$ -CD leads to selective separation of the target analyte from sample matrices. Under the optimized experimental conditions, the limit of detection and enrichment factor for gemfibrozil were  $3 \text{ pg mL}^{-1}$  and 100, respectively.

Yang *et al.* [44] presents a novel microextraction technique combining magnetic solid-phase microextraction (MSPME) with ionic liquid dispersive liquid-liquid microextraction (IL-DLLME) to determine four fungicides (azoxystrobin, chlorothalonil, cyprodinil and trifloxystrobin) in environmental water samples by high-performance liquid chromatography. Under the optimum conditions, the limits of detection were between  $0.02$  and  $0.04 \text{ } \mu\text{g L}^{-1}$ .

In other research, Gong *et al.* [45] prepared carboxymethyl-hydroxypropyl- $\beta$ -cyclodextrin polymer modified magnetic particles  $\text{Fe}_3\text{O}_4$  (CM-HP- $\beta$ -CD-CP-MNPs) and applied to magnetic solid phase extraction of rutin combined with UV-Visible spectrometry detection. Calibration curve was linear in the range of  $0.05$ – $8.00 \text{ } \mu\text{g mL}^{-1}$  and the limit of detection was  $7.0 \text{ ng mL}^{-1}$ .

#### MSPE involving carbon nanotube (CNT)-based magnetic nanoparticles

Because of their excellent mechanical, electrical, and thermal properties, carbon nanotubes (CNTs) have been the focus of intensive study since their discovery by Iijima in 1991 [46].

Because of their relatively large specific area,

CNTs have attracted researchers' interest as a new type of powerful solid-phase extraction adsorbent. However, the poor solubility of CNTs and the difficulty of collecting them from their dispersing media can cause much inconvenience in their practical application. To simultaneously overcome these two disadvantages, functionalization of the CNTs became necessary. Addition of the property of magnetism to CNTs enables convenient separation of the sorbent in addition to high adsorption capacity [47]. The prepared magnetic CNTs can be well dispersed in water and easily separated from the medium by the use of a magnet [48]. Different strategies for the preparation of the M-CNT composite by the combination of the MNP and CNTs are shown in Fig. 5 [49]. More recently (2015), Herrero-Latorre *et al* have reviewed magnetic solid-phase extraction using carbon nanotubes as sorbents [16]. CNT-modified MNPs have been used for the extraction of thiamine [50], estrogens [51], flavonoids [52], fluoroquinolones [53], gatifloxacin [54], naproxen [55], sulfonamide antibiotics [56,57], aconitines [58], methylprednisolone [59], puerarin [60], pyrethroids [61], aryloxyphenoxypropionate herbicides [62], bisphenol A [63], linear alkylbenzene sulfonates [64] and 4-nonylphenol [65] from different matrices.

Daneshvar Tarigh and Shemirani [50] proposed an ultrasound-assisted dispersive solid phase extraction method with MWCNT- $\text{Fe}_3\text{O}_4$  as the sorbent and subsequent spectrofluorimetric

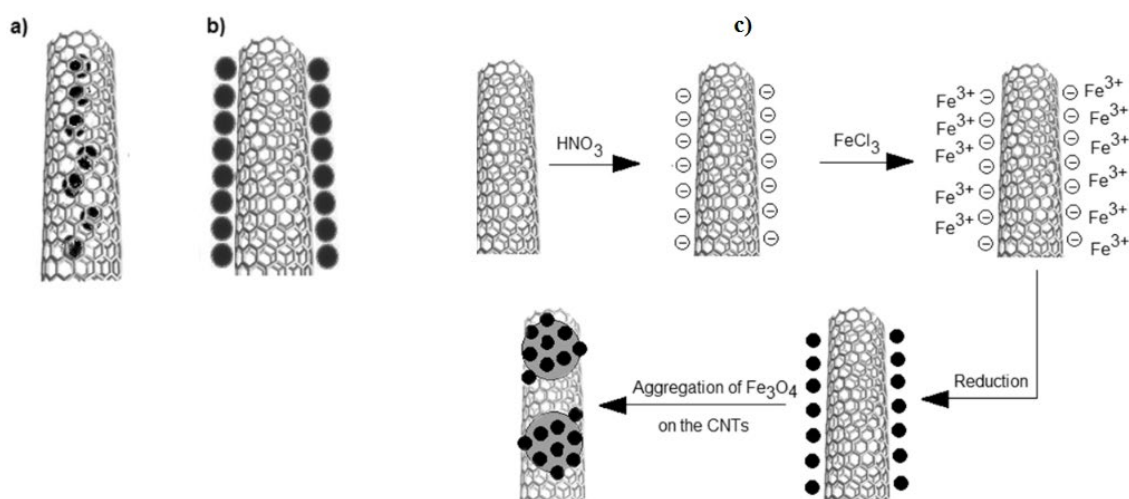


Fig. 5. Different strategies for the preparation of the M-CNT composite by the combination of the M-NP and CNTs. a) Endohedral functionalization; b) Exohedral functionalization; c) Preparation of M-CNT composites by exohedral functionalization. Schematic description of the self-assembly of magnetite beads along MWCNTs in the hydrothermal synthesis [39]

determination of thiamine (Vitamin B1) in diverse biological, pharmaceutical and foodstuff samples. The sensitivity and precision obtained are comparable to, or even better than those of other methods for the determination of Vitamin B1 and, in addition, the sample clean up system proved to be an excellent procedure for complex matrices. Different types of estrogens have been determined in milk [51].

An interesting way to increase the selectivity of M-CNTs for target analytes is by modification of their surface in different ways by chemical or physical functionalization. This approach can be used to introduce diverse functional groups, biomolecules and onto the surface. It is clear that this functionalization (through both chemical and physical strategies) seems to be one of the future trends in M-SPE. The attachment of functional groups with directed selectivity for some analytes (or even specific ones in the case of molecularly imprinted polymers: MIPs) appears to be one of the most interesting approaches for future developments. Zhang *et al.* [63] applied this strategy by developing an M-SPE procedure based on the synthesis of a MWCNT-Fe<sub>3</sub>O<sub>4</sub>-MIPs composite for the extraction of bisphenol A. In spite of the complex synthesis method for the MIP-based sorbent material, involving several steps, the high selectivity and binding capacity of the composite make this a very interesting sorbent for analytical separations.

Other functionalization methods have been employed for analytical separations of different natural substances. Xiao *et al.* [52] functionalized MWCNT-Silica/Fe<sub>3</sub>O<sub>4</sub> with 1-hexadecylmethylimidazolium bromide (C<sub>16</sub>MIM Br) for the separation of flavonoids from human urine.

Three different pyrethroids (insecticides used in the majority of commercial household formulations) were also determined after magnetic extraction with MWCNT-Fe<sub>3</sub>O<sub>4</sub>. Betacyfluthrin, cyhalothrin and cyphenothrin were successfully separated from tea samples and were subsequently measured by HPLC [61]. The authors stated that magnetic nanotubes are ideal vehicles for loading pyrethroids and they proposed the extension of these studies to organophosphorus pesticides in complex matrices.

Recently, Luo *et al.* [62] have proposed a new method for the HPLC and UHPLC-MS/MS determination of four aryloxyphenoxy-propionate herbicides (AOPPs) and their metabolites in

water samples using a novel magnetic ionic liquid modified carbon nanotube (M-IL-MWCNTs) as a sorbent for magnetic extraction. The appropriate  $\pi$ - $\pi$  electron-donor/acceptor interactions and anion exchange ability allowed the sorbent to be used for the simultaneous extraction of analytes with different polarities, namely non-polar AOPP esters and their polar acid metabolites. This approach compares favorably with similar procedures in which M-MWCNTs and other M-NPs are employed as sorbents. The authors suggested that the MWCNT part of the M-IL-MWCNT has a similar adsorption mechanism to M-MWCNT, while the ionic liquid part not only changed the polarity of the MWCNT but also offered an anion exchange group to interact with ionic analytes. Therefore, the sorption of analytes onto the M-IL-MWCNT can be explained by a variety of adsorption mechanisms, including  $\pi$ - $\pi$ , van der Waals and ionic interactions.

#### **MSPE involving graphene-based magnetic nanoparticles**

Graphene (G) is another carbon-based material with many unique features, including a two-dimensional planar structure coupled with one-atom thickness, large surface area, and extraordinary electrical, thermal, and mechanical properties [66]. Because of its large delocalized  $\pi$ -electron system, G can form a strong  $\pi$ -stacking interaction with the benzene ring and might be a good adsorbent for the extraction of benzenoid compounds [67]. Introduction of magnetic properties into G could combine its high adsorption capacity with the separation convenience of magnetic materials [68]. Therefore, it is believed that magnetic graphene nanoparticles would have good functionality and performance in separation applications [69-81].

Wang's group synthesized a G-based magnetic nanocomposite (Fe<sub>3</sub>O<sub>4</sub>-G) and successfully applied it in MSPE for preconcentration of some benzenoid compounds, for example neonicotinoid insecticides [70], imide fungicides [71], carbamate pesticides [72], fuchsine [73], triazine herbicides [74], chloroacetanilide herbicides [75] and triazoles [76] in environmental water samples. Also, G-based magnetic nanocomposite have been used for extraction of PAHs [77], sulfonamide antibiotics [78], polychlorinated biphenyls, polyaromatic hydrocarbons and phthalates [79], perfluoroalkyl and polyfluoroalkyl substances [80] and preservatives [81] by other research groups.

Very recently, a kind of  $\text{Fe}_3\text{O}_4\text{-G}$  has been prepared and used as adsorbent for preconcentration of four neonicotinoid insecticides (thiamethoxam, imidacloprid, acetamiprid, and thiacloprid) from environmental water samples [70]. In this study, pure  $\text{Fe}_3\text{O}_4$  MNPs and two different magnetic carbon materials, i.e.,  $\text{Fe}_3\text{O}_4\text{-G}$  and  $\text{Fe}_3\text{O}_4\text{-MWCNT}$ , were all tested as adsorbents for extraction of the target analytes. The results indicated that  $\text{Fe}_3\text{O}_4$  nanoparticles alone barely extract the target compounds from sample solution, and that MWCNT or G was responsible for adsorption of the neonicotinoids. The results also showed that the extraction efficiency of  $\text{Fe}_3\text{O}_4\text{-G}$  ( $225\text{ m}^2\text{ g}^{-1}$ ) was much better than that of  $\text{Fe}_3\text{O}_4\text{-MWCNT}$  ( $196\text{ m}^2\text{ g}^{-1}$ ), which could be attributed to its slightly larger surface area and the high adsorption ability of G. The research group also used  $\text{Fe}_3\text{O}_4\text{-G}$  for efficient enrichment of some trace triazoles from environmental water samples [76].

It is well known that graphene oxide (GO) sheets are highly negatively charged when dispersed in aqueous solution, as a result of ionization of carboxylic acid and phenolic hydroxyl groups on the GO sheets. Han *et al.* reported a facile strategy for preparing  $\text{Fe}_3\text{O}_4\text{-GO}$  nanocomposites by electrostatic interaction—simple addition of  $\text{Fe}_3\text{O}_4$ , which has a positively charged surface. This synthesis of  $\text{Fe}_3\text{O}_4\text{-GO}$  nanocomposites was mild, rapid, and no toxic reagents were used; the procedure is illustrated schematically in Fig. 6 [77]. The hybrid materials obtained were used as MSPE sorbent to preconcentrate several PAHs in environmental water samples before HPLC–UV analysis. To avoid tedious chemical modification, an easy-to-handle approach was devised by Luo *et al.* With the aid of sonication, graphene was easily immobilized on the silica-coated magnetite particles (denoted  $\text{Fe}_3\text{O}_4\text{-G}$ ) [78]. Thus, the  $\text{Fe}_3\text{O}_4\text{-G}$

$\text{SiO}_2\text{-G}$  had magnetic properties, enabling easy removal of the material after dispersion. The graphene in the  $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-G}$  magnetic sorbent still had its own properties, indicating potential adsorption ability. This synthesized  $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-G}$  was used to extract six sulfonamide antibiotics (SAs) from water samples.

More recently, chem. *et al.* [81] synthesized size-controlled magnetite nanoparticles with a graphene and polymeric ionic liquid coating ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{G@PIL}$ ). The adsorbent (Fig. 7) used as the modified QuEChERS adsorbent for the determination of 20 preservatives residues in vegetables by gas chromatography/mass spectrometry (GC–MS) analysis. It not only exerted the nanometer features of magnetic nanoparticles, but also displayed the large specific surface area of graphene (G) and the solvent effects of polymeric ionic liquids (PILs). Various experimental parameters have been investigated. Under the optimized conditions, the detection limits of the proposed method for 20 preservatives ranged from 0.82 to 6.64  $\mu\text{g}/\text{kg}$ .

#### MSPE involving polymer-coated magnetic nanoparticles

Magnetic polymer composites can be prepared by coating or encapsulating the magnetic inorganic particles, for example magnetite ( $\text{Fe}_3\text{O}_4$ ), with natural or synthetic polymers. These polymer-modified MNPs combine the high extraction capacity of polymer with the easy separation property of MNPs, and can be used for the sample preparation. Recently, some recent applications of magnetic polymer composites and magnetic molecularly imprinted polymers have been reviewed by some research groups [13,15,17].

Hybrid polymer-magnetic NPs can be powerful materials for (micro) the extraction. These

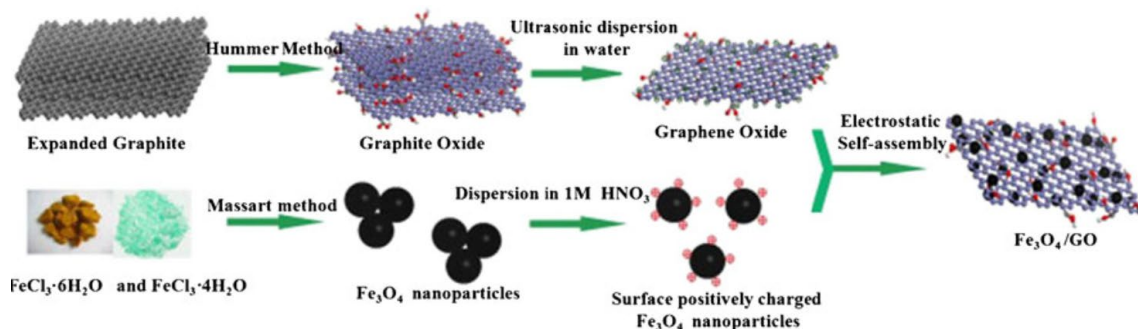


Fig. 6. Schematic illustration of fabrication of the  $\text{Fe}_3\text{O}_4\text{-GO}$  nanocomposite [67]



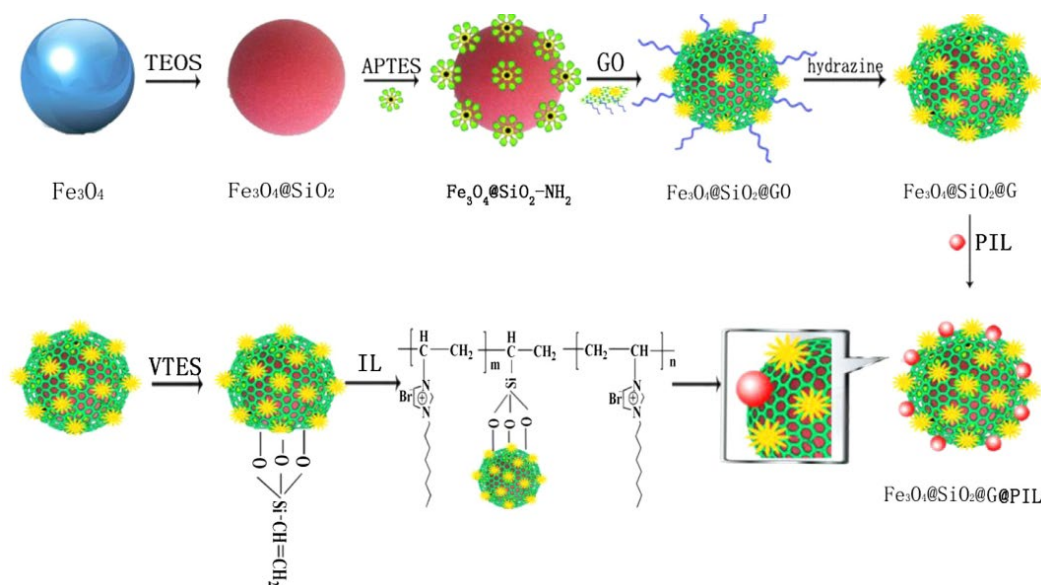


Fig. 7. Preparation of magnetite nanoparticles by a graphene and polymeric ionic liquid coating [71]

hybrid MNPs coated with a polymer network can be anchored by electrostatic interaction [82,83] or by covalent bonding [84-88]. Covalent bonding is usually involved when polypyrrole [84,87], polythiophenes [88], polyaniline [75] or molecularly imprinted polymers (MIPs) [54,89-108] are used as polymeric coatings, whereas electrostatic interactions occur when such biopolymers as chitosan [82] or alginate [83] are used. In the latter case, the biopolymers are usually used to enhance the dispersibility of the derivatized MNPs.

Zhang *et al.* reported the preparation of chitosan-coated octadecyl-functionalized MNPs [82]. The magnetite NPs were first modified with an octadecyl group by silylation; the surface of the  $\text{Fe}_3\text{O}_4$ -C18 was then further coated with a layer of hydrophilic chitosan-tripolyphosphate polymer by ionotropic gelation. The resultant materials have an interior hydrophobic octadecyl group and exterior hydrophilic chitosan polymer coating. Another method used to solve the problem of  $\text{Fe}_3\text{O}_4$ -C18 being difficult to disperse in aqueous solution is to coat a hydrophilic barium-alginate ( $\text{Ba}^{2+}$ -ALG) polymer on the surface of C18 [83]. The sorbents were used to preconcentrate PAHs and phthalate ester pollutants from environmental water samples. It required only 30 min to extract trace levels of analytes from 500 mL water samples compared with 2-3 h for a traditional SPE column equipped with a vacuum pump.

There has recently been increasing interest in the use of conducting polymers as extractants [84-87]. Conducting polymers are multifunctional materials with a variety of interesting properties, for example extraordinary stability and simplicity of the synthesis from an inexpensive monomer. Polypyrrole (PPy)-coated  $\text{Fe}_3\text{O}_4$  magnetic microspheres have been successfully synthesized and used as a magnetic sorbent to extract and concentrate the phthalates from water samples on the basis of formation of  $\pi$ - $\pi$  complexes and hydrophobic interaction between polypyrrole and analytes [84]. For a similar reason,  $\text{Fe}_3\text{O}_4$ -PPy showed excellent performance in estrogen extraction [87]. Estrogens could be captured directly by  $\text{Fe}_3\text{O}_4$ -PPy from milk samples without protein precipitation.

Mehdinia *et al.* [85] reported the application of polyaniline-coated  $\text{Fe}_3\text{O}_4$  nanoparticles ( $\text{Fe}_3\text{O}_4$ -PANI NPs) with diameters between 50 and 100 nm for extraction of methylmercury. In this research, hydrophobic and  $\pi$ - $\pi$  interactions were important in the extraction of anionic ionizable compounds. Recently,  $\text{Fe}_3\text{O}_4$  nanoparticles coated with sulfate-doped PANI have been synthesized and used for sampling the ionizable compounds parabens [86]. Because sulfate-doped PANI is positively charged, electrostatic interactions and hydrophobic and  $\pi$ - $\pi$  interactions have a significant role in adsorption of target analytes by the sorbent.

In recent years, because of their chemical

stability in air and/or humid environments, polythiophenes have been coated on Fe<sub>3</sub>O<sub>4</sub> NPs (Fe<sub>3</sub>O<sub>4</sub>-PTh NPs) and used as efficient sorbents for extraction and preconcentration of several typical plasticizers from environmental water samples before gas chromatography with flame-ionization detection (GC-FID) [88]. Coating of NPs with polythiophene not only increased adsorption capacity for the target analytes but also improved the stability of the NPs and their dispersibility in aqueous media.

Molecular imprinting of highly cross-linked materials imitates the recognition mechanism of antigens and antibodies. The imprinting process uses a template molecule and a functional monomer for co-polymerization in the presence of a cross-linking agent, leading to formation of a polymer with a three-dimensional structure. After removal of the imprinted molecules, the imprinted cavities enable the polymer to selectively rebind the imprint molecule and its analogues from a mixture. Magnetic molecularly imprinted polymer microspheres prepared by molecular imprinting of magnetic nanoparticles have combined the advantages of both molecular imprinting and

magnetic separation. These molecularly imprinted polymers (MIPs)-modified magnetic NPs have both good superparamagnetism and highly selective adsorption and are very promising as selective sorbents for SPE. In continue, some most recently published magnetic molecularly imprinted polymer methods have been reviewed [89-109].

Xiao *et al.* [54] synthesized a novel composite imprinted material, on the basis of magnetic carbon nanotubes (MCNTs)-incorporated layer using gatifloxacin as a template, methacrylic acid as a functional monomer, glycol dimethacrylate as a cross-linker, by a surface imprinting technique (Fig. 8). The results showed that magnetic carbon nanotubes molecularly imprinted polymers (MCNTs@MIP) display a rapid dynamic adsorption and a high adsorption capacity of 192.7 µg/mg toward GTFX. Applied MCNTs@MIP as a sorbent, a magnetic solid phase extraction method coupled with high performance liquid chromatography (MSPE-HPLC) was developed for the determination of GTFX in serum samples. The recoveries from 79.1 ± 4.8% to 85.3 ± 4.2% were obtained. MCNTs@MIP can not only be collected and separated fast by external magnetic

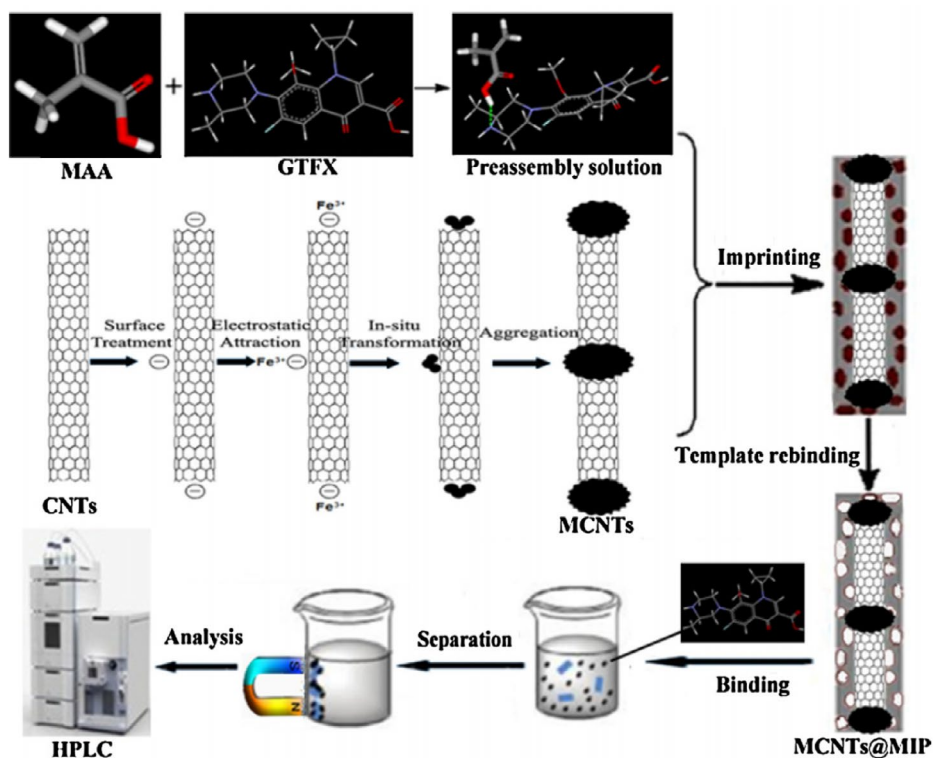


Fig. 8. Scheme of the synthetic route for MCNTs@MIP and their application for SPE of GTFX with the help of an applied magnetic field [44]

field but also have high surface-to-volume ratio, outstanding mechanical properties and specific recognition toward template molecule. In addition, the MCNTs@MIP could be regenerated, which could be used for five cycles with lost of less than 7.8% of its recovery on average.

Yuan *et al.* [89] introduced a new strategy for the extraction of bisphenol A (BPA) from milk using surface-imprinted core-shell magnetic beads. In order to obtain highly selective recognition cavities, they chose an enhanced imprinting method based on binary functional monomers, e.g. 4-vinylpyridine (4-VP) and  $\beta$ -cyclodextrin  $\beta$ -CD), for BPA imprinting (Fig. 9). The adsorption experiments revealed that  $\text{Fe}_3\text{O}_4$ -MIPs showed better extraction capacity and selectivity toward BPA and its analogues than the non-imprinted polymers (NIPs). In milk samples, the present method displayed a lower detection thresholds, down to 3.7  $\mu\text{g/L}$ .

More recently, Peng *et al.* [90] prepared photonic-magnetic responsive molecularly imprinted microspheres (PM-MIMs) by seed polymerization, through suitable functionalization of magnetic nanoparticles for further coating with photoresponsive functional monomer and imprinted layers (Fig. 10), and then successfully applied to the fast and selective extraction of  $17\beta$ -estradiol ( $17\beta$ -E2) from milk powder and drinking water samples by HPLC-UV. The PM-MIMs displayed excellent photoresponsive properties and could be rapidly separated from solutions under an external magnet. The PM-MIMs proved to be an ideal photoswitch with the ability of reversible uptake and release of  $17\beta$ -E2 upon alternate 365 and 440 nm irradiation: 45.0% of  $17\beta$ -E2 released from the PM-MIMs upon 365 nm irradiation, and 94.0% of the released  $17\beta$ -E2 was rebound to the PM-MIMs at 440 nm. The method limit of detection (LOD, S/N = 3) for

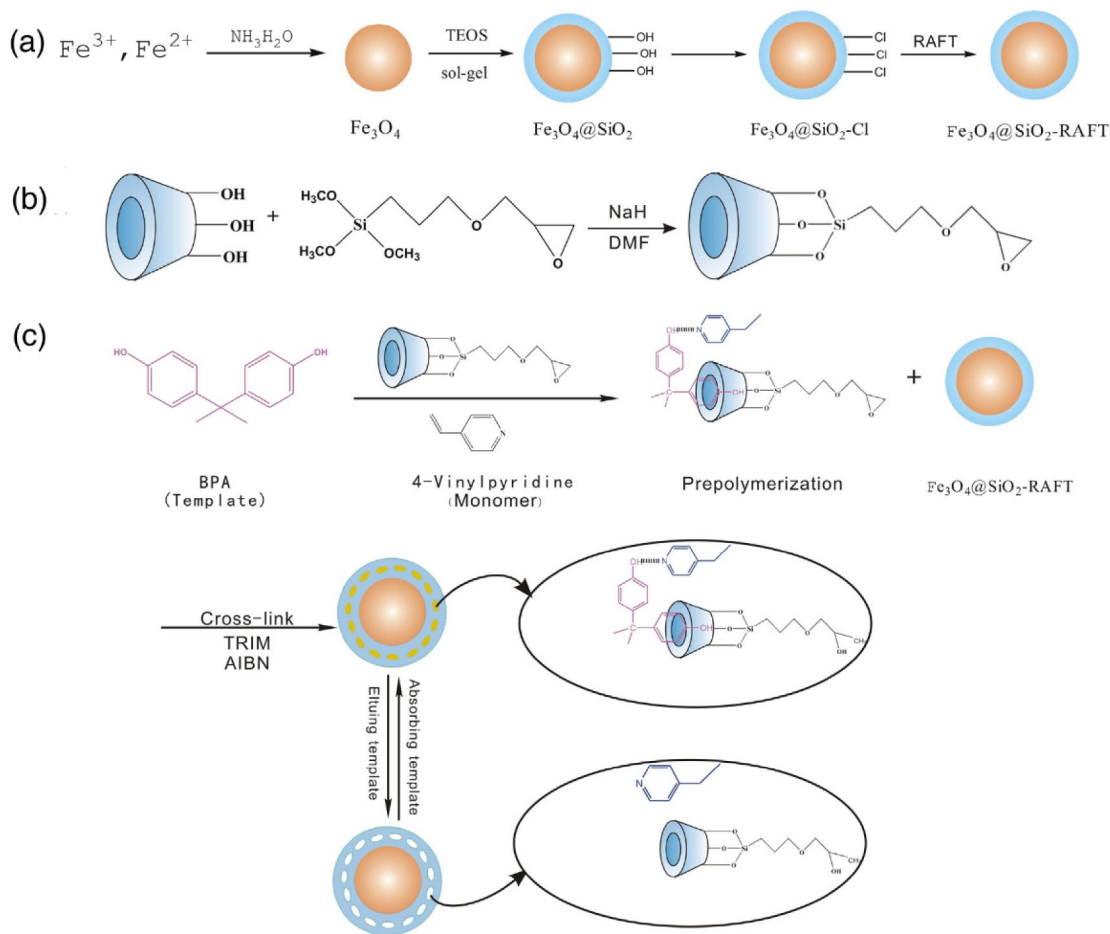


Fig. 9. Synthesis route of surface-imprinted core-shell magnetic beads and their application for the extraction of BPA [79]

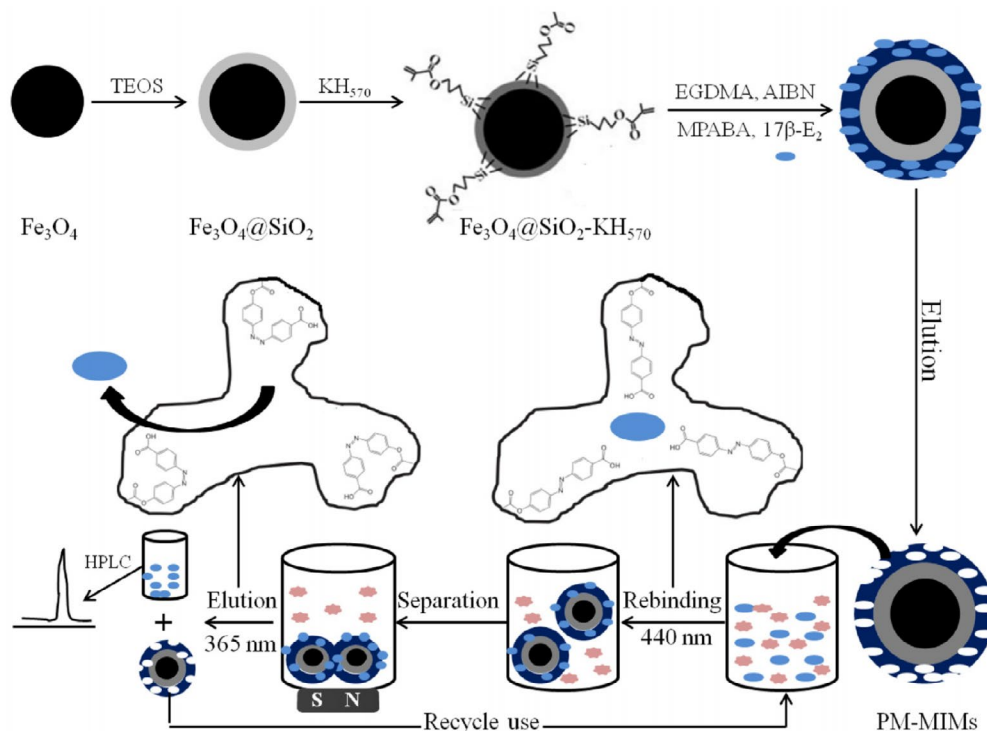


Fig. 10. Schematic illustration for the preparation process of the PM-MIMs, possible mechanism of photoregulated uptake and release and the extraction procedure [80]

17 $\beta$ -E2 was 0.18  $\mu\text{mol L}^{-1}$ . The proposed method reasonably combined photonic response, magnetic separation and surface imprinting, which endowed the PM-MIMs with significant advantages of high adsorption capacity and fast binding kinetics, convenient separation and recycled use, and simple rapid eco-benign adsorption/elution processes for template molecules.

Versatile molecularly imprinted polymers (MIPs) have been widely applied to various sample matrices, however, molecular recognition in aqueous media is still difficult. Stimuli-responsive MIPs have received increasing attentions due to their unique feature that the molecular recognition is regulated by specific external stimuli. More recently, Wu *et al.* [104] prepared water-compatible temperature and magnetic dual-responsive MIPs (WC-TMMIPs) with hydrophilic brushes prepared via reversible addition-fragmentation chain transfer precipitation polymerization for reversible and selective recognition and extraction of bisphenol A (BPA). The resultant WC-TMMIPs (Fig. 11) showed excellent thermosensitivity and simple rapid magnetic separation. Controlled adsorption and release of BPA by temperature regulation were investigated systematically, and the maximum

adsorption and removal efficiency toward BPA in aqueous solutions were attained at 35°C and 45°C, respectively, as well as a good recoverability which exhibited a precision less than 5% through five adsorption-desorption cycles. Using the two modes followed by HPLC-UV determination, excellent linearity was attained in the range of 0.1–14.5  $\mu\text{M}$  and 1.3–125 nM, with low detection limits of 0.02  $\mu\text{M}$  and 0.18 nM, respectively. Satisfactory recoveries for spiked seawater samples were achieved ranging from 86.3–103.5% and 96.2–104.3% with RSD within 2.12–4.33%. The intelligent WC-TMMIPs combining water-compatibility, molecular recognition, magnetic separation, and temperature regulation proved potentially applicable for selective identification, controlled adsorption/release and high-efficiency enrichment/removal of trace targets in complicated aqueous media.

#### **MSPE involving Octadecylsilane(ODS)-modified magnetic nanoparticles**

ODS-modified NPs have been widely used for preconcentration of environmental pollutants because of their favorable separation ability, excellent stability, and long lifetime [99]. ODS

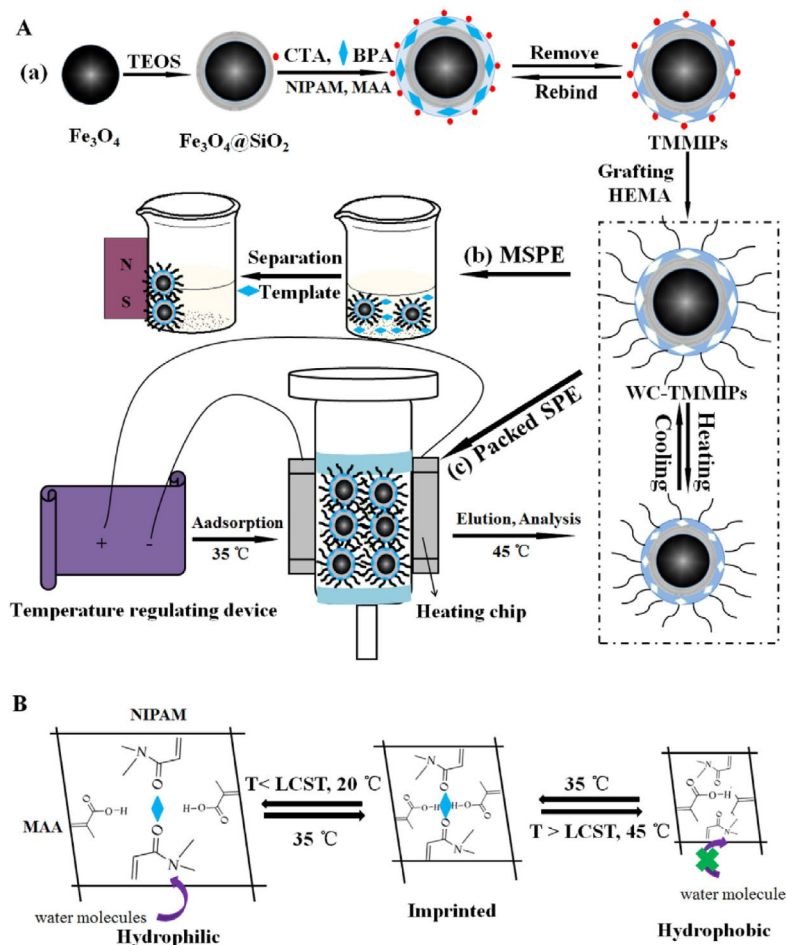


Fig. 11. (A) Schematic illustrations of the preparation process and temperature-regulated shrinking/swelling behavior (in the dotted box) of WC-TMMIPs (a), and their applications to MSPE (b) and packed SPE (c). (B) Schematic representation of the adsorption and release process of BPA by the WC-TMMIPs and possible molecular recognition mechanism regulated by temperatures [94].

modified magnetic NPs are therefore expected to have excellent performance in adsorption and separation of substances from complex samples. One of the most promising and advanced composite materials is  $\text{Fe}_3\text{O}_4$ -silica nanoparticles coated with alkyl C18 ( $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$ -C18). Sha *et al.* reported  $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$ -C18 magnetic nanoparticles for extraction and determination of ergosterol in tobacco [110] for the first time. After that C18-functionalized MNPs were used for the extraction of PAHs [111,112], methylprednisolone (MP), lidocaine, or puerarin in rat plasma [113–115], phthalates [116], sudan dyes [117], OPPs [118], phthalates esters [119], fat-soluble vitamins [120], pesticides residues [111] and anionic perfluorinated compounds [122].

By fabricating a C18-functionalized mesoporous silica shell on the surface of a  $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$  core,

Zhang *et al.* also synthesized  $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$ - $\text{SiO}_2$ -C18 magnetic microspheres [112]. These microspheres had high extraction efficiency for PAHs and efficiently prevented interference from natural organic matter, thus enabling easy isolation from the aqueous solution after extraction. When  $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$ - $\text{SiO}_2$  microspheres without modification by use of C18 groups were used for comparison, PAHs were hardly extracted over the whole pH range, indicating that the C18 group is mainly responsible for adsorption of PAHs on the  $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$ - $\text{SiO}_2$ -C18 magnetic sorbent.

Sorbents with mixed functional ligands may enhance adsorption ability toward targets with different functional groups. Zhang *et al.* developed novel silica-coated MNPs functionalized with both C18 and  $\text{NH}_2$  groups, and used as the extractant for anionic organic pollutants under acidic conditions

[112]. Owing to the hydrophobic interaction and electrostatic attraction of the anionic perfluorinated compounds jointly provided by the mixed groups on the surface, more than 90 % of the targets can be extracted from 500 mL aqueous solution by 0.1 g  $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-C18+NH}_2$  NPs at pH 3.

Ultrafine  $\text{Fe}_3\text{O}_4$  NPs prepared by chemical coprecipitation have a smaller diameter, and larger surface area that can be more easily dispersed in aqueous samples compared with those prepared by solvent-thermal method. These C18-functionalized ultrafine magnetic silica nanoparticles were utilized as adsorbent to extract four kinds of Sudan dye (Sudan I, II, III, and IV) from water samples before determination by UFLC [116]. The LODs for Sudan I, II, III, and IV were 0.066, 0.070, 0.120, and 0.120  $\text{ng mL}^{-1}$  respectively.

Application of magnetite nanoparticles for cleanup and enrichment of pesticides is a relatively new area of research. Maddah *et al.* reported a method for sample preparation of trace amounts of organophosphorus pesticides (OPPs) in environmental water using magnetite octadecylsilane nanoparticles as adsorbent [117]. The enrichment factors of this method were 172 and 184 and the LODs for both analytes, enitrothion and diazinon, were 0.014 and 0.019  $\text{ng mL}^{-1}$  with good precision—relative standard deviations (RSD) were 5.4 % and 7.2 %, respectively.

#### Automation of M-SPE

As stated previously, it is clear that M-SPE has advantages over standard column SPE due to the simplicity of the solid sorbent separation. However, in spite of the minimal sample manipulation required for M-SPE, automation involving the use of flow injection analysis (FIA) and related procedures would constitute an appreciable contribution to improve the analytical figures of merit of M-SPE-based methods. These ameliorations are focused on analysis time (by faster sample throughput) as well as on precision and accuracy (by reduction of human intervention). In addition, other benefits for the analytical process provided by automation include a reduction in the consumption of reagents and solvents and minimization of the analysis time, all of which have associated cost savings.

In general, automation of M-SPE involves the use of an FIA (or related technique) system in which the magnetic sorbent is immobilized onto a microcolumn by applying a magnetic field generated by magnets arranged around the column. The main two drawbacks of this approach are (i)

the effective immobilization of a magnetic sorbent by the application of an external magnetic field alone continues to be a great challenge [123] and (ii) the uniformity and strength of the magnetic field are critical factors to achieve a well-packed column and to avoid the formation of undesired channels in the magnetic sorbent [21]. The first attempt to automate M-SPE was carried out by Lee *et al.* [124] in 2009. These authors proposed a new method for the determination of multiple heavy metals by inductively coupled plasma mass spectrometry (ICP-MS) employing an M-SPE sample preparation procedure in which iron based magnetic nanoparticles modified with polyacrylic acid were used as the sorbent. In this case, in addition to the magnetic field, frits and plugs at both ends of the microcolumn were used to immobilize the magnetic material and to avoid material losses. An FIA on-line M-SPE process in which the magnetic sorbent was coated onto the inner walls of a laboratory-made knotted reactor (KR) was developed for selective chromium speciation [125] and for the preconcentration and determination of several trace noble metals [126], with detection by ICP-MS. In both cases, the particular design of the reactor, combined with the magnetic field applied, was sufficient to immobilize the magnetic sorbent and avoid the need for any frits or plugs. Another recently applied strategy is the lab-on-chip M-SPE method [127-129]. In these cases, integrated microfluidic chips consisting of reaction, mixing and extraction units along with two magnets, were designed and fabricated for M-SPE.

In addition to the general benefits of M-SPE, the principal advantages of this approach are the miniaturization of the procedure, which in turn leads to a very low sample requirement, very low consumption of solvents and reagents, and good compatibility with biological samples (such as cells). In contrast, the preparation of microfluidic devices with several inlet and outlet flow channels, microvalves and magnets is highly specialized and involves soft lithography and rapid prototyping with polydimethylsilicone technology [128].

In addition to FIA, the other related technique employed for MSPE automation is sequential injection analysis (SIA). Over the past few years the use of SIA has been extended to encompass a variety of complex online sample manipulation and pretreatment procedures. For example, Giakisikli and Anthemidis [122] recently developed an SIA-M-SPE approach for the preconcentration of

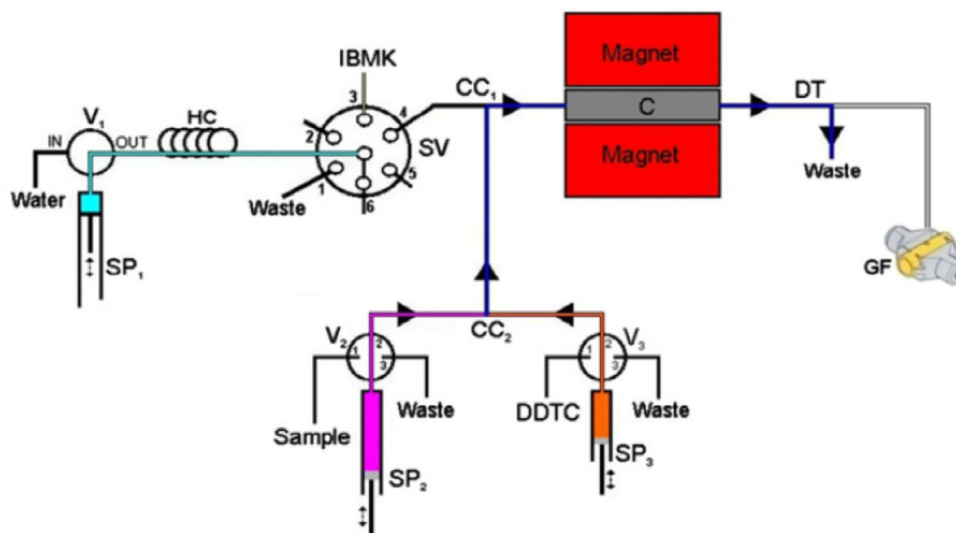


Fig. 12. Schematic diagram of the SI-MSPE-ETAAS system for cadmium determination. SV, selection valve; SP<sub>1</sub>, SP<sub>2</sub>, SP<sub>3</sub>, syringe pumps; HC, holding coil; CC<sub>1</sub>, CC<sub>2</sub>, confluence connectors; DT, delivery tube; C, microcolumn; GF, graphite furnace of ETAAS; IBMK, isobutylmethylketone; DDTC, diethyldithiocarbamate [113]

aqueous cadmium samples prior to determination by electrothermal atomic absorption spectrometry (ETAAS). A schematic diagram of the proposed system is shown in Fig. 12.

One of the drawbacks of the repeated use of permanently packed M-SPE columns in FIA and SIA networks is that this might lead to several problems such as contamination, deactivation of the surface and even loss of analyte retention capability. Furthermore, incomplete elution of the retained species from the magnetic sorbent might produce carry-over effects between consecutive runs. Therefore, in both FIA and SIA procedures it is essential to use magnetic materials that are robust to a large number of adsorption/ elution cycles without performance loss. A new SIA-approach, namely sequential injection analysis-bead injection-solid phase extraction (SIA-BI-SPE), has recently been developed to overcome the aforementioned drawbacks by facilitating the renewal of the solid sorbents [130].

#### **Magnetic nanoparticles in microextraction techniques** **Magnetic nanoparticles for retrieving solvents in dispersive liquid-liquid microextraction**

In conventional DLLME, organic solvents with higher density than water should be used for easily separation from the aqueous phase. A disperser solvent with high miscibility in both extractant and aqueous phase, such as methanol or acetone, is generally needed. When extractant and disperser

agent are added to the aqueous sample, small droplets are formed, hence facilitating extraction. To recover the sediment phase at the bottom of the vial, it is necessary to centrifuge the cloudy solution. Typically, solvents used in DLLME include chloroform and chlorobenzene, which are very toxic, and extraction efficiency is not good for all analytes. On the other hand, when using low-density organic solvents less toxic than chlorinated solvents (e.g., octanol), additional operations to isolate the extractant phase are required, since, apart from centrifugation, refrigeration and thawing need to be applied [131]. Other extractants with enhanced greenness and potential application in DLLME are ILs. ILs used as extractants in LPME have a number of advantages, such as negligible vapor pressure, good thermal stability, and tunable miscibility with water and organic solvents.

The replacement of those solvents by environment-friendly solvents, such as ILs, is therefore very attractive, but centrifugation is still necessary for phase separation. A possibility for the recovery of ILs after DLLME is the combination in sequence of DLLME with dispersive micro-SPE (D-micro-SPE). The latter technique can be considered a miniaturized version of conventional SPE, using dispersion of hydrophobic magnetic NPs (MNPs). Most MNPs contain Fe, Ni, Co and their oxides as the magnetic core [1-3].

Several applications following this dual extraction have appeared in the literature for

polyaromatic hydrocarbons (PAHs) [131], triazine Herbicides [132], pyrethroids [133,134], benzoylurea, insecticides [135], lead [136,137], 4-n-nonylphenol [138], carbaryl [139], cadmium [140,141], gatifloxacin [142], zearalenone [143], triazole fungicides [144], aflatoxins [145], fungicides [146], aflatoxin M1 [147] and arsenic [148]. In this technique, MNPs are employed as sorbents for retrieving the extractant containing the analytes, which are finally desorbed (e.g., by sonication). MNPs, employed in nanoscale magnetic separations, display a large surface area and high sorption capacity and can be isolated from the sample solution by an external magnetic field. In this way, centrifugation is not needed and extraction solvents are not limited to high-density solvents. In principle, any extractant solvent immiscible with water could be employed in DLLME and the whole procedure could be automated.

Moreover, MNPs can be modified for the extraction of different organic solvents. In these applications, the extractant solvent used in DLLME becomes the target phase to be extracted by D-micro SPE. For example, solvents, such as 1-octanol, have been employed for DLLME of pyrethroids, and the extract subjected to D-micro SPE with  $\text{Fe}_2\text{O}_3$ -NPs functionalized with 3-aminopropyl triethoxysilane. [131]. DLLME of Cd(II) after derivatization with ammonium pyrrolidine-dithiocarbamate (APDC) to yield a hydrophobic compound is performed using a non-ionic surfactant and 1-octanol in aqueous medium. The extractant phase is collected by highly hydrophobic polysiloxane-coated core-shell  $\text{Fe}_3\text{O}_2$ @C-MNPs [140].

Addition of a disperser solvent so that small droplets are formed could be omitted, since high-speed stirring to break 1-octanol into fine droplets could be enough to achieve fast extraction [121]. However, a drawback could be the need for vigorous vortex stirring, which requires the use of specialized vortex apparatus.

Yang *et al.* [146] proposed a novel effervescence-assisted microextraction technique based on ionic liquid-dispersive liquid-liquid microextraction with the magnetic retrieval of the extractant for the detection of four fungicides. Magnetic effervescent tablet composed of  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles, sodium carbonate, sodium dihydrogen phosphate and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonimide) was used for extractant dispersion and retrieval. The limits of detection were between 0.02 and  $0.10 \mu\text{g L}^{-1}$  and the intra-day precision and inter-

day precision both are lower than 4.9%.

Amoli-Diva *et al.* [147] developed simple and fast low-density solvent based dispersive liquid-liquid microextraction (LDS-DLLME) followed by vortex-assisted dispersive solid phase extraction (VA-D-SPE) as a new approach for extraction and preconcentration of aflatoxin M1 in milk samples prior to its micelle enhanced spectrofluorimetric determination. In VA-D-SPE approach, hydrophobic oleic acid modified  $\text{Fe}_3\text{O}_4$  nanoparticles were used to retrieve the analyte from the DLLME step. It is noteworthy that the target of VA-D-SPE was 1-heptanol rather than the aflatoxin M1 directly. Under the optimum conditions, the method was linear in the range from  $0.02$  to  $200 \mu\text{g L}^{-1}$  with the correlation coefficient ( $R^2$ ) of 0.9989 and detection limit of  $13 \text{ ng L}^{-1}$ .

#### **Sequential approaches using solid and liquid-phase extraction**

The combination of SPE and DLLME has provided further improvements in EFs, which is advantageous for detection at ultratrace levels. Ebrahimipour *et al.* [149] used MSPE with nano polypyrrole-coated magnetic nanoparticles followed by dispersive liquid phase microextraction (DLLME) for trace determination of megestrol acetate and levonorgestrel by liquid chromatography/ultraviolet detection in biological and wastewater samples. After magnetic solid phase extraction, the eluent of MSPE was used as the disperser solvent for DLLME. Emulsion resulted from DLLME procedure was passed through the in-line filter for phase separation. Finally the retained analytes in the filter was washed with mobile phase of liquid chromatography and transferred to the column for separation. This approach offers the preconcentration factors of 3680 and 3750 for megestrol acetate and levonorgestrel, respectively. This guarantees determination of the organic compounds at trace levels.

Mukdasai *et al.* [133] developed dispersive liquid microextraction (DLME) combined with dispersive  $\mu$ -solid phase extraction (D- $\mu$ -SPE) as a new approach for the extraction of four pyrethroids (tetramethrin, fenprothrin, deltamethrin and permethrin) prior to the analysis by high performance liquid chromatography (HPLC) with UV detection. 1-Octanol was used as the extraction solvent in DLME. Magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$ ) functionalized with 3-aminopropyl triethoxysilane (APTS) were used as the disperser in DLME and as the adsorbent in D- $\mu$ -SPE. Under the



optimum conditions, the enrichment factors were in the range of 51–108. Also, detection limits were 0.05–2 ng mL<sup>-1</sup> (water samples) and 0.02–2.0 ng g<sup>-1</sup> (vegetable samples).

Yamini *et al.* [150] prepared octadecyl functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> as sorbent for the use in solid-phase extraction combined with dispersive liquid-liquid microextraction (DLLME) for the extraction of the plasticizers dibutyl phthalate, di(2-ethylhexyl) adipate and di(2-ethylhexyl) phthalate from water samples by GC-FID. Under optimal conditions, the calibration plots are linear in the range from 0.01 to 100 µg·L<sup>-1</sup>, and very high enrichment factors (mean value ~20,000) were obtained. As a result of the high enrichment factors, the detection limits were as low as 2–3 ng·L<sup>-1</sup>.

Mehdinia *et al.* [151] developed sequential extraction of PAHs using Au-immobilized magnetic mesoporous silica NPs for magnetic SPE followed by DLLME with chloroform. Detection was carried out by GC-flame-ionization detection (GC-FID). This combined procedure allows achieving EFs in the range of 5519–6271 and LODs of 0.002–0.004 µg/L.

#### **Dispersive liquid-liquid microextraction using nanoparticles directly dispersed in the extractant phase**

Different nanomaterials can be directly dispersed in an organic extractant and applied to the preconcentration of analytes following the DLLME technique. For example, Shi *et al.* [152] introduced a new LPME approach based on the use of silica-coated MNPs and 1-octanol as the extractant solvent for the preconcentration of 16 PAHs prior to determination by GC-MS. 1-octanol was efficiently confined within the silica-coated NPs, which prevented it from being lost. EFs and LODs were in the range 102–173 and 16.8–56.7 ng/L, respectively. Agitation by reciprocating movement of the external magnet was applied so as to facilitate microextraction.

More recently, Casado-Carmona *et al.* [153] synthesized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> functionalized with ionic liquid methylimidazolium hexafluorophosphate (MIM-PF<sub>6</sub>) and evaluated its potential in dispersive microextraction for the isolation of 11 endocrine disrupting compounds (benzophenones, bisphenol A and parabens) from water samples by liquid chromatograph with tandem mass spectrometric detection (HPLC-MS/MS) for analyte separation and quantification. The proposed microextraction method allows the determination of the target

compounds with limits of detection in the range from 0.16 to 1.21 µg/L and the linearity was maintained between the limits of quantification and 500 µg/L. The precision, expressed as the relative standard deviation, was better than 8.3%. The recovery study was performed on different water samples obtaining percentages higher than 87%, demonstrating the applicability of the hybrid sorbent for the selected analytical problem

Reyes-Gallardo *et al.* [154] synthesized magnetic nanoparticles-nylon 6 composite and applied in the microextraction field. The extraction performance of the composite under a dispersive micro solid phase extraction format has been evaluated by determining four polycyclic aromatic hydrocarbons (benzo[*b*] fluoranthene, fluoranthene, indeno[1,2,3-*cd*]pyrene and phenanthrene) in water using ultra performance liquid chromatography (UPLC) combined with photo diode array detection. The developed methodology allows the determination of the analytes with limits of detection in the range from 0.05 µg/L (benzo[*b*] fluoranthene) to 0.58 µg/L (phenanthrene). The repeatability of the method was better than 6.9% at the limit of quantification level. The relative recoveries varied in the interval 80–111%.

In other research, Abbasghorbani *et al.* [155] used solvent-assisted micro-SPE for the determination of parabens in water and cosmetic samples. Aminopropyl-functionalized MNPs together with hexyl acetate were used. EFs in the range 217–1253 were achieved with LODs in the range 50–300 ng/L.

Bouri *et al.* [156] used a magnetic material based on N-methylimidazolium ionic liquid (ILs) and Fe<sub>3</sub>O<sub>4</sub> MNPs incorporated in a silica matrix to extract and preconcentrate sulfonylurea herbicides (SUHs), such as thifensulfuron methyl, metsulfuron methyl, triasulfuron, tribenuron methyl and primisulfuron methyl from polluted water samples. It was reported that hydrophobic interaction became predominant as the five SUHs were absorbed by the ionic liquid magnetic sorbent at pH of 5. The results obtained allow concluding that the ILs-MNPs can be a very suitable alternative for the clean-up and the preconcentration of pesticide residue analyses.

#### **Nanoparticle-assisted hollow-fiber-liquid-phase microextraction (solid/liquid microextraction)**

In hollow-fiber-liquid-phase microextraction (HF-LPME), analyte extraction occurs in the pores of a hydrophobic hollow fiber, where the extractant

is previously immobilized. This microextraction technique displays an improved stability to the extractant phase at high stirring rates in the sample vial. Reviewing literature showed that carbon nanotubes have been extensively used in HF-LPME techniques as reviewed by Bendicho *et al.* [157]. However magnetic nanoparticles more recently have been used in this technique [158].

Es'haghi and Esmaeli-Shahri [158] developed  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanocomposite dispersed in 1-octanol as a novel highly efficient sorbent in hollow fiber-solid phase micro-extraction (HF-SPME) technique for the extraction and determination of six non-steroidal anti-inflammatory drugs; acetylsalicylic acid, naproxen, piroxicam, diclofenac, indomethacin and mefenamic acid, in hair samples. The  $\text{TiO}_2$  mixed oxide displays improved adsorptive characteristics in comparison with pure  $\text{TiO}_2$ . The large surface area and the porosity of the nanosorbent allow EFs in the range 405–2450.

Martinez *et al.* [22] reported in-tube solid phase microextraction approach, named magnetic in-tube solid phase microextraction (magnetic-IT-SPME). This system, taking advantage of magnetic microfluidic principles, was developed to improve the extraction efficiencies of acetylsalicylic acid, atenolol, acetaminophen, diclofenac, and ibuprofen, yielding to extraction capacities between 70 and 100%, which are much higher than those achieved using an IT-SPME approach (in the range of 10–30%).

#### **Magnetic nanoparticles in enantioseparation**

Chirality is an important, universal phenomenon in nature. For the in-depth study of pharmacology and biology, efficient enantioselective technologies are indispensable. Nanomaterials with large surface-to-volume ratio and specific physical and chemical properties have demonstrated great potential in chiral discrimination [159]. At the same time, by applying magnetic nanoparticles introduce another important advantage, easy and fast collection of the complexes from the solution by applying magnetic field [160] which compared with conventional separation methods, this process is noted for its speed, simplicity and cost effectiveness. Many publications show that utilization of nanomaterials could improve the selectivity, stability and efficiency of enantioseparation which some of them have been reviewed in ref [159].

MNPs, immobilized with an appropriate

chiral selector, have been successfully used for enantioseparation [161–164]. MNPs tagged with an appropriate chiral selector were expected to interact selectively with a single enantiomer and form complexes, which were easily removed by an external magnet. Ghosh *et al.* [161] synthesized carboxymethyl- $\beta$ -cyclodextrin-bonded  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  core-shell NPs, and applied these MNPs in the enantioselective adsorption of chiral amino acids. Adsorption-equilibrium experiments demonstrated that the adsorption capacities were higher for L-enantiomers than the corresponding D-enantiomers. However, the enantioselective adsorption ability for racemic solution has not been investigated yet.

Choi *et al.* [162] developed a method employing racemic amino-acid solutions as model compounds for further study. First, MNPs with (S)-chiral selector (MNPs/(S)-CS) were added into the racemic solution for enantioselective adsorption. The enantiomeric excess was evaluated by chiral HPLC and confirmed the enantioselectivity of MNPs/(S)-CS. However, the enantioselectivity was not stratified. Consequently, another method was developed, employing equal non-magnetic silica particles tagged to the antipode (R)-chiral selector (MNPs/(R)-CS) and MNPs/(S)-CS at the same time. After extraction, the MNPs/(S)-CS-enantiomer complexes were collected by a magnet, while the MNPs/(R)-CS-enantiomer complexes were collected by decantation after centrifugation.

These results of chiral HPLC separation demonstrated that the enantioselectivity is improved when MNPs/(R)-CS is simultaneously used. This method indicated that the two contrary chiral selectors could have some synergistic effects for enantioseparation and provides a new insight to the development of a highly efficient enantioselective method.

In most conditions, washing to retrieve the target molecules is necessary for further experiments. However, elution made the method complicated, and the organic solvent was not economic or environmentally friendly. As an alternative, Chen *et al.* [163] developed a photo-controlled inclusion-and-exclusion method to induce the release of the adsorbed enantiomers in reverse (Fig. 13). The chiral selective system also employed  $\beta$ -CD-functionalized  $\text{Fe}_3\text{O}_4$  NPs as chiral adsorbents. After extraction, pure optical enantiomer adsorbed on the NPs was released via the photo-controlled inclusion-and exclusion reactions of azobenzene

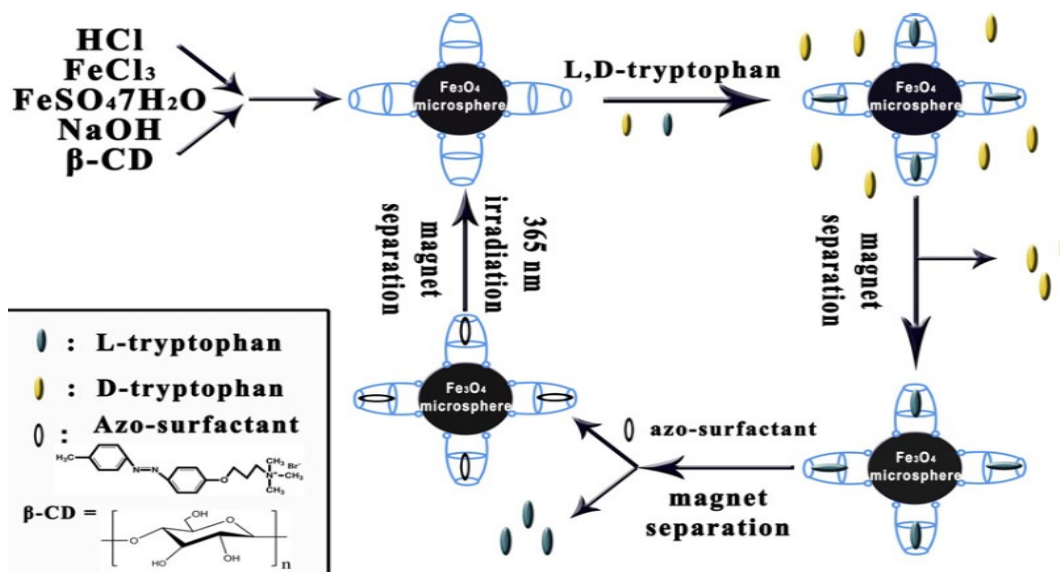


Fig. 13. Preparation procedures and separation mechanism of  $\beta\text{-CD}$  modified  $\text{Fe}_3\text{O}_4$  nanoparticles for amino acids enantiomers [155]

derivatives with  $\beta\text{-CD}$ . The reversible photo-controlled inclusion-and-exclusion process enabled recycled use of  $\beta\text{-CD}$ -functionalized  $\text{Fe}_3\text{O}_4$  NPs in enantioseparation. It is worth mentioning that after more than 5 times repetitions  $\beta\text{-CD}$  modified  $\text{Fe}_3\text{O}_4$  NPs still showed good enantioselectivity for L-tryptophan, indicating that  $\beta\text{-CD}$ -modified  $\text{Fe}_3\text{O}_4$  NPs were highly applicable in repeated recycling.

Another solution, packing chiral MNPs into microchip channels, was developed to achieve complete enantioseparation [164]. Molecularly-imprinted MNPs, with Sofloxacin as the template molecule, were located as stationary phase in the microchannel of the microfluidic device. Under optimized conditions, efficient molecular recognition of ofloxacin enantiomers was achieved in 195 s with good reproducibility and precision. Compared with a conventional device, the MNPs could be conveniently localized to the predetermined position by applying an external magnetic field, and the length of the packing zone could be easily tuned by changing the length of the magnet.

#### Magnetic nanoparticles in chemosensors

The design and fabrication of nanoparticle-based chemosensors have attracted a great interest in a variety of scientific communities ranging from biological and environmental sciences to engineering. Nanoparticle-based chemosensors can detect biologically as well as environmentally

relevant target species with high precision and accuracy [23].

The desired goals for the next generation of nanoparticle-based chemosensors include cost-effective production, simple analysis methods and in-field readable results. Such attributes are required for modern-day analytical schemes as a response to battlefield detection of biowarfare agents and applications in biomedical diagnostics in economically depressed regions [23].

Among the chemosensors for detection and separation applications based on magnetic nanoparticles which are composed of both inorganic and organic motifs [165], core-shell type MNPs have been investigated as promising method for colorimetric sensing applications [23] due to their high surface area, strong magnetic responsivity and good dispersibility in various solvents [166-169]. One of the most important properties of the diverse chemosensors is recoverability.

One of the most important properties of the diverse chemosensors is recoverability. To obtain this attractive property and get rid of those drawbacks such as thickness control [170], inner-layer analyte diffusion [171] and harsh manipulations [172] brought by the reported methods, Zhang *et al.* introduced adamantane-modified salicyl rhodamine B and  $\beta$ -cyclodextrin-modified  $\text{Fe}_3\text{O}_4@SiO_2$  by the host-guest interactions which induced novel inclusion complex magnetic nanoparticles (SFIC MNPs) colorimetric sensitive for  $\text{Cu}^{2+}$  [173]. The MNPs exhibit a clear color

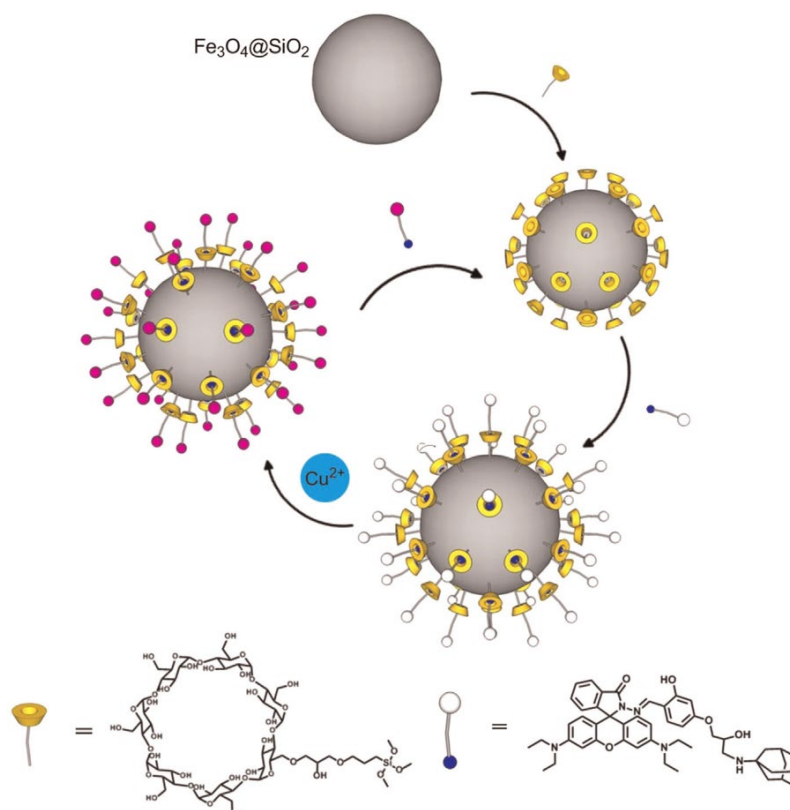


Fig. 14. Chemical and schematic illustration of the preparation of SFIC NMPs sensor for  $\text{Cu}^{2+}$  [165]

change from colorless to pink selectively (Fig. 14) and sensitively with the addition of  $\text{Cu}^{2+}$  in the experiments of UV-Visible spectra, and the detection limit measures up to  $5.99 \times 10^{-6}$  M in solutions of  $\text{CH}_3\text{CN}-\text{H}_2\text{O}=1:10$ . The SFIC magnetic nanoparticles are superparamagnetic according to magnetic measurements and can be separated and collected easily with a commercial magnet in nine seconds. In addition, the microspheres have also showed good ability of separating for other ions from aqueous solutions due to a large number of hydroxyl groups on the surface.

In other research, Zeng *et al.* prepared di(2-picolyl)amine derivatives functionalized inorganic/organic hybrid magnetic network for selective detection and removal of Zn (II). A significant visual color change from colorless to pink-red was observed under the irradiation of 365 nm UV lamp [174].

Tian *et al.* [175] also developed a highly selective and sensitive method for recognition of  $\text{Zn}^{2+}$  and hydrogen sulfide ( $\text{H}_2\text{S}$ ) in aqueous solution by using a quinoline fluorescent sensor functionalized magnetic silica nanoparticles

(R1). The chemosensor R1 shows excellent fluorescence sensitivity and selectivity toward  $\text{Zn}^{2+}$  and  $\text{H}_2\text{S}$  in aqueous media, and displays off-on-off type fluorescence change with alternately adding  $\text{Zn}^{2+}$  and  $\text{H}_2\text{S}$  to the media along with reversible association-dissociation of the complex. Furthermore, the magnetic nanocomposites can be easily separated from solutions by adding an external magnetic field.

## CONCLUDING REMARKS AND FURTHER TRENDS

Functionalized MNPs combine the advantages of magnetic particles and modified layers in sample preparation, enantioseparation and chemosensor techniques. The small MNPs have a high surface area-to-volume ratio, which results in high sensitivity and rapid extraction. The magnetism of the NPs simplifies the separation process and improves the rate of separation; this enables completion of the extraction process within a few minutes or even seconds.

Depending on application, different functionalized MNPs are needed. For example,

LDH modified MNPs are good for ionic compounds; C18-modified MNPs are good for hydrophobic organic compounds, for example pesticides, phthalates, and PAHs. On the other hand, carbon-based functionalized MNPs are suitable for the hydrophilic compounds, for example esters or sulfonates, because of the carboxyl and hydroxyl groups found on the surface. Surfactant or polymers-coated MNPs are useful for selective extraction of organic analytes from complex matrices, especially magnetic molecularly imprinted polymers (MMIPs), which enable high selective adsorption of specific analytes. Moreover, functionalized MNPs with suitable chiral selector such as  $\beta$ -CD are needed in enantioseparation techniques.

Among the future expected improvement and perspectives in this field, it can be pointed out the development of new methods of synthesis and functionalization of new MNPs and the increase in their physicochemical stability, lifespan and selectivity. In consequence, new application of magnetic supports will appear in the future in different stages of analytical processes: sample treatment, separation and detection. The integration of magnetic particles with other existing nanomaterials, and the use of emerging technologies (microfluids, micro-flow analysis, etc.), are other potential areas of applications.

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