Adsorptive remediation of environmental pollutants using magnetic hybrid materials as platform adsorbents

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Abstract

Effective separation and remediation of environmentally hazardous pollutants are burning areas of research because of a constant increase in environmental pollution problems. An extensive number of emerging contaminants in the environmental matrices result in serious health consequences in animals, humans, and plants, even at trace levels. Therefore, it is of paramount significance to quantify these undesirable pollutants, even at a very low concentration, from the natural environment. Magnetic solid-phase extraction (MSPE) has recently achieved huge attention because of its strong magnetic domain and easy separation through an external magnetic field compared with simple solid-phase extraction. Therefore, MSPE appeared the most promising technique for removing and pre-concentration of emerging pollutants at trace level. Compared to the normal solid-phase extraction, MSPE as magnetic hybrid adsorbents offers the unique advantages of distinct nanomaterials and magnetic hybrid materials. It can exhibit efficient dispersion and rapid recycling when applying to a very complex matrix. This review highlights the possible environmental applications of magnetic hybrid nanoscale materials as effective MSPE sorbents to remediate a diverse range of environmentally toxic pollutants. We believe this study tends to evoke a variety of research thrust that may lead to novel remediation approaches in the forthcoming years.

Keywords: Environmental pollutants; Magnetic solid-phase extraction; Adsorbents; Carbon nanotubes; Metal-organic frameworks; Magnetic hybrid materials

1. Introduction

The effective separation and removal of toxic pollutants are among the hot research topics because of the constant increase in ecological inconsistency and environmental pollution in recent years (Khan et al., 2020; Ali et al., 2020a; Zeb et al., 2020). The environmental matrices are full of some typical pollutants and can be very harmful to both land and aquatic life. Some of the emerging contaminants are pesticides, polychlorinated biphenyls (PCBs), heavy metals, polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PAEs), bisphenol A (BPA), perfluorinated compounds (PFCs), organic phosphate flame retardants (OFRs), and so on (Ali et al., 2018; Ahmad et al., 2021; Clarke et al., 2011). Therefore, even at a low concentration level, it is important to quantify and determine these destructive pollutants from various sources. In addition, sample pretreatment procedures need enhanced proficiency and selectivity because of the complicacy and diversity of the sample matrices (Aziz et al., 2020; khan et al., 2021a). It is imperative to design and construct some new adsorbents with high extraction efficiency, such as amberlite resins, silica gel, graphene oxide, chelating resin, carbon nanotubes, activated carbon, graphene and so on (Arabi et al., 2017; Bagheri et al., 2019; Ma et al., 2018; Azzouz et al., 2018).

Generally, the most effective and simple technique is dispersive-SPE (DSPE). Followed by the elution process, in which the reversible interactions between adsorbent and target in a suitable column through adsorption are the base of the following technique (Ötles et al., 2016; Khan et al., 2021b). A key concern for DSPE is selecting the right adsorbents such as silica bonded to C18 and frequently used HLB-based hybrid materials. However, the traditional SPE can be hampered because of the clogging of the adsorbent, the necessity of toxic solvent in excess during extraction, and high column pressure (Khan et al., 2019). Carbon dots (C-dots), a new addition to the carbon family, have been widely reported for many applications. A large number of novel materials can be fabricated using C-dots as a starting material, such as synthetic, biological, and natural sources of carbon. A set of desried features like inertness, biocompatibility, easy to functionalization, low toxicity, and the property of photoluminescence redner C-dots preferable for different applications, such as imaging, drug delivery and biosensing (Wang et al., 2016). Therefore, a new class of DSPE called MSPE uses magnetic materials as an effective adsorbent to differentiate and targeted compounds in environmental samples (Ali et al., 2019).

Shortly, the process of solid-phase extraction can be carried out while using MSPE by diffusing an adsorbent that is magnetic in the specimen sample to enable the adsorption process of the desired analyte (Ali et al., 2015a; Zhang et al., 2016a). An external magnet is used to separate the magnetic adsorbent material, which contains the analyte from the targeted sample matrix after the adsorption process is performed (Scheme 1). The desired analyte is further desorbed from the MSPEs sorbent and then dissolved in some suitable desorption solvent after the elution process. For later determination, the desorption solution can be collected, which is enriched with the target analyte. After that, the recycling process of the magnetic adsorbent is held. Traditional SPE requires more time, and the whole filtration and centrifuging processes are very slow, which can be avoided in MSPE. MSPE shows some promising advantages such as quick separation, better recycling of sorbent, convenient operation with high extraction efficiency (Fig. 1).

A key factor for accomplishing better extraction performance is to select some good magnetic adsorbents. The addition of magnetic domain imports significantly influences the anti-interference capability, selectivity, extraction efficiency, and enrichment factor (Zhang et al., 2016a; Ali et al., 2015b). Various types of magnetism can be exhibited by magnetic materials such as diamagnetism, ferromagnetism, antiferromagnetism, paramagnetism, and ferrimagnetism. Magnetic materials that show paramagnetism or ferromagnetism are mainly employed as magnetic cores to construct MSPE adsorbents. Magnetic nanoparticles are generally made from Ni, Fe, Co and the metal oxides of these metals, which normally exhibits strong magnetic properties, i.e., ferromagnetism, e.g., magnetite (Fe_3O_4) (Ali et al., 2015c), maghemite, and $CoFe_2O_4$ (Yang et al., 2021a; Ali et al., 2020b; Zhang et al., 2013). The methods preparing MNPs consist of coprecipitation synthesis, hydrothermal synthesis, sol-gel synthesis, and solvothermal synthesis. When the MNPs are used as adsorbents, the magnetic cores agglomerate prepared by the above methods resulting in a reduction in their magnetic properties. An appropriate method was needed to fabricate the magnetic core with some functionalized materials is needed to overcome this limitation (Khan et al., 2021c). Due to their structure and peculiarities, porous and carbonaceous materials are the most widely used coating materials. These increase the surface area with abundant active reacting sites and maintain the oxidation state, followed by improving the stability of MNPs. In addition, silicon nanomaterials, metallic nanomaterials, chitosan (Ali et al., 2020c,d; Aziz et al., 2020; Khan et al., 2021d; Yang et al., 2021b), ionic liquids (ILs), and surfactants (Ali et al., 2020a) are the main MSPE sorbents materials. The mode of interaction between MSPE sorbent and the target analytes is due to the electrostatic attraction, hydrophobic force, van der Waals forces, hydrogen bonding, and metal ionic coordination (Zaman et al., 2019). However, the adsorbent may be interfered with by a complicated matrix due to these non-selective interactions. Therefore, a beneficial method is the MNPs with cautiously designed materials known as molecularly imprinted polymers (MIPs) (Zhang et al., 2015; Nawaz et al., 2020; Ali et al., 2015d). In the last few years, few reviews published addressing the preparation, properties, and applications of MSPE sorbent materials. Also, there is lacking some fruitful publications to effectively reviewed the applications of MSPE sorbents for the enhanced removal of environmental pollutants. Therefore, in this current work, we tried to sum up the latest available literature in the advance's magnetic hybrid material as MPSE sorbents and their applications for the efficient remediation of environmental pollutants.

2. Carbon-based magnetic materials as adsorbents

Various carbon-based materials are frequently reported, such as graphitic carbon nitride (g-C_3N_4) carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene (G) and graphene oxide (GO), reduced graphene oxide (RGO), carbon-based quantum dots, etc. (Speltini et al., 2016; Azzouz et al., 2018). Most own superior features, including better mechanical, chemical, and thermal stability, large surface area, and active sites. To use these carbons based MSPE sorbent material for the effective removal of environmental pollutants from complex wastewater matrices. This is possible because MSPE sorbent gives high specificity and selectivity with reduced medium interference. In this article, we discussed two main types of magnetic carbonaceous materials as MSPE sorbents. Table 1 explains some of the carbon-based magnetic materials as adsorbents.

2.1. Graphene-based composites

Graphene is a well-known carbon-based material that comprises sp2 hybridized carbon atoms in a single-atom-thick with a two-dimensional (2-D) structure and hexagonal structural arrangement in the form of lattice (Hu et al., 2018; Shen et al., 2015). Graphene gives good applications in extracting organic compounds with a benzene ring with a π-π stacking in their structure. In the structure of graphene, there are delocalizedπ-electrons and a large surface area (Ersan et al., 2017). However, the recycling of graphene from the sample solutions is challenging because of its hydrophobicity and low weight. If a polar pollutant contains hydrophilic chemical groups (Lim et al., 2018), Graphene is ineffective for its absorption (Huang et al., 2018). Hence, to get some practical applications and meet the specific requirements, proper modification is needed. The chemical oxidation of graphene leads to graphene oxide (GO), which contains some more functional groups such as phenolic hydroxyl (-OH), carboxyl (-COOH), epoxy groups (-C-O-C-). These functional groups can further be modified by fabrication which may show more affinity for targeted analytes based on the presence of active sites of interaction. Chemical reduction method used for the preparation of reduced graphene oxides (RGO) nanosheets. Compared to graphene oxides (GO) RGO contains very few vacancy defects and oxygen-containing functional groups (He et al., 2016). Incorporating the magnetic domain to GO and RGO leads to form a very stable magnetic composite MGO and MrGO, which can be easily recovered and separated from the targeted sample solution and prevent the loss of MGO sorbent material during the MSPE process.

There are many methods for fabricating magnetic graphene oxides composite materials, such as in-situ coprecipitation, solvothermal, and hydrothermal (Sherlala et al., 2018; Lingamdinne et al., 2019). Yang et al. used the solvothermal method for the fabrication of G-doped magnetic nanoparticles to form (Fe_3O_4/G) composite material and then checked the prepared material for the effective removal of 4-bromodiphenyl ether (BDPE), tetrabromobisphenol A (TBBPA), 2,4,6-tribromophenol (TBP), and 4,4'-dibromodiphenyl ether (DBDPE) (Yang et al., 2015). Graphene component provides an extensive system of π-electron. Therefore, the limitations of the simple graphene oxides (GO) can be reduced by the applications of magnetic content, which can give quick isolation and separation from the reaction mixture and give more space for the targeted aromatic compounds byπ-π stacking and hydrophobic interactions. Fe_3O_4/G shows 59.9 emu gL^{-1} of maximum saturation magnetization (Ms) value, which proved good superparamagnetism. Also, the LOD limits of detection are low in the range of 0.2-0.5 μg L^{-1}, and good recovery rate of about 85.0-105.0% after coupling with high-performance liquid chromatography-ultraviolet detector (HPLC-UV) to check BFRs in wastewater samples of water were gained. Without modification, pure magnetic graphene-based materials usually fail to provide adequate extraction performance because of lean applications with insufficient adsorption properties for complex and diverse environmental pollutants. Hence, if Graphene-based materials are further functionalized, they can considerably help to improve the target analytes selectivity and reduce the interference from the sample matrices.

As graphene oxide is an excellent carbon-based hybrid material containing organic and inorganic parts and a large surface area with thermal and mechanical stability. Furthermore, the applications of magnetic graphene oxide are very much promising for both graphene oxides and magnetic components. An ultrafast, direct, non-toxic, and green was used to prepare magnetic graphene hybrid materials (GO–Fe_3O_4) (Liu et al., 2018a). Compared to other conventional synthetic methods, this reaction is a very simple and one step without any production of dangerous pollutants during the whole synthetic process. Also, the preparation of Fe_3O_4@GO magnetic hybrid material was confirmed through the characterization using different instrumental techniques. Furthermore, the prepared Fe_3O_4@GO was successfully checked for the adsorption of Methylene blue, and the material show effective adsorption within 30 min. Therefore, Fe_3O_4@GO demonstrates potential applications as an environmental adsorbent.

Organophosphorus pesticides (OPPs) detection in water samples, a graphene-based tetraethoxysilane-methyltrimethoxylane magnetic composite (Fe_3O_4@G-TEOS-MTMOS) was fabricated by Nodeh et al. (2017) as an MSPE adsorbent. The synthetic process included using the sol-gel method to modify graphene nanosheets and Fe_3O_4 nanoparticles, followed by their coating using silica-based porous material. These functional ingredients of the Fe_3O_4@G-TEOS-MTMOS adsorbents exhibit selective adsorption sites and can be used to effectively adsorption of polar OPPs (phosphamidon, dimeyhoate) via hydrogen-bonding and non-polar OPPs (diazinon, chlorphyrifos) via π-π stacking. The adsorption capacity of the Fe_3O_4@G-TEOS-MTMOS adsorbents is very high of about 37.18-76.34 mg g^{-1} for both TEOS-MTMOS or Fe_3O_4@G or their composites (Fig. 2). Li et al. (2017a) successfully prepared a magnetic polyethyleneimine-functionalized RGO-based (Fe_3O_4@PEI-RGO) nanohybrid material for the quick adsorption of MSPE to increase the concentration of the sample with acidic herbicides in food materials. The RGO component of the modified material import a large surface area for the exchange of anions can give a large surface area for anion and make the exchange of PEI, a positively charged polymer. Therefore, the as-synthesized Fe_3O_4@PEI-RGO nanocomposite shows the maximum adsorption of five different herbicides (chiefly through π-π stacking electrostatic attraction) as compared to Fe_3O_4/RGO, Fe_3O_4@PEI-GO, and Fe_3O_4@PEI under optimized extraction conditions (Fig. 3).

Magnetic graphene oxide Fe_3O_4/GO hybrid material was prepared through self-assembly method and checked their solid phase remediation of polyaromatic hydrocarbons (PAH) while using different environmental samples (Han et al., 2012). The super hydrophilic nature of graphene oxides mixed with the charged surface of iron oxide and form a hybrid material in solution under the electrostatic interaction. Also, different amounts of iron oxide were also used to effectively control the change in the initial precursor particles. The structure and surface morphology of the prepared material confirmed through different characterization techniques such as XRD, VSM, TEM, and XPS, etc. To check the application of Fe_3O_4/GO, five samples of PAH contaminated water were selected for the DSPE. The prepared Fe_3O_4/GO exhibits excellent adsorption efficiency due to the π–

π stacking of the hydrophobic interaction. Under optimized conditions, the final results show that PAH recovery remains in between 76.8–103.2%, with 1.7% to 11.7 % of relative standard deviations. Furthermore, the detection limit was between t 0.09 to 0.19 ng mL^{-1} (Fig. 4).

2.2. CNT-based composites

Many studies have investigated the use of graphene oxides and other carbon materials for environmental remediation of food and biological samples. Especially graphene and carbon nanotubes (CNT) have been assessed for adsorptive removal of hydrocarbon compounds, dyes, and metals (Jon et al., 2019). The functionalization of carbon materials with some good ionic liquids generates CNM/ILs, which are the promising sorbent materials with high selectivity for different pollutants. The viscosity, miscibility, and high thermal stability of CNM/ILs make them suitable for adsorption because the CNM/ILs contains organic and ionic moieties in their structure. CNM/ILs are considered excellent adsorbents for the environmental remediation of different organic pollutants.

Carbon nanotubes (CNTs) are one of the allotropic forms of carbon made from graphene nanosheets. The structure of CNT can be changed to various shapes like one-dimensional hollow tubular shape. Single wall carbon nanotube (SWCNTs) and multi-walled carbon nanotube can be designed according to the number of graphene layers. The adsorption of different environmental pollutants is due to adsorption sites' presence on the surface of carbon nanotubes (CNTs) (Liang et al., 2014). To change the surface properties to be more hydrophilic, the base or the sidewall of the carbon nanotubes (CNT) can be modified with different oxygen-containing functional groups. Also, for enhanced separation and purification efficiency, the modification of carbon nanotubes to magnetic material as MCNT is very popular recently. MCNT gives rapid separation in various environmental media because of their large surface area and recycling property.

Magnetic-based carbon nanotubes (CNTs) hybrid material show promising applications, especially in solid-phase extraction. This is because of their unique physicochemical properties and well-engineered surface morphology (Li et al., 2019). In the case of MCNTs hybrid material for solid-phase extraction application, new procedures were introduced that extended the application's profile to both organic and inorganic pollutants determinations such as pesticides, foods, chemical pollutants, drugs. In the end, they give fruitful suggestions for future research direction. In another very recent study, multi-walled carbon nanotubes polyamide-amine dendrimers (PAMAM)) were designed and further modified with Fe_3O_4 nanoparticles to (MMWCNTs). The prepared MMWCNTs were used in very efficient and sensitive methods for the remediation of polyaromatic hydrocarbons (PAH) under solid-phase extraction and gas chromatography with quadrupole mass spectra detector (GC/MS/MS) (Zhou et al., 2021). Different reaction and testing parameters such as adsorbent dose, generation of PAMAM, adsorption time, pH, elution volume, time, and humic acid concentration were thoroughly investigated. After optimization, the concentration of dibenzothiophene, carbazol, and 7-methyl quinoline range from 0.005–20 μg L^{-1}, with excellent linearity. Furthermore, the concentration of about 0.001–20 μg L−1 4-methyldibenzothiophene, 9-methylcarbazole, and 4,6-dimethyl dibenzothiophene also shows excellent good linearity. In all cases, the correlation coefficients are high as 0.996. The sharp recoveries were noted in between 87.0% to 15.1%. The given results concluded that this is a reliable method and can be used to remove aromatic poly hydrocarbons from different wastewater samples.

A collection of many studies was reported for the remediation of many inorganic and organic pollutants while using magnetic carbon nanotubes (MCNTs). First, the environmental effects of different trace and toxic metals, different dyes were discussed in detail. The contamination of these pollutants severely impacts both humans and plants and can be carcinogenic and harmful to nature. Therefore, priority is given to remove these toxic pollutants from the different environmental media (Khan et al., 2021e). Carbon nanotubes (CNTs) give the possible solution to remove toxic metal and dyes from wastewater, further modifying CNTs with Fe_3O_4 nanoparticles to design new magnetic carbon nanotube MCNTs hybrid materials make this emerging material as an adsorbent more applicable. The remarkable properties of magnetic carbon nanotube such as easy separation procedure, reusability, large surface area, and surface to volume ratio increase the importance of these materials for the rapid removal of trace metals and different kinds of dyes (Fig. 5). Buckypaper (BP) as separation membranes also give excellent results like magnetic carbon nanotubes (MCNTs), and give favourable remediation because of their high adsorption, strength, and porosity. The utilization of

Buckypaper (BP) membranes s limited to aqueous samples, and their application for dyes and metals removal is very less.

Multi-walled magnetic carbon nanotubes were constructed by the covalent grafting of β-cyclodextrin on multi-walled carbon nanotubes (MMWCNTs) to develop a novel material named β-CD@Fe_3O_4/MWCNTs. Different high sophisticated instruments characterize the prepared material such as XRD, FT-IR, Raman Spectroscopy, SEM, TGA, surface area (BET) VSM.β-CD@Fe_3O_4/MWCNT has a large pore volume and surface area. Furthermore, the application for the removal of Ni ions is excellent at optimized conditions such as pH, adsorption time, and temperature (Lin et al., 2021). Also, the adsorption follows the Langmuir and pseudo-first-order kinetics, and thermodynamically, the process is exothermic with a maximum of 103 mg/g of Ni^{+2} ion on the surface of β-CD@Fe_3O_4/MWCNT at ambient temperature. Andβ-CD@Fe_3O_4/MWCNT shows the recycling capacity of about five times in a row. Therefore, Lin and his coworkers presented an environment-friendly and novel adsorbent material (β-CD@Fe_3O_4/MWCNT) having the potential to effectively remove Ni^{+2} ion from aqueous samples.

3. MOF- and COF-based porous magnetic materials as MSPE adsorbents

The most enhanced class of materials for the effective removal of different kinds of organic and inorganic pollutants are porous hybrid materials such as magnetic MOFs, Magnetic COFs, and other mesoporous (PCOMS), metal-organic frameworks (MOFs), and mesoporous materials. These materials show large pore size and surface area with high adsorption capacity and can be easily modified by grafting magnetic nanoparticles. Furthermore, the adsorption process can speed up by combining magnetic nanoparticles and porous material in a single hybrid entity.

3.1. MOF-based magnetic hybrid material

MOFs are composed of (metal ions/clusters) as an inorganic component strongly linked with organic compounds having carboxylic or nitro-containing functional groups as organic via strong through a coordinate covalent bond. The coordination of the organic and inorganic entities leads to various functional materials with some promising properties and multi-dimensional geometries (Ali et al., 2020e). The solid-phase extraction is possible on MOFs surface because of the superhydrophobicity of π-π bonds (Wen et al., 2021). Generally, the non-spherical surface morphology of MOFs is the drawback because the separation of MOFs is very difficult from the targeted adhered compound in the solutions. To solve this problem, the mixing of MOFs and MNPs to prepare strong MNPs/MOFs can be separated from the aqueous solution through an external magnet (Jiang et al., 2021). Also, the use of some conventional methods such as filtration and centrifugation can be avoided. In this part of the review, we discuss the different methods for the magnetization of MOFs, such as encapsulation, mixing, layer by layer, etc. (Ricco et al., 2013). Glycopeptides and glycoproteins detection in humans' fluids are important with clinical importance for the detection of disease biomarkers. However, the interfering liquids make this quantitative detection with low abundance in humans fluids more challenging. Therefore, the application of magnetic MOFs as an MSPE is more advantageous due to their low price, easy preparation, and high magnetic domain (Qi et al., 2021). Table 2 explains some of the magnetic MOFs as an MSPE adsorbent for the glycopeptides and glycoproteins.

A single step and direct carbonization process was adopted to prepare magnetic porous carbon (MPC) material leading to the cobalt-metal organic framework (Co-MOF). The prepared Co-MNPC material were characterized for their structure, surface morphology, and magnetic domain while using SEM, TEM, XRD VSM, and N_2 adsorption. Co-MNPC exhibits large pore volume, surface area, and super magnetic properties. Furthermore, the material was checked for solid-phase extraction applications to remove insecticides neonicotinoid from the samples of fat melon and water, and the final results were confirmed by high-performance liquid chromatography. The experimental parameters and the extraction coefficient were investigated for their possible effects on the whole remediation process. The final results mentioned the efficient adsorption capacity of magnetic Co-MNPC material (Hao et al., 2014).

Fe_3O_4@MOF-808) as a facile MNPs/MOFs was designed and prepared through the solvothermal method and was employed as a DSPE to remove benzoyl urea (BUs), a famous insecticide from different juice and tea samples (Jia et al., 2020). The surface morphology, functional groups, and the magnetic domain were checked through SEM, FT/IR, XRD, and VSM. Furthermore, a detailed investigation was made for the adsorption process regarding the amount of adsorbent and extraction time. Also, suitable solvent for elution, elution time, and volume were also optimized. Fe_3O_4@MOF-808 MNPs/MOFs applications are promising because they can be recycled much time without ant decrease in efficiency. The rapid adsorption process is because of the different attractive forces between Fe_3O_4@MOF-808 and benzoyl urea (BUs), such as hydrophobic interaction, π-π interactions, and hydrogen bonding. In the end, a very simple and sensitive method was designed by the connection of HPLC coupling with Fe_3O_4@MOF-808-based for the improved MSPE. The detection limits are low, i.e., 0.04 to 0.15 ng/mL, with wide linear ranges of about 0.15 to 50 ng/mL, and the recovery rate is about 84.6 to 98.3% which is quite satisfactory (Jia et al., 2020). The proposed Fe_3O_4@MOF-808) as an MNPs/MOFs coupled with HPLC give rapid and safe results as an MSPE tool for the removal of s benzoyl urea (BUs) BUs from tea and beverages samples.

Fe_3O_4@SiO_2@MOF/TiO_2 with core-shell morphology was prepared while using the encapsulation method and was checked as a suitable adsorbent for MSPE to efficiently remove triazole fungicides from environmental samples (Su et al., 2016). Five different triazole fungicides samples as target such as tebuconazole,triadimenol, hexaconazole, myclobutanil, and diniconazole were used for MSPE. After the adsorption of these samples on Fe_3O_4@SiO_2@MOF/TiO_2 microspheres, the adsorbed material was separated from the adsorbent while using an external magnet. LC/MS was used for the determination of the desorbed analytes solution in methanol. The final extraction efficiency was affected by changing some extraction parameters, and response surface methodology was used to optimize these parameters. The detection and quantification limits were 0.19 to1.20 ngL^{-1} and 0.61 to 3.62 ng L^{-1}. Fe_3O_4@SiO_2@MOF/TiO_2 was successfully used for the fungicide concentration in many environmental wastewater samples, and it was noted that the method gives a satisfying recovery of up to 90 to 104 % for four samples and exhibits promising applications as MSPE for the quick removal of fungicides from wastewater samples.

Wang and co-workers reported another very effective magnetic Cu-MOFs magnetic nanocomposites as MSPE adsorbent. A chemical bonding method was used for the preparation of Fe_3O_4 (MNPs), Cu-MOFs, and graphene oxide (GO). In this method, GO MNPs and CU-MOFs were loaded onto graphene oxides working as a platform (Fig. 6). The prepared Magnetic Cu-MOFs composite exhibits a strong magnetic domain with quick separation and large surface pore size, allowing them as promising adsorbent

(Wang et al., 2018a). The silica is working as a shell to protect MNPs from oxidation and work as a platform to integrate MNPs and GO. The integration process is actually the silica shells modification by amino group followed by the bonding of amino group and carboxylic group on the surface of GO sheets. Different techniques were used, such as SEM, TGA, TEM, XRD, FT-IR, and nitrogen adsorption, to characterize the prepared Magnetic Cu-MOFs magnetic nanocomposites. Furthermore, the magnetic Cu-MOFs were checked as MSPE to remediate six different aromatic insecticides from actual samples, then HPLC was successfully used for the quantification. All experimental parameters such as extraction temperature and time, oscillation rate, adsorbent amount, desorption times were optimized for excellent results. Good linearity of more than 0.9931 and relative standard deviations of 1.9 to 2.7% was noted under optimal conditions. Six insecticide samples were checked, and LOQ and LOD were found as low as 1.0–5.2 μg L^{-1} and 0.30–1.58 μg L^{-1}, respectively. Remarkably, the prepared Fe_3O_4@SiO_2-GO-MOFs nanocomposites demonstrate promising results for the adsorption of six different insecticides remediation (Wang et al., 2018b).

Peter Behrens prepared MOF-801 for the first time by the strong coordinating covalent bond between Zr^{4+} as central metal ion and fumaric acid as organic ligand. The prepared MOFs exhibits spherical shape, large surface area, and pore size with three-dimensional surface morphology. Furthermore, the preparation method of MOF-801 is very simple and can easily be controlled; MOF-801 shows chemical and thermal stability and pH resistance (Zahn et al., 2014). Therefore, MOF-801 can be used as a special material for solid-phase adsorption. To further improve the applications of MOF-801 as an MSPE material, magnetic MOF-801 was generated by the in-situ growth of MOF-801 on MNPs surface through amidation reaction. The surface of polyethyleneimine magnetic nanoparticles (PEI-MNPs) contains an amino group that makes an amidation reaction with the carboxyl group of fumaric acid as organic ligand. The resulting PEI-MNPs@MOF-801 MNPs-MOF-801 was characterized while using TEM, FT-IR, XRD, XPS, and the extraction mechanism was also investigated. The prepared PEI-MNPs@MOF-801 shows an excellent application for the adsorption of sulindac indometacin, acemetacin under drug treatment (Wan et al., 2021). MSPE-HPLC-UV method was used on PEI-MNPs@MOF-801 for human plasma. The extraction performance of MSPE-HPLC-UV shows high extraction efficiency under the optimized condition with 96 to 118 of enrichment factor, 0.03 to 0.05 ng/mL limit of detections, and R ≥0.9987 linearity, high level of reproducibility, i.e., RSD ≤ 4.30 %.

3.2. Porous covalent organic materials-based composites

One of the expanded chemistries with 2D and 3D crystalline structures is in the form of Covalent organic frameworks (COFs) (Diercks et al., 2017). The covalent linkage constructs the entire body of COFs with a high level of physicochemical properties and crystallinity (Waller et al., 2016). The reported range of the linkage is from reversible imine (Uribe-Romo et al., 2009), boroxine (Cote et al., 2005) or hydrazone (Uribe-Romo et al., 2011) to less reversible dioxin (Zhang et al., 2018), phenazine (Guo et al., 2013), triazine (Kuhn et al., 2008), oxazole (Wei et al. 2018). In the present research era, we need high crystallinity and chemical stability in the structures of porous COFs. Specially to focus on the C=C bond for the construction of COFs, which contains good stability and less reversibility. To solve the problems of COFs, such as low density and hydrophobicity, the induction of magnetic nanoparticles in the structure of COFs gives a proper remedy in the preparation of chemical stable magnetic COFs. The construction of porous covalent organic framework PCOFs can be divided into four board groups, such as a one-step method for the synthesis of PCOFs and MNPs, indirect mixing of MNPs and PCOFs, the deposition of PCOFs on MNPs surfaces, and deposition of MNPs on PCOFs surface, among all these four methods, the last two methods are mainly used methods (Yu et al., 2019).

Dye is one of the typical pollutants which is a serious environmental problem and threat to human health. Therefore, the effective remediation of these toxic dyes is one of the emerging research areas and got attention from scientists. Magnetic porous organic framework (M-POFs) shows promising applications in the removal of dyes and other environmental pollutants from wastewater, i.e., as MOP magnetic nanoparticles (Huang et al., 2019), PANI (Kharazi et al., 2019), PAA (Zhou et al., 2013) and so on (Tables 3 and 4). Hu and co-workers (2020) reported a new magnetic porous covalent organic framework MPCOFs sorbent material for the fluoroquinolones andβ-agonists enrichment in pork and milk samples. During the enrichment process, the reaction of amino-modified MNPs and the 1,3,5-tri formyl phloroglucinol as reactive monomers and

2,5-diaminobenzenesulfonic acid DABA through Schiff base-condensation reaction leading to prepare the composite of a porous magnetic covalent organic framework called TFP-DABA MNS. After the extraction process optimization, and coupling with HPLC-MS/MS, a reproducible and effective process was developed to quantify the traces of fluoroquinolones and β-agonists in the selected food sample. The final results show excellent linearity (R2 ≥ 0.9916), as well as low LOQs in the range of 0.1 to 0.2 ng g−1 for both fluoroquinolones and β-agonists (Hu et al., 2020). They also reported a novel magnetic COFs, having bouquet-shape and composed of a flower-shaped MNPs and COF stem. The 1,3,5 triformylphoroglucinol monomer was grown on the surface of amino-functionalized MNPs while using a solution-phase reaction and will structure magnetic COFs was generated.

He et al. (2017) reported a novel magnetic COFs, having bouquet-shape and composed of a flower-shaped MNPs and COF stem. The 1,3,5 triformylphoroglucinol monomer was grown on the surface of amino-functionalized MNPs while using a solution-phase reaction. As a result, well-structured magnetic COFs were generated, which was mandatory for the subsequent formation of the COFs and directed growth. To effectively construct the nanofibers of COFs, the surface of MNPs was modified with p-phenylenediamine at room temperature. The prepared bouquet-shaped magnetic COFs exhibits large pore volume and surface area, but the BET surface area is low of about 247.8 m^2 $g^{-1,}$ and this is because of the addition of MNPs. The magnetic domain of the prepared magnetic COFs are from 40.1 to 69.4 emu g^{-1}. The magnetic COFs showed excellent application as a sorbent and was successfully utilized for the extraction of polyaromatic hydrocarbon (PAHs); this is because of the hydrophobic interactions, hydrogen bonding. After coupling with HPLC-FID, the material shows low LODs of about 73-110 % and high recovery good recovery of 0.24 to 1.01 ngL^{-1}. Lu et al. (2020) used a solvothermal method for the preparation of nitro functionalized magnetic covalent organic framework (Fe_3O_4@COF-$(NO_2)_2$) and was tested as adsorbent for the MSPE of insecticides and neonicotinoid in different vegetable samples. The prepared Fe_3O_4@COF-$(NO_2)_2$ functional material shows thermal, chemical stability, and hydrophilic nature, which help in the MSPE of polar compounds. The strong hydrophilic interaction of Fe_3O_4@COF-$(NO_2)_2$ enriching neonicotinoids very efficiently (Lu et al., 2020). The reported method exhibits a very good linearity of about 0.1 to n30 ng mL^{-1}, followed by a low range of detection limit, which is about 0.02 to 0.05 ng mL^{-1}). The enrichment factors are high in the range of170 to 250, and the recovery rate is about 77.5% to 110.2%, which is looking satisfactory. The reported results show that the extraction efficiency increased for different pollutants after the functionalization and modification of (Fe_3O_4@COF-$(NO_2)_2$) (Fig. 7).

3.3. Magnetic mesoporous composites materials

Generally, nanoscale mesoporous materials possess pore size in the range of 2- 50 nm with a unique surface morphology (Zhao et al., 2012). The biocompatibility, promising structural features, i.e., control particle size, large pore size, and surface area, engineered mesoporous structure the reported mesoporous materials exhibited high-value application (Yang et al., 2012). The mesoporous features in the entire structures of the material create some active sites for effective interactions, making it possible to use these mesoporous materials for different applications such as sensing, catalysis, adsorption, and targeted drug delivery. A novel adsorbent was prepared by the fabrication of aminopropyl and octyl groups onto the surface of magnetic mesoporous silica (mOAS). In the first stage, the pseudomorphic transformation was used to prepare magnetic mesoporous silica (Zhu et al., 2012), followed by the surface modification with aminopropyl and octyl groups. The material was characterized for its surface morphology and other physical and chemical properties by XRD, SEM, XPS, nitrogen adsorption (NAM), VSM, and FTIR. Furthermore, the mOAS was checked as sorbents and was employed for MSPE phenoxy carboxylic acid in different environmental aqueous samples. Then the detection was confirmed through HPLC-MS/MS having triple-quadrupole tandem (Zhang et al., 2020a). Finally, MSPE-UHPLC-MS/MS method was optimized and established for the effective MSPE of phenoxy carboxylic acid in the environmental sample (Fig. 8). The final results explain the great potential of mOAS has as MSPE sorbent, especially for acidic pollutants from different wastewater samples.

Magnetic nanoparticles were coated with the layer of mesoporous silica modified with methyl dimethoxy, and p-toluenesulfonic acid (PTSA) was used as a catalyst and finally, a will defined Fe_3O_4/mSiO_2-Me-PTSA material was prepared (Qin et al., 2018a). The prepared Fe_3O_4/mSiO_2-Me-PTSA material was used as MSPE sorbent for the efficient removal of polychlorinated biphenyls from wastewater samples. The sol-gel process was used for the synthesis of $Fe_3O_4/mSiO_2$ as magneto porous silica. In the process, cetyltrimethylammonium bromide (CTAB) was used as a surfactant and silica (TEOS) as a precursor. Then the surface of $Fe_3O_4/mSiO_2$ was coated with methyl dimethoxy. p-toluenesulfonic acid PTSA was used as a catalyst to speed up the reaction. The $Fe_3O_4/mSiO_2$-Me-PTSA exhibits a strong magnetic domain of about 33 $emug^{-1}$ and a large surface area of about 197.1 m^2 $g^{-1}$and, therefore, gives a very quick magnetic separation. Also, the adsorption time of the targeted polychlorinated biphenyls is about 10 min. Furthermore, the polychlorinated biphenyls enrichment factors are very high from 119 to 147, and the adsorption efficiency of the $Fe_3O_4/mSiO_2$-Me-PTSA for polychlorinated biphenyls was noted as 46.3 mg g^{-1}. Therefore, the reported method shows promising results with 85.25-118.60% recoveries and low LODs, which is about 0.16-0.91 ng L^{-1} (Qin et al., 2018b).

In another study, Fe_3O_4@RF@mTiO_2 with proper core-shell like surface morphology was designed and prepared and tested as MSPE sorbent for the effective removal of arsenic from highly acidic samples. The surface Fe_3O_4 was first fabricated with resorcinol-formaldehyde (RF) followed by mesoporous TiO_2 with a shell thickness of about 50 nm and a surface area of about 337 m^2 g^{-1}, and a large pore volume of 0.42 cm^3 g^{-1}. The prepared Fe_3O_4@RF@mTiO_2 material gives quick adsorption (1.16 g mg^{-1} h^{-1}) and 139 mg g^{-1} adsorption capacity, which was calculated through the Langmuir model at pH in the range of 3 to 3.5. The entire structure of the Fe_3O_4@RF@mTiO_2 is composed of 130 nm of Fe_3O_4 inner core and 50 nm of RF@mTiO_2 shell, which makes this material strongly magnetic and can be separated while using an external magnetic field and can be recycled many times. Moreover, the resorcinol-formaldehyde shows hydrophobic nature and makes about 10 nm shell and helping the entire Fe_3O_4 core from etching against acid solution (Zhao et al., 2018). Also, in the adsorption process, Fe_3O_4@RF@mTiO_2 core-shell material shows some surface complexation and electrostatic forces between TiO2 crystals arsenate and hence can be used as promising multi-layer material for wastewater treatment in the long run.

4. Other magnetic composites as MSPE adsorbents

Along with those above magnetic hybrid materials, MNPs can be fabricated by coupling with some other functionalized materials, including metallic nanomaterials, silicon, chitosan, and surfactants, to prepared excellent MSPE sorbents. The summary of some other magnetic hybrid MSPE sorbents for the remediation of environmental pollutants is mentioned in Table 5. Silica and silicon magnetic materials show promising applications as MSPE due to some unique features such as easy surface modification, availability, low cost, mechanical stability. Because of these unique properties, magnetic silicon materials exhibit excellent adsorption applications. Three different cores, i.e., γ-Fe_2O_3, $MnFe_2O_4$, and $CoFe_2O_4$, were successfully fabricated with a modified silica shell followed by alkyl modification and were used for the MSPE sorbent of triclosan under environmentally friendly and one-pot process. The prepared γ-Fe_2O_3@SiO_2 andγ-Fe_2O_3@SiO_2-C18 material was characterized through VSM, TGA, XRD, FTIR, BET area, DLS, contact angle, and zeta potential. All three magnetic materials show cores shell surface morphology and hydrophobic wettability. The shell thickness is about 2 nm. The magnetic core is about 13 nm with effective organofunctionalization and shows effective adsorption of triclosan (Caon et al., 2020). Furthermore, after coupling with HPLC, the results revealed that the 0.4–102.4 μg L^{-1} linear range, $R^2 > 0.99$ of very good linearity, and the quantification limit detection of about 0.36 to 1.20 μg L^{-1}, noted respectively. The prepared magnetic nano adsorbent as MSPE can be reused with high efficiency under the 4.76 signal enhancement (Fig. 9).

In another study, a novel Fe_3O_4@SiO_2-NH_2/F_{13} magnetic silica hybrid material was prepared through a one-step reaction. First, the surface of SiO_2 was modified with an amino group and the chain of octyl-perfluorinated while using the sol-gel procedure (Zhou et al., 2016a). After the complete experiment, the prepared Fe_3O_4@SiO_2-NH_2/F_{13} material shows excellent adsorption of perfluorinated compounds from the selected water samples and the results was further confirmed through HPLC-MS/MS. For example, in a 500 mL water sample, 50 mg of Fe_3O_4@SiO_2-NH_2/F_{13} as MSPE sorbent was dispersed, and within 30 min, the adsorption equilibrium was reached. The high adsorption efficiency is because of the fluorine-fluorine (F-F) interactions and high electrostatic attraction followed by the size exclusion effect. The noted recoveries were 90.65 to 106.67% and 0.029-0.099 ng L^{-1} of low LODs. Therefore Fe_3O_4@SiO_2-NH2/F_{13} composite can be extensively applied as a useful adsorbent, particularly for aqueous solutions with large volume, to rate the concentration levels of average PFCs in environmental water systems (Zhou et al., 2016a).

The composites of natural polymers such as chitosan with MNPs also show promising applications as an MSPE sorbent. Chitosan is a well-known natural polymer with amino and carboxylic groups on its surface, which import some excellent properties such as biodegradability and biocompatibility followed by simple modification (Khan et al., 2019; Khan et al., 2020b; Aziz et al., 2020; Ali et al., 2020d). More recently, generating magnetic chitosan hybrid material was designed and fabricated by the dispersion ferrites of the entire chitosan matrix, giving the microspheres of ternary ferrites chitosan (TFCM) (Nawaz et al., 2020; Ali et al., 2018). The co-precipitation method was used to prepare the nanoparticles of ternary ferrites, followed by the induction of chitosan matrix to synthesize magnetic chitosan as an effective adsorbent for methylene blue dye. The composition of the design photocatalysis ($Fe_2Zn_0.5Ni_{0.5}O_4$). The crystalline nature of the magnetic chitosan material is because of the inside metals, which are helping in the redox coupling and decrease the effect of recombination of the conduction and valance bands (Nawaz et al., 2020).

Generally, the induction of chitosan effectively assists the growth of MNPs but also stop their accumulation. Tolessa et al. fabricated magnetic chitosan hybrid materials in the size of 2 um through suspension cross-linking method as used as MSPE sorbent to remove silver (Ag) nanoparticles (Tolessa et al., 2017). Their study dispersed MNPs in 1% chitosan; next, toluene was added to the mixture containing the Span-80 emulsifier. Then the mixture was stirred at 500 rpm for 30 min; during this process, NaOH and glutaraldehyde solution was eventually added. In the end, external magnetic was to separate magnetic chitosan composite material. After coupling with ICP-MS (inductively combined plasma-mass spectrometry), the LODs are low with different size and coating for three Ag particles, i.e., 0.016-0.023 ug/L. The high extraction efficiency of silver (Ag) nanoparticles is because of the positive charges on the chitosan surface, making them a good adsorbent. The extraction efficiency was reported in the range of 84.9 to 98.8%, which shows negative charges because of organic matter coating onto their surface (Fig.

10). The prepared magnetic chitosan hybrid material can be reused, and the efficiency remains about 77.2 + 2.2% after three-time recycling.

5. Conclusions and perspectives

In this current article, we summarized the progress and development in the field of MSPE sorbents and their effective usage as an adsorbent for the extraction of many environmental toxic pollutants such as organic solvents, dyes, and trace metals. The main toxic and dangerous pollutants which are found in the biological, environmental, and food matrix are heavy metals, drugs residue, pesticides, pesticides, phthalate esters, polyaromatic hydrocarbons, polychlorinated biphenyls, bisphenol A, perfluorinated compounds. Due to their diverse surface morphology, structure, and physicochemical properties, the MSPE sorbents material needs accurate design and fabrication for their promising extraction applications. Magnetic solid-phase extraction shows superior adsorption advantages over simple conventional solid-phase extraction because of integrating the magnetic components. The magnetic domain imports some good properties to prepared MSPE sorbent material, such as high adsorption sites, large surface area, mechanical and chemical stability, and quick separation by the external magnetic field from the complex sample matrix. Therefore, the induction of magnetic components makes this MSPE sorbent material more promising after coupling with suitable detection techniques and can be employed for quantitative and qualitative analysis of trace pollutants.

In the near future, to utilize more MSPEs sorbent as a versatile material, need more efforts in the direction to overcome some of the limitations facing during the design and fabrication process, MSPE adsorption process, and then their practical application. Therefore, in the first step, we need to identify the problem, such as overcoming the poor chemical stability, heterogeneous shapes, dispersibility, and recycling in harsh environmental conditions. Furthermore, it is needed to simplify the synthesis and fabrication strategies with optimization and use fewer harmful reagents. Also, to explore some novel environment-friendly materials to reduce harmful effects and the contamination of MSPEs sorbent material and further introduce green chemistry. Need main focus to generate some new applications of these MSPEs sorbents by coupling with suitable analytical techniques. The objective should be to achieve miniaturization, automation, and clear sample analysis with high throughput to get a fast, portable, and satisfactory application. Solving these problems will make the utilization of these MSPEs sorbent materials eventually lead us to remarkable progress for sample pretreatment.

Acknowledgments

Consejo Nacional de Ciencia y Tecnología (CONACYT) is thankfully acknowledged for partially supporting this work under Sistema Nacional de Investigadores (SNI) program awarded to Hafiz M.N. Iqbal (CVU: 735340).

Conflict of interests

The author(s) declare no conflicting interests.

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Table 1 Summary of some magnetic carbon based solid-phase extraction sorbent materials

Adsorbent	Sample	Pollutant	Adsorption (mg g^{-1})	Separation technique	Recoveries (%)	References
G/Fe_3O_4@PT	Water	PAHs		GC-FID	83-107	(Mehdinia et al., 2015)
GOePAR@Fe_3O_4	Food, water	Pb(II)	133	ETAAS	94.3-107	(Akbarzade et al., 2018)
GO-Fe_3O_4@PS	Water	PAHs		GC-FID	95.8-99.5	(Amiri et al., 2018)
Fe_3O_4@MWCNTs	Water, human urine	Parabens		GC-MS	81-119	(Pastor-belda et al., 2018)
Mag-MMWCNTs	Environmental water	β-blockers		Chiral UPLC-MS/MS	82.9-95.6	(Wang et al., 2018)
c-MWCNT-MNPs	Sesame oil	Herbicides phenolic		HPLC-MS/MS	83.8-125.9	(Wu et al., 2016)
m-G/CNF	Environmental water	PAHs		GC-FID	95.5-99.9	(Rezvani-Eivari et al., 2016)
g-C_3N_4/Fe_3O_4	Water	PAEs	4.14-18.02	HPLC-UV	79.4-99.4	(Wang et al., 2015a)
g-C_3N_4/Fe_3O_4	Water	PAHs		HPLC-UV	80.0-99.8	(Wang. M et al., 2015b)

Table 2 Summary of some MOF based magnetic solid-phase extraction sorbent materials

Adsorbent	Sample	Pollutant	Adsorption (mg g^{-1})	Separation technique	Recoveries (%)	References
$Fe_3O_4eNH_2$@MIL-101(Cr)	Water	Pyrethroids		GC-ECD	72.1-106.8	(He et al., 2018)
Fe@MIL101(Cr)	River water	PAHs		HPLC-VWD	85.7-97.3	(Zhou et al., 2017a)
Fe_3O_4@SiO_2-MIL-101(Cr)	Water	Pesticides		HPLC-DAD	80.2-107.5	(Ma et al., 2016a)
Fe_3O_4@MIL-101(Fe)	Human hair, urine	OPPs		GC-FPD	74.9-94.5	(Zhang et al., 2014)
magnetic MIL-100(Fe)	Environmental water	PAHs		GC-FID	88.5-106.6	(Hou et al., 2017)
MAA@Fe_3O_4-ZIF-8	Water	PAEs		HPLC-DAD	85.6-103.6	(Liu et al., 2015)
Fe_3O_4@PDA@ZIF-7	Rainwater, PM2.5	PAHs		GC-MS	82.1-99.4	(Zhang et al., 2016b)
PSA@Zr-MOF@Fe_3O_4	Environmental	Herbicides		UPLC-HRMS	86.2-104.6	(Pan et al., 2019)
Fe_3O_4@HKUST-1	Water, fruit-tea	PAHs		UPLC-FLD	75-94	(Rocío-Bautista et al., 2016)
Magnetic MOF-5	River water	heterocyclic	81-181	HPLC-FLD	80.20-108.33	(Ma et al., 2018)
Fe_3O_4@DMcT@HKUST-1	Baby food	Cd(II), Zn(II), Pb(II)	155-190	FAAS	90.0-106	(Ghorbani et al., 2015)
Fe_3O_4@IRMOF-3	Water	Cu(II)	2.4	ETAAS	98.0-102.0	(Wang et al., 2014)
COF-LZU1@PEI@Fe_3O_4	Water, soil	PAHs		HPLC-FLD	85.1-107.8	(Wang R et al., 2017a)

Table 3. Representative magnetic MOFs as adsorbents for glycoproteins and glycopeptides.

Magnetic MOFs material	Samples	Selectivity	Sensitivity	Identified glycopeptides	Reference
L-Cys-Fe_3O_4@mSiO_2	Human saliva (healthy volunteer; gastric cancer volunteer)	HRP:BSA = 1:100 (mass ratio)	1 fmol/μL HRP digest	46; 36	(Chen et al., 2019a)
MagG@PEI@HA	Human serum	HRP:BSA = 1:1000 (molar ratio)	2 fmol/μL IgG digest	376	(Zhan et al., 2019)
Fe_3O_4-GO@PDA-Chitosan	Human renal mesangial cells	HRP:BSA = 1:10 (molar ratio)	0.4 fmol/μL HRP digest	393	(Changfen et al., 2020)
SPIOs@SiO_2@MOF	Mouse liver	IgG:BSA = 1:500 (mass ratio)	10 fmol/μL IgG digest	152	(Luo et al., 2019)
MoS_2-Fe_3O_4-Au/NWs-GSH	Human urine exosome; serum	IgG:BSA = 1:1000 (mass ratio)	0.5 fmol/μL IgG digest	1250; 489	(Zhang et al., 2020b)
Fe_3O_4-PEI-pMaltose	Human renal mesangial cells	HRP:BSA = 1:100 (mass ratio)	10 fmol/μL HRP digest	449	(Qi et al., 2021)
Fe_3O_4@TpPa-1	Human serum	IgG:BSA = 1:100 (molar ratio)	28 fmol/μL IgG digest	228	(Wang et al., 2017b)
AEK8-maltose functionalize d SiO_2@Fe_3O_4	Human serum	HRP:BSA = 1:150 (mass ratio)	0.001ng/μL HRP digest	282	(Zhang et al., 2019a)
MCNCs@COF@PBA	Exosomes secreted from the	HRP:BSA = 1:600 (mass ratio)	100 amol/μL HRP digest	32	(Gao et al., 2019)
magOTfP5SOF-Ga^{3+}	Hela cell human lung adenocarcinoma cells; mouse liver tissue	HRP:BSA = 1:2000 (mass ratio)	0.1 fmol/μL HRP digest	147	(Zheng et al 2020a)
MMP	Human serum	HRP digest:BSA protein = 1:50 (mass ratio)	–	365	(Zhang et al., 2018)
Fe_3O_4-GO@nSiO_2-PAMAM	Mouse liver	–	0.5 fmol/μL IgG digest	1529	(Wan et al 2015)
CFMZOF	Exosomes from human urine	HRP:BSA = 1:100 (mass ratio)	0.5 fmol/μL HRP digest	335; 375; 389	(Zheng et al., 2020b)
mCTpBD	Human saliva (healthy people; patients with inflammatory bowel disease)	HRP digest:BSA protein = 1:1000 (mass ratio)	0.5 fmol/μL HRP digest	32; 39	(Wu et al., 2020)
MagG@Mg-MOFs-1C	Human urine	HRP digest:BSA	0.1 fmol/μL HRP digest	406	(Wang et al 2019)

		protein = 1:500 (mass ratio)			
magHN/Au-GSH nanofiber	Human serum	IgG:BSA = 1:500 (molar ratio)	2 fmol/μL IgG digest	246	(Huan et al., 2019)

Table 4 Data explaining the application of MNPs-COFs for removal of metals, dyes and others.

Magnetic porous organic framework (M-POFs)	Medium	Pollutant	Pore size (nm)	Analytical Techniques	Adsorption (mg.g^{-1})	References
Magnetic porous organic polymers MOP	Water	Methylene blue » Methylene Orange	e	Uv-visible	1153	(Huang et al., 2017)
Tannin-based magnetic porous organic polymers (TA-MOPs)	Water	Methylene blue/Pb	9.6	inductively coupled plasma optical emission spectrometer and Uv-Vis	1326 to 1727	(Huang et al., 2019)
Magnetic carboxyl functional nanoporous polymer	Water	Methylene blue	20 to 40	Uv-visible	57.74	(Su et al., 2018)
Magnetic covalent triazine-based framework (CTF/Fe_2O_3)	Water	Methylene Orange	21 to 40	UV-visible	291	(Zhang et al., 2011)
Fe_3O_4@3-aminophenol-formaldehyde	Water	Methylene blue	e	e	e	(Zhao et al., 2015)
Fe_3O_4/Hypercrosslinked polymers	Water	Methylene Orange and fuchsin basic	0.73 and 1.36	UV-visible	211 to 231	(Pan et al., 2016)
Yolk–shell magnetic porous organic nanoparticles	Water	Methylene blue	e	Uv-visible	134	(Zhou et al., 2019)
Magnetic β-cyclodextrin (β-CD) porous polymer nanospheres (P-MCD)	Water	Methylene blue	5.59	UV-visible	305.8	(Liu et al., 2019)
Copper ferrite-polyaniline nanocomposite CuFe/PANI	Water	Methylene Orange	-	UV-visible	345.9	(Kharazi et al., 2019)
Triazine-based polymeric network/MNPs	Water	Methylene Orange	-	UV-visible	80.6	(Faraji et al., 2018)
poly(acrylic acid)/Fe_3O_4	Water	methylene blue	-	Uv-visible	73.85	(Zhou et al., 2013)
Sodium acrylate (SA)/Fe_3O_4 nanoparticles (SA-MMNPs)	Water	Rhodamin e B	-	e	216	(Li et al., 2017b)
Magnetic 1,3,5-triphenylbenzene- benzi dine (Fe_3O_4/TpBD)	Water	Bisphenol s	-	UV-visible	160.6 to 236.7	(Li Y et al., 2017c)
Magnetic hyper-cross-linked polymers	e	Antibiotics	-	UV-visible	114.94 to 212.7	(Liu Y et al., 2018b)

Fe_3O_4/COF-LZU-1	Water	Iodine	1.1 to 1.3	UV-visible	797	(Liao et al., 2017)

Table 5 Preparation and application of M-POFs in the determination of heavy metal and other emerging organic contaminants.

M-POFs	Matrix	**Pollutant**	SBET ($m^2 g^{-1}$)	Analytical instruments	Recovery (%)	References
Magnetic TpPa-1	Water	PAHs	-------	HPLC-FLD	73 to110	(He et al., 2017a)
Fe_3O_4/TpBD	Grilled fish, wild fish,	PAHs	248	HPLC-DAD	84.3 to 104.3	(Li et al., 2018)
COF-LZU1-PEI/ Fe_3O_4	Soil, water and coffee	PAHs	115	HPLC-UV/FLD	85.1 to 105	(Wang et al., 2017)
Fe_3O_4/COF(TpDA)	Edible oil, grilled fish and chicken	PAHs	-------	HPLC-DAD	85.7 to 104.2	(Shi et al., 2018)
Fe_3O_4/SiO_2-TCPP	Water	PAHs	-------	GC-MS	71.1 to 106.0	(Yu et al., 2018)
Fe_3O_4/SiO_2@PAF-6	Cigarette smoke and water	Phenols,	-------	HPLC-UV/FLD	84.0 to 94.0	(Chen et al., 2018)
TpBD-DS MNS	Urine	PAHs,	180	UPLC-MS/MS	95.4 to 129.3	(Zhang et al., 2019b)
CTC-COF-MCNT	Fried chicken, roast beef	HAAs	-------	UPLC-MS/MS	73.0 to 117	(Liang et al., 2020)
CTF/Fe_2O_3	Water	PFCs	-------	HPLC	81.9e114	(Ren et al., 2018)
Fe_3O_4/TpPa-F4	Milk	PFCs	120	HPLC-MS/MS	73.27 to 128.07	(Zhang M et al., 2020c)
Fe_3O_4/COF(TpDA)	Fruits, vegetables	PGRs	-------	HPLC-DAD	83.0 to 105.0	(Li M et al., 2020)
Fe_3O_4/COF-$(NO_2)_2$	Vegetables	Neonicotinoids	171	HPLC	77.5 to 110.2	(Lu et al., 2020)
Ni-POFs	Urine	Alkaloids	429	UHPLC-MS/	93.5 to 99.2	(Hu et al., 2020)
M-CTF-TPC	Slimming tea	Anthraquinone		MS UHPLC-FLD	94.5 to 105.4	(Shi et al., 2019)
Fe_3O_4/PPy	Water	Nitrophenols	-------	HPLC-UV	84 to 109	(Tahmasebi et al., 2013)
Fe_3O_4/SiO_2 GMA-S-SH	Farmland water,	$MeHg^b$	188	ICP-MS	84.3 to 116	(He et al., 2019)
g-Fe_2O_3/CTF-1	Water, soil and rice samples	$PhHg^b$	255	ICP-MS	-----	(Leus et al., 2018)
MOP	Urine, cell	Pt^{4b}, Au^{3b}	-------	ICP-MS	86 to 110	(Chen et al., 2019b)
Fe_3O_4/PANI	Seawater	Bi^{3b} $MeHg^b$	293	GC-MS	98 to 105	(Mehdinia et al., 2011)

Table 6 Miscellaneous magnetic nanomaterials for magnetic solid-phase adsorption

Magnetic adsorbents	Samples	**Pollutant**	Adsorption (mg g^{-1})	Detection techniques	Recovery (%)	Reference
GO-Chm	water, rice	herbicides	29.41 to 35.71	HPLC-UV	94.33 to 102.67	(Shah et al., 2018)
Fe_3O_4@SiO_2	Urine	paraquat	2.4	UVeVis	92.9 to 105.2	(Sha et al., 2017)
polythiophene@CS@MNPs	water	triazines	-----	GC-FID	96 to 102	(Feizbakhsh et al., 2016)
Fe_3O_4@SiO_2@MgeAl LDH	water	PAEs	------	HPLC-UV	63 to 102	(Zhao et al., 2015)
Fe_3O_4@Au@2-ME	water	Cd(II),Pb(II), Hg(II)	------	HPLC-VWD	97.5 to 103.2	(Zhou et al., 2017b)
Fe_3O_4@SiO_2eNH$_2$&F$_{13}$	environmental water	PFCs	------	UPLC-MS/MS	90.05 to 106.67	(Zhou et al., 2016b)
MCM	water	silver nanoparticles	------	ICP-MS	84.9 to 98.5	(Tolessa et al., 2017)
Fe_3O_4@SiO_2@(PSS-PIL)n	water	pesticide	------	HPLC-UV	82.5 to 109.3	(He et al., 2017b)
FeO_4@Au@DDT	water	diphenols, PAHs	------	HPLC-UV	63.8 to 110.7	(Li et al., 2014)
Fe_3O_4@DC193C	water	parabens	------	HPLC-UV	86.0 to 118.0	(Ariffin et al., 2019)
3D-IL@mGO	vegetable oil	PAHs	7[e]	GC-MS	80.2 to 115	(Zhang et al., 2017)
Fe_3O_4@SiO_2eC16	water	PCBs	------	GC-MS/MS	75.17 to 101.20	(Fan et al., 2017)
Fe_3O_4@MnO_2	water	As(III), As(V)	------	CHG-AFS	85.6 to 111.7	(Yang et al., 2018)
Fe_3O_4@SiO_2@GO@ILs	water	CPs	------	HPLC-MS/MS	85.3 to 99.3	(Cai et al., 2016)
Fe_3O_4@SiO_2@TiO_2@CPC	water	BPA	------	HPLC-UV	92e105	(Sobhi et al., 2017)
MPIL@CC[4]A	water,	PAEs	52.90 to 63.7	HPLC-UV	84.3 to 110.8	(Zhou S.et al., 2018)
PIL-MNPs	tea	OPPs	-------	HPLC-UV	81.4 to 112.6	(Zheng et al., 2014)
SDS@ Fe_3O_4	food	cationic dyes	47.4 to 270.3	HPLC-DAD	70.1 to 104.5	(Qi et al., 2016)
Fe_3O_4eNH$_2$@MIL-101(Cr)	Water	Pyrethroids	72.1-106.8	GC-ECD		(He et al., 2018)
Fe_3O_4@PEI-RGO	Rice	Polar acidic	76.34	HPLC-DAD	87.41-102.52	(Li et al., 2017a)
Fe_3O_4@G-TEOS-MTMOS	Water	OPPs	37.18	GC-mECD	83-105	(Nodeh et al., 2017)
GOPA@Fe_3O_4	Vegetable oil	Herbicides PAHs		HPLC-DAD	85.6-102	(Ji et al., 2017)

PPy-RGOx-Fe_3O_4	Bottled water, beverages	PAEs		GC-MS/MS	87.5-99.1	(Pinsrithong et al., 2018)
Fe_3O_4@mSiO_2-Ph-PTSA	Soil	PAHs		GC-MS	86.85-110.01	(Qin et al., 2018)
Fe_3O_4@Cr(VI) IIPs	Water	Cr(VI)	2.50	FAAS	98.0-99.2	(Qi et al., 2017)
Fe3O4@mSiO2 eNH2	Water, food seafood	highly chlorinated		GC-MS	88.4-103.2	(Liu et al., 2016)
Fe_3O_4@mSiO_2-Me-PTSA	Water	PCBs	46.3	GC-ECD	85.25-118.60	(Qin et al., 2018)
PEMs/Fe_3O_4@SiO_2	Water, rice	Cu(II)	14.7	FAAS	94.4-114.1	(Xiang et al., 2014)
Fe_3O_4@SiO_2@g-MPTS	Water, human hair	Hg(II), MeHg(I)		ICP-MS	75.6-99.6	(Ma et al., 2016b)
Fe_3O_4@P(MMA-AA-DVB)	Emulsion	Water in water			98	Ali et al., 2015a)

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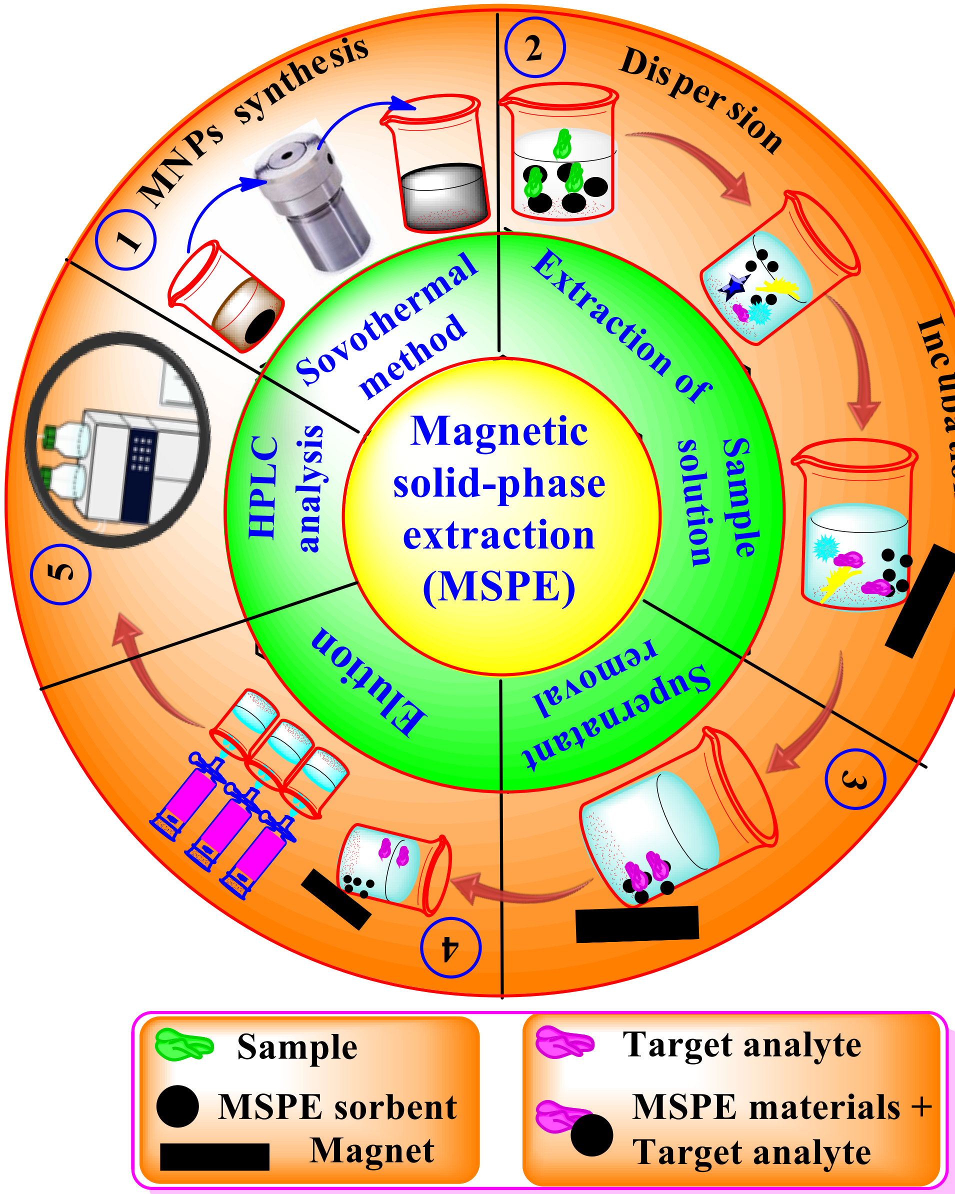

Scheme 1. Schematic illustration of magnetic solid-phase extraction process.

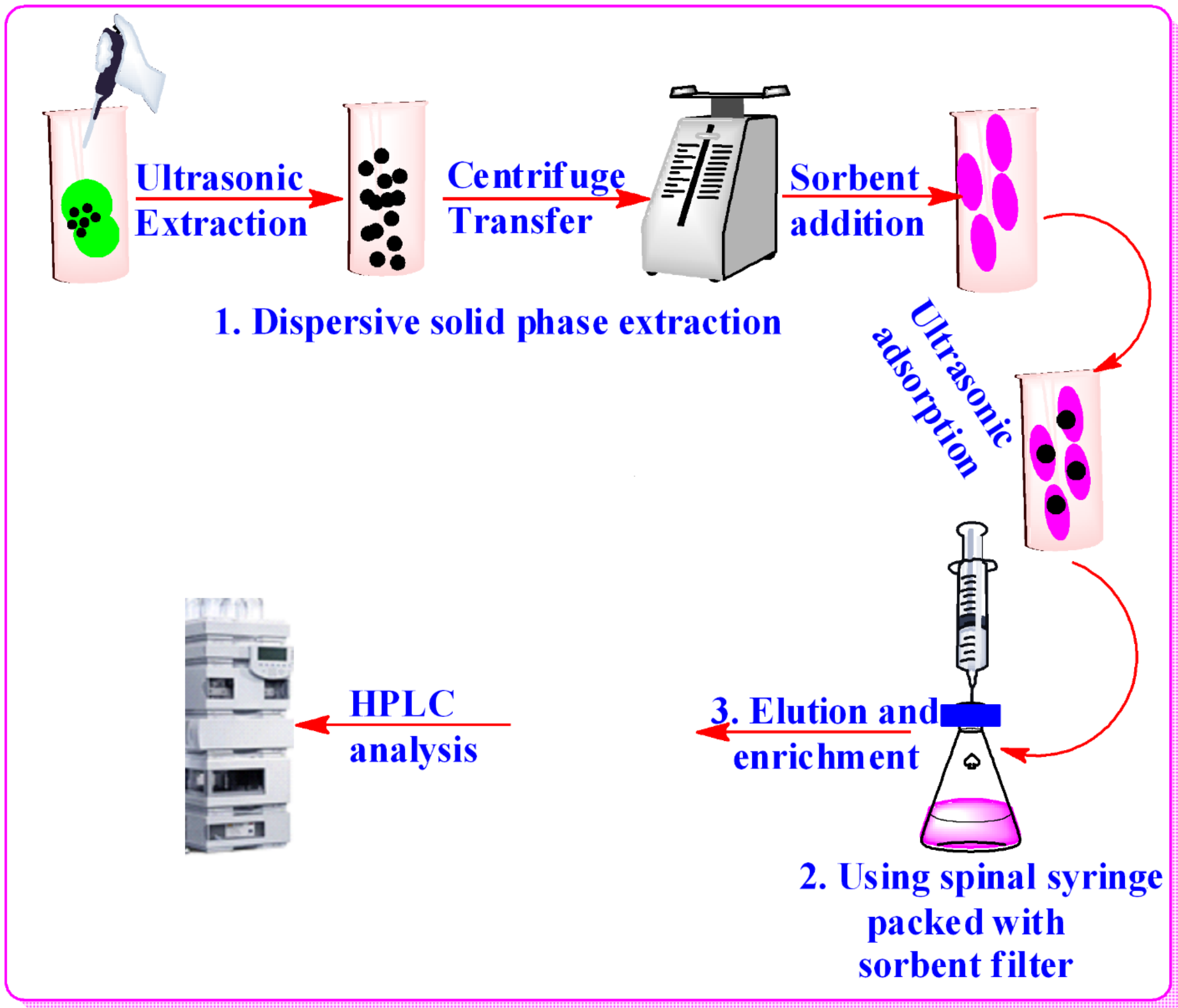

Fig. 1 Schematic of the solid-phase extraction process.

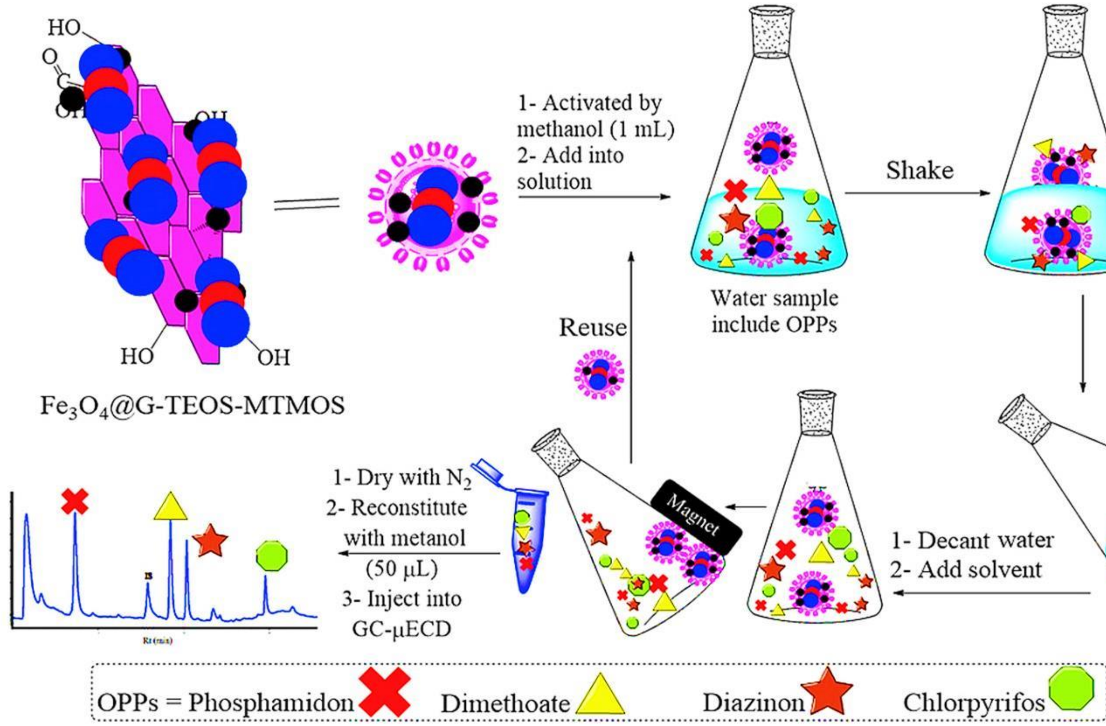

Fig. 2 Synthesis and MSPE applications of Fe_3O_4@G-TEOS-MTMOS. Reprinted from Nodeh et al. (2017) with permission from Elsevier. License Number: 5086230780822.

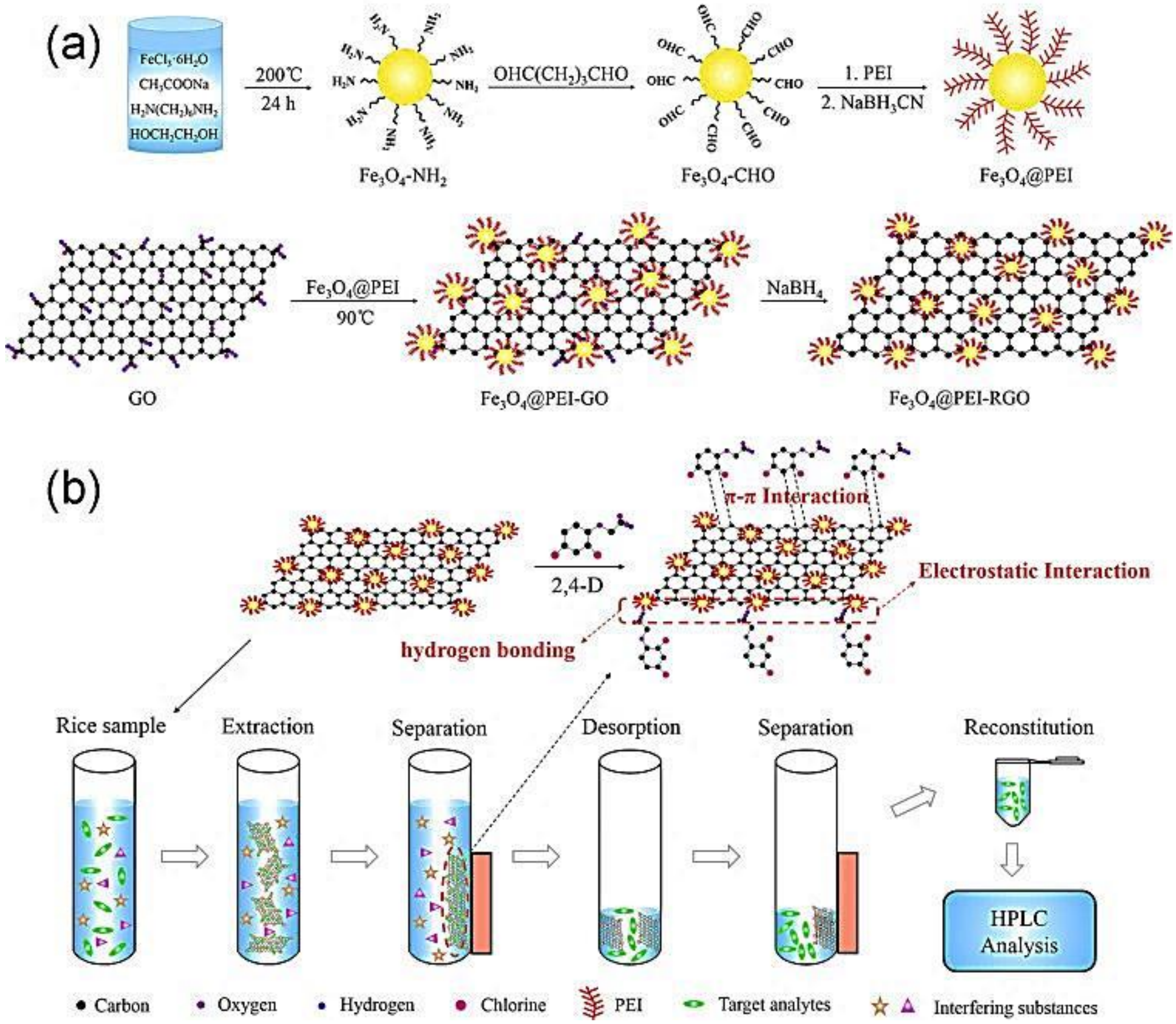

Fig. 3 Schematic illustration for the synthesis of Fe_3O_4@PEI-RGO and their MSPE removal application. Reprinted from Li et al. (2017a) with permission from Elsevier. License Number: 5086250405992.

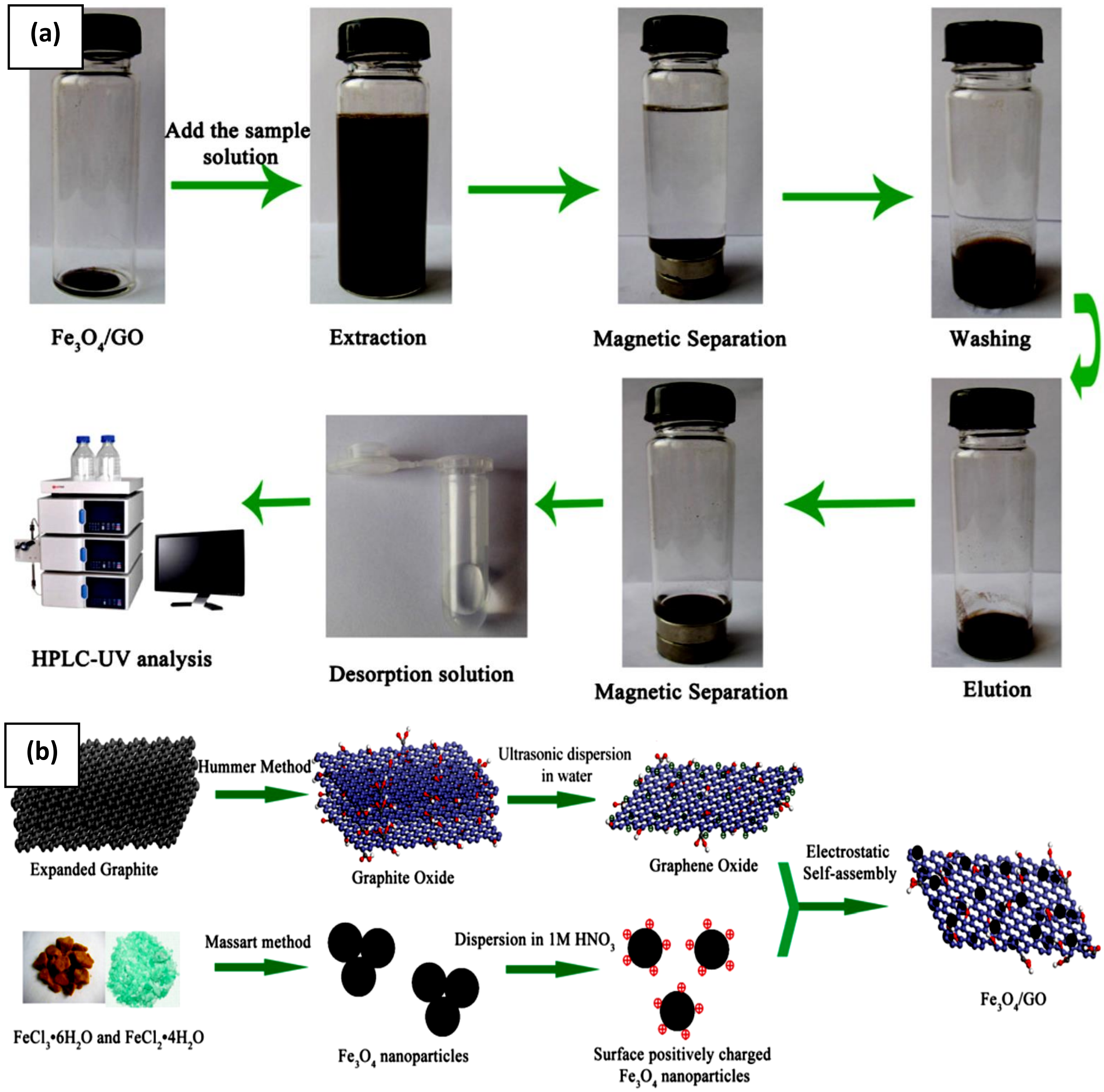

Fig. 4 (a) Experimental process for solid-phase extraction using Fe_3O_4/GO. (b) Schematic explanation of Fe_3O_4/GO nanocomposite fabrication. Reprinted from Han et al. (2012) with permission from Elsevier. License Number: 5086230981636.

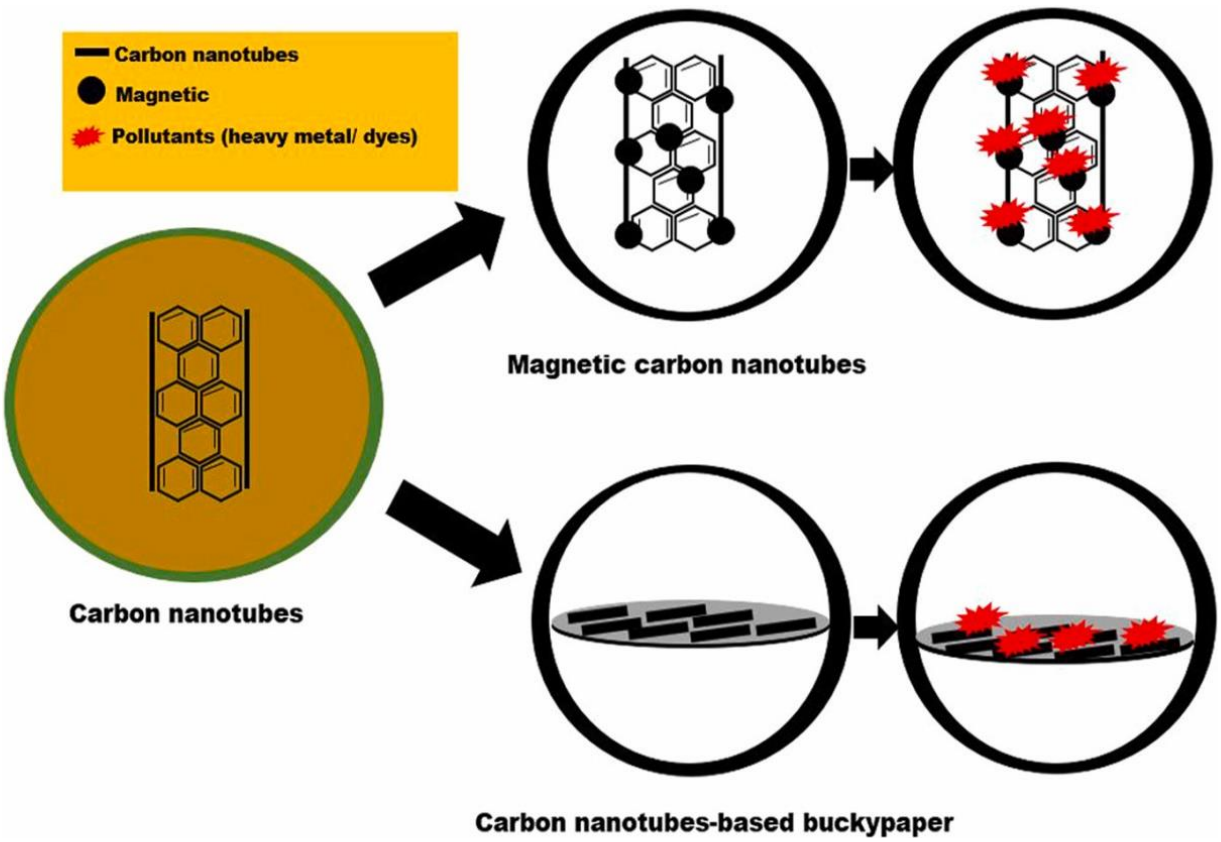

Fig. 5 Schematic illustration of MCNTs and carbon nanotube buckypaper for the effective removal of dyes and heavy metals. Reprinted from Khan et al. (2021e) with permission from Elsevier. License Number: 5086231420185.

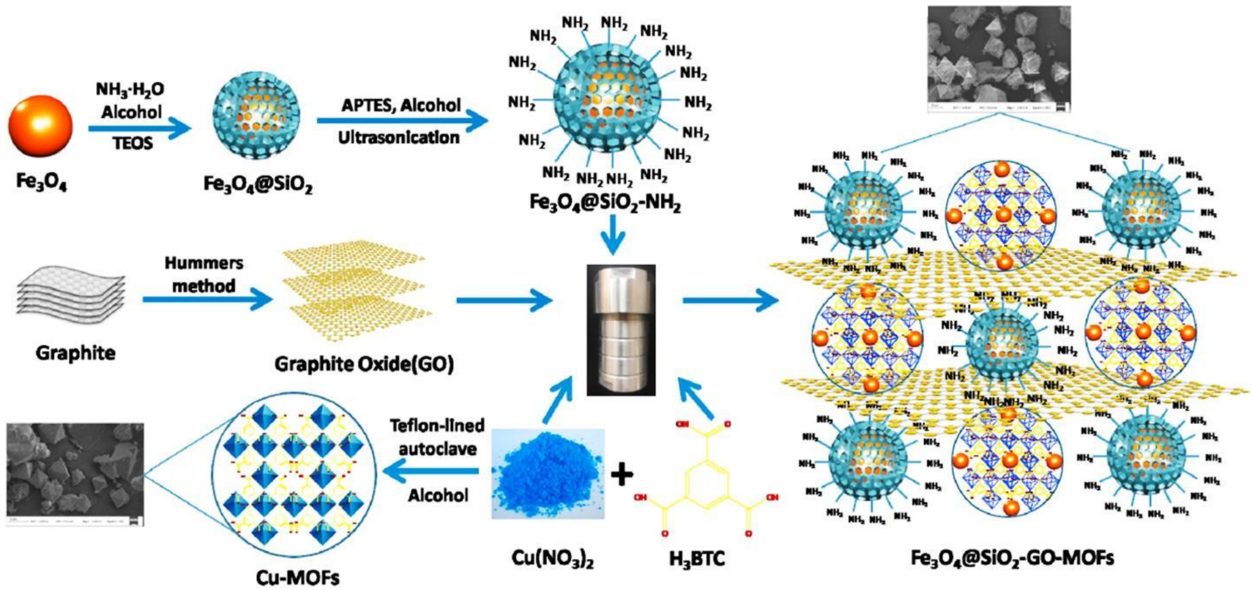

Fig. 6 The layer-by-layer fabrication of Cu-MOFs and Fe_3O_4@SiO_2-GO-MOFs magnetic nanocomposites. Reprinted from Wang et al. (2018b) with permission from Elsevier. License Number: 5086240269387

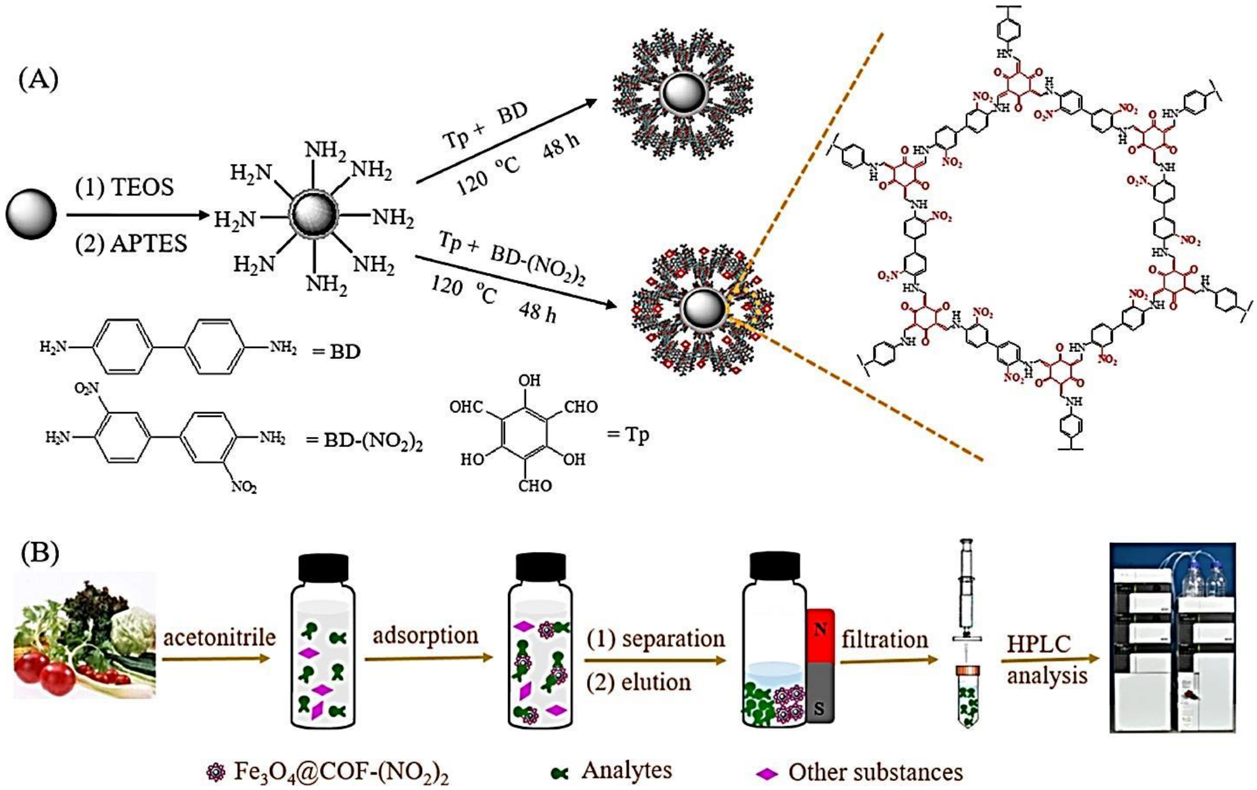

Fig. 7 (A) Schematic of the Fe_3O_4@COF-$(NO_2)_2$ microspheres synthesis. (B) MSPE applications of Fe_3O_4@COF-$(NO_2)_2$ of different vegetable sample as sorbent. Reprinted from Lu et al. (2020) with permission from Elsevier. License Number: 5086240628363.

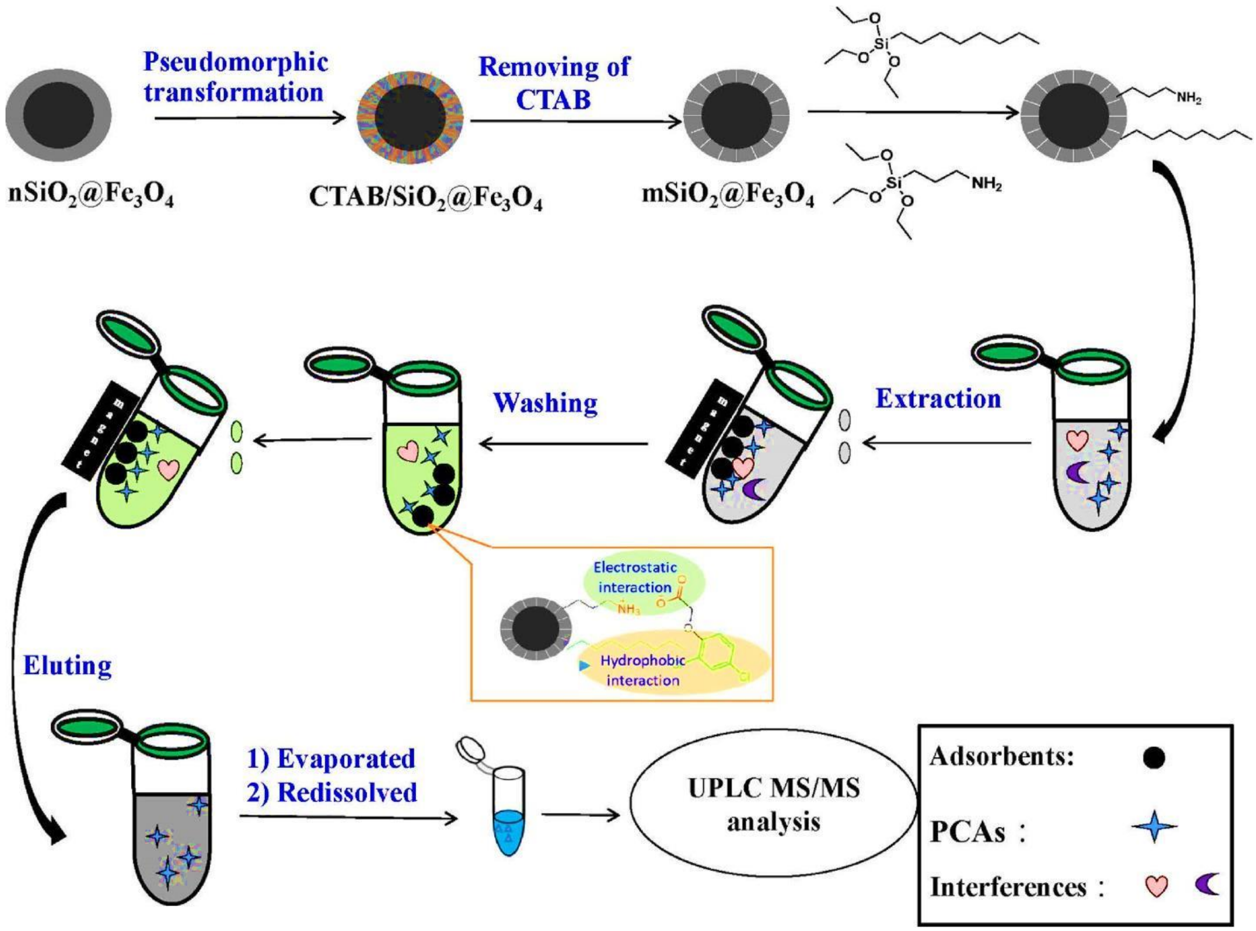

Fig. 8 Schematic illustration of mOAS synthesis and their application as an MSPE sorbent of PCAs from wastewater. Reprinted from Zhang et al. (2020) with permission from Elsevier. License Number: 5086250015810.

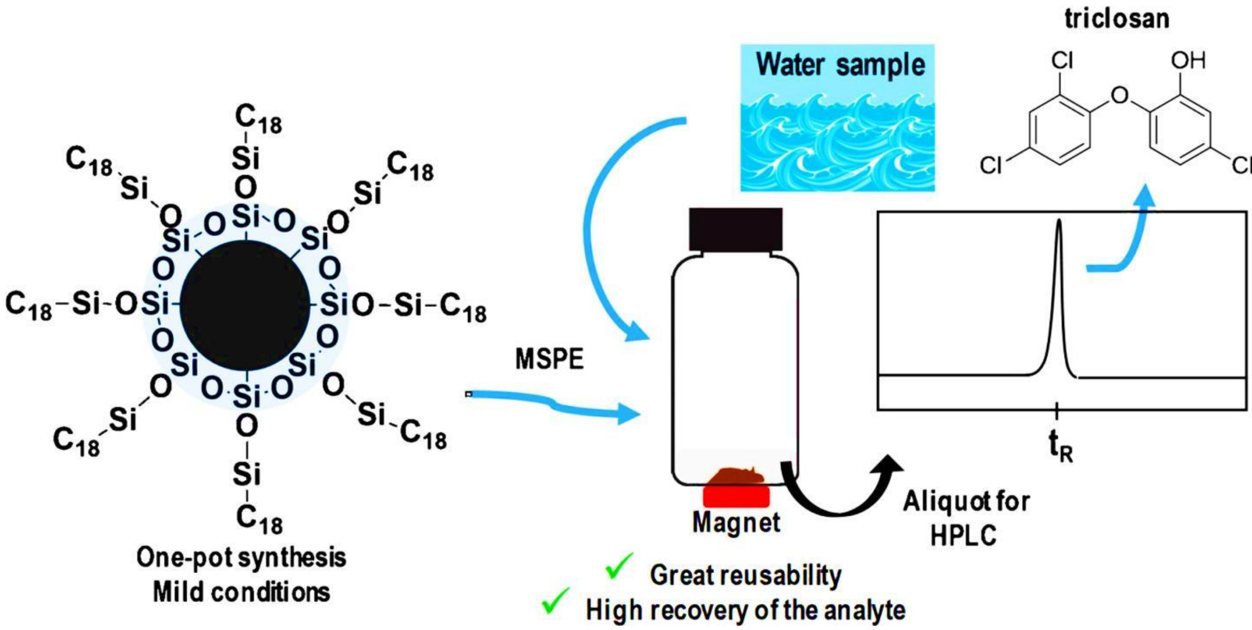

Fig. 9 One pot synthesis of $Fe_2O_3@SiO_2$-C18 and their adsorption applications as MSPE of triclosan. Reprinted from Caon et al. (2020) with permission from Elsevier. License Number: 5086240852460.

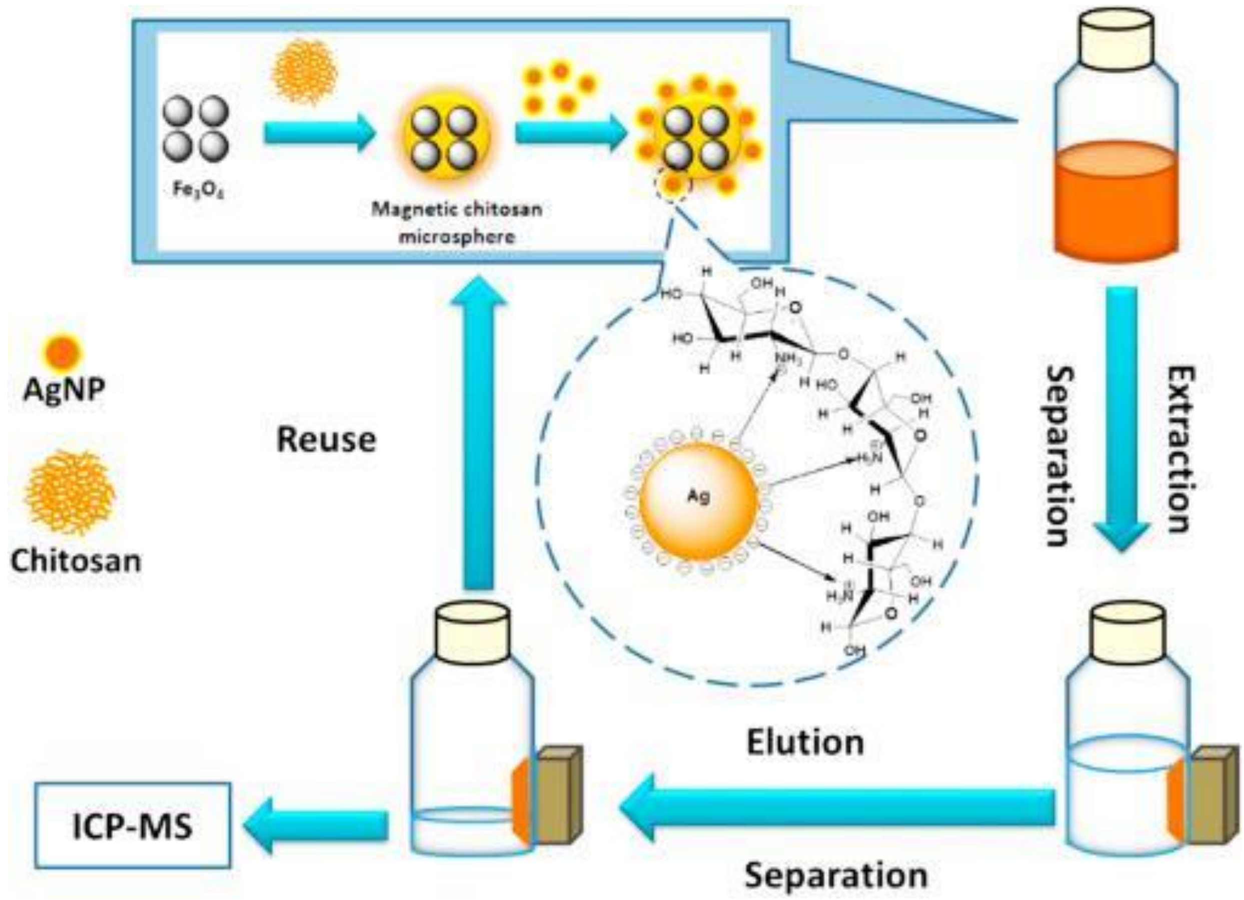

Fig. 10 Schematic synthesis of magnetic chitosan microspheres sorbent and their application as MSPE sorbent of silver nanoparticles waste waters samples prior to the analysis of ICP-MS. Reprinted from Tolessa et al. (2017) with permission from Elsevier. License Number: 5086241063395.