Review Article

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Review on functionalized magnetic nanoparticles for the pretreatment of organophosphorus pesticides

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Abstract: Organophosphorus pesticides are currently extensively applied on the control of agricultural and forestry pests. The number of poisonings and deaths caused by organophosphorus pesticides are increasing year by year. Because of the complex matrix, numerous interfering substances, and low poison content, pretreatment methods are crucial for the detection and analysis of such cases. As an adsorbent used for pretreatment, magnetic nanoparticles have the advantages of simple preparation, convenient modification, superparamagnetism, and hydrophilicity. Microextraction can be performed with small amount of magnetic nanoparticles in a short time, and the target substances can be separated with an external magnetic field. In this paper, the latest research achievements are reviewed. Based on the introduced characteristics and preparation methods of magnetic nanoparticles, this paper outlines the applications of different functionalized magnetic nanoparticles for the pretreatment of organophosphorus pesticides and predict the potential research prospects.

Keywords: organophosphorus pesticide, magnetic nanoparticle, pretreatment, functionalized materials

1 Introduction

Organophosphorus pesticides (OPPs), which are organic phosphates or thiophosphates, are used for the control of agricultural and forestry diseases and insect pests. Based on the characteristics of high efficiency, broad spectrum of activity, and low levels of residues, OPPs have been frequently used as pesticides [1]. However, death cases of suicide, homicide, poisoning, and other incidents caused by OPPs have become a common social concern. According to the statistics of World Health Organization, almost one million poisoning cases are related to OPPs every year [2,3]. Although detection methods for OPPs have been developed in recent years [4–6], simpler and more efficient pretreatment technologies are needed for rapid detection and identification since the target substances are generally distributed in complex substrates, such as water environment, fruit and vegetable products, and biological tissues [7–9]. Magnetic nanoparticles (MNPs) with superparamagnetism can serve as adsorbents in the pretreatment process. With an external magnetic field, the adsorbents and substrates can be rapidly separated, free of a large amount of organic solvent, special equipment, and slow and time-consuming processes, which are the shortcomings of traditional pretreatment methods. The samples have not been filtered or centrifuged which makes the whole process more convenient and faster [10–12]. In addition, MNPs have the characteristics of large specific surface area, good compatibility, great reusability, excellent adsorption and extraction performance, and convenient surface modification with a variety of materials to improve versatility and selectivity. In the view of the aforementioned advantages, MNPs have attracted tremendous attention in the pretreatment methods for the extraction of OPPs [13,14]. In this paper, the characteristics and preparation methods of MNPs are summarized, and the applications of different modified MNPs for the extraction of OPPs are emphasized for the future studies in this field.

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2 Overview of magnetic nanoparticles

As important nanomaterials, MNPs have been widely applied in catalysis, biological separation and purification, medical diagnosis, environmental protection, and other fields [15–22]. MNPs can be prepared with iron, cobalt, nickel, and other elements in different chemical forms and phases, such as metal oxides (Fe_3O_4 and γ-Fe_2O_3), composite metal oxides ($NiFe_2O_4$, $MgFe_2O_4$, $MnFe_2O_4$, and $CoFe_2O_4$), pure metals (Fe, Co, and Ni), and alloys ($CoPt_3$ and FePt) [23]. Among them, Fe_3O_4 MNPs have become the most popular magnetic nanomaterials for the pretreatment of samples containing OPPs since they have the advantages of convenient preparation and modification, superparamagnetism, large specific surface area, good hydrophilicity, and low toxicity [24].

The preparation approaches of Fe_3O_4 MNPs include physical, chemical, and microbial methods [25]. The physical methods include gas-phase deposition, electron beam etching, and so on. The chemical methods include coprecipitation, hydrothermal synthesis, sol–gel, oxidation etching, electrochemistry, sonochemical decomposition, and so on. The biosynthesis can be realized with fungi, bacteria, cultures with mixed microorganisms, etc. Considering the complexity and compatibility of substrates, operation difficulty, preparation cost, particle-size distribution, and magnetic saturation strength, coprecipitation and hydrothermal synthesis methods are prevalent in the recent research on Fe_3O_4 MNPs for the pretreatment of samples containing OPPs.

Surface chemical properties of MNPs can be modified to generate new functional groups and effectively improve stability, so the MNPs could have the adsorption capacity for target compounds [26–30]. In the pretreatment methods for the extraction of OPPs, core-shell-structured MNPs are most commonly fabricated by modification methods [31]. Coating a layer of material on the surface of MNPs can effectively prevent the MNPs from agglomeration and erosion by the external environment and this can be done via surface deposition or immersion methods. Moreover, MNPs can be further modified with the functional groups on the layer [32,33]. The common materials for the functionalization of MNPs for the pretreatment of samples containing OPPs include carbon-based materials, inorganic materials, polymer materials, metal organic framework materials, mixed micelles, ionic liquids (ILs), and so on. These different materials show different adsorption characteristics.

3 Applications of MNPs functionalized with different materials in the pretreatment of OPPs

3.1 Carbon-based materials

Carbon materials have the characteristics of large specific surface area, high adsorption efficiency, and good hydrothermal stability [34–36]. The coating of carbon materials on MNPs can improve the stability and lead to new superficial properties [37,38]. Glucose (Glc), as a kind of carbon material, was uniformly coated on the surface of Fe_3O_4 MNPs. The core-shell Fe_3O_4@Glc particles were obtained by a hydrothermal method [39]. Fenitrothion, diazinon, and ethion in tap water samples could be fast isolated with the Fe_3O_4@Glc particles. These particles can be readily prepared and conveniently applied, but they are usually poorly dispersed, leading to low recovery rates. Maddah's group [40] also studied the adsorption capacity of octadecyl-functionalized materials for OPPs. Octadecylsilane-modified Fe_3O_4 MNPs were prepared by concerted coprecipitation, sol–gel polymerization, and alkylation procedures. Due to high hydrophobicity of C_{18} groups, trace amounts of diazinon and fenitrothion could be adsorbed on this material. Nie et al. [41] adopted mercapto-olefin click chemistry to bind octadecyl mercaptan with MNPs functionalized with vinylphosphoric acid (VPA). The synthesis process is illustrated in Figure 1. This material contained not only hydrophobic C_{18} groups, but also phosphate groups to enhance the selectivity.

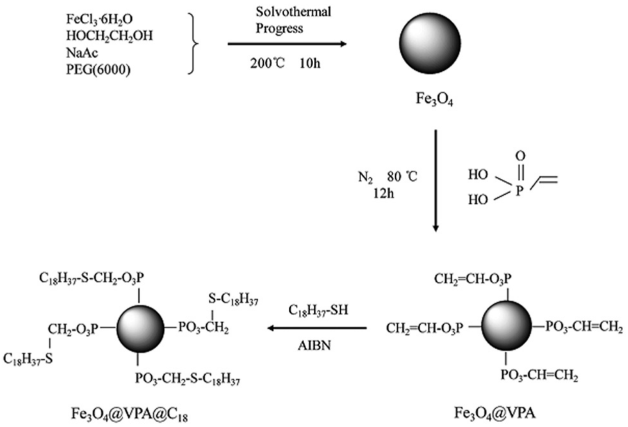

Figure 1: Schematic preparation procedure of magnetic composites Fe_3O_4@VPA@C_{18} [41].

Compared to the research results of Maddah et al., the enrichment factors for OPPs were significantly improved, and this material could be employed in more complex water environment.

Graphene (G), a honeycomb-like monolayer nanomaterial, is composed of sp^2 hybridized carbons. It has good stability and a large specific surface area, and it is rich in delocalized π bonds. By oxidizing G, graphene oxide (GO) with a large number of hydroxyl and carboxyl groups can be obtained. As an adsorbent, GO can effectively enrich and extract organic compounds through hydrogen bonding, hydrophobic, electrostatic, and π–π stacking interactions [42,43]. Nodeh et al. [44] studied the extraction of polar and nonpolar OPPs from milk with Fe_3O_4@G modified with cyanopropyl triethoxysilane (CNPrTEOS) as the adsorbent. Hydrophobic interactions occurred between G and nonpolar chlorpyrifos and diazinon, and strong π–π interactions took place between the delocalized electrons in G and benzene rings of both pesticides. In addition, CNPrTEOS interacted with polar phosphoramides and dimethoate molecules through dipole-dipole and hydrogen-bond interactions. The adsorption mechanism is shown in Figure 2. The enrichment factors for these four OPPs reached 2400. This research group [45] also modified Fe_3O_4@G with tetraethoxysilane methyltrimethoxysilane (TEOS-MTMOS) to prepare a magnetic sol–gel hybrid adsorbent. The pretreatment and detection procedures are shown in Figure 3. Compared to Fe_3O_4@G-CNPrTEOS, the enrichment factors for these four OPPs were largely declined by using Fe_3O_4@G-TEOS-MTMOS as the extraction reagent. This is because Fe_3O_4@G-CNPrTEOS can bind with OPPs through five functional groups, especially the hydrophilic –CN groups in CNPrTEOS, which can interact with the polar P═S, P═O, and –Cl in amine phosphate and dimethoate to enhance the adsorption capacity for OPPs. Mahpishanian et al. [46] reported that the reduced GO sheets anchored with Fe_3O_4 MNPs simultaneously self-assembled into a 3D hydrogel with interconnected networks driven by combined hydrophobic and stacking interactions, then a black magnetic 3D-G aerogel was generated via vacuum freeze drying. The aerogel had good magnetic properties, three-dimensional nanoporous structure, and a larger specific surface area. The number of OPPs species extractable with this material was much greater than those with other materials, and the recovery rates were higher than those with Fe_3O_4 MNPs and 2D-G-Fe_3O_4 materials. Mahpishanian et al. [47] and Wang et al. [48] studied the extraction of OPPs with covalently bonded MNPs-G composites, and the results showed that the stability of the material was significantly improved.

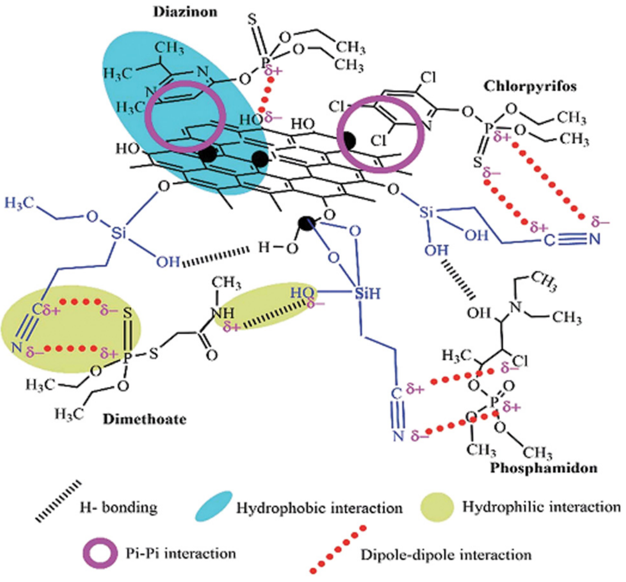

Figure 2: Adsorption mechanism of OPPs on Fe_3O_4@G-CNPrTEOS [44].

3.2 Inorganic materials

Hydroxyapatite (HA) is an important inorganic component of human and animal bones. The crystal surface of HA and its derivatives have positively charged regions (C sites) composed of cations and negatively charged regions (P sites) composed of phosphate ions. Therefore, they are often used as good adsorbents for a variety of anionic and cationic compounds [49–51]. Chahkandi et al. [52] synthesized potassium-substituted hydroxyapatite (KHA) with a sol–gel method. After mixing with Fe_3O_4 MNPs, KHA/Fe_3O_4 magnetic nanocomposites were prepared with a hydrothermal method. The nanocomposites were used as the adsorbent to extract and preconcentrate five OPPs, such as diazinon, fenitrothion, and fenthion, from three water samples (tap water, wastewater, and river water) and three fruit juice samples (apple juice, grape juice, and peach juice). Compared to elevated temperature–dispersive liquid-liquid microextraction (ET-DLLME), single-drop microextraction (SDME), QuEChERS, and other pretreatment methods, magnetic solid-phase microextraction based on KHA/Fe_3O_4 nanocomposite is an ultrasensitive and reproducible method, which can be exploited as a routine method for the pretreatment of samples containing OPPs. This is due to the positive and negative charges on HA surface and introduction of K ions, the biochemical regulation and nucleation ability of apatite were greatly improved, and the binding with OPPs was promoted. Therefore, this method exhibits a relatively lower detection limit and a relatively wider linear range.

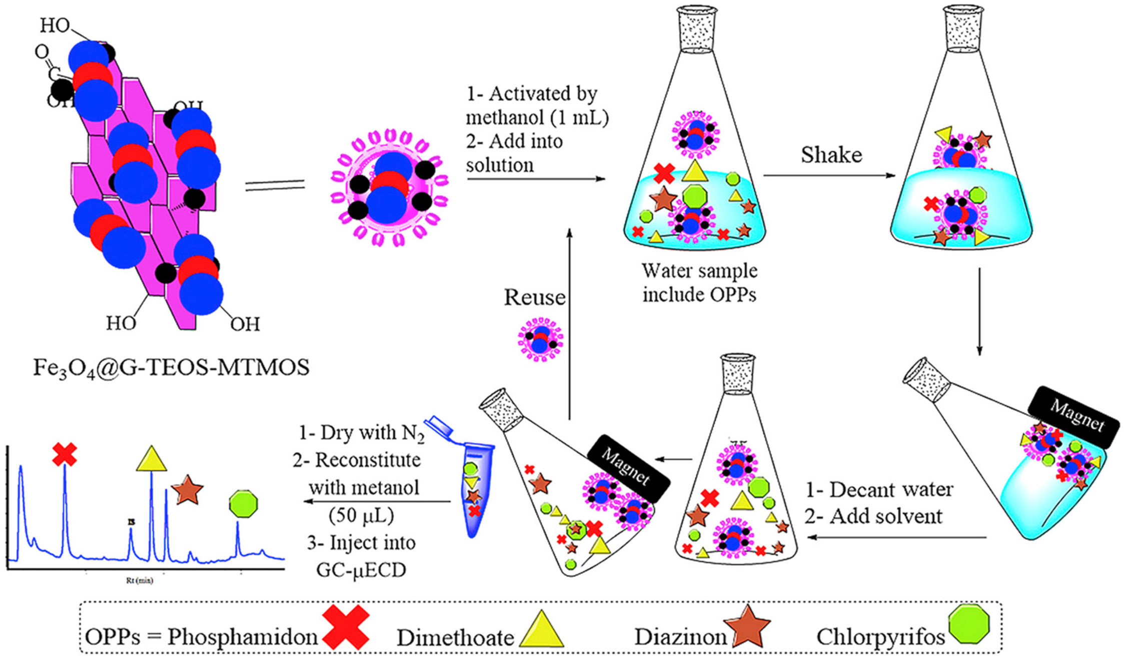

Figure 3: Pretreatment and detection of OPPs with Fe_3O_4@G-TEOS-MTMOS [45].

Hydrotalcites (LDHs) are intercalated bimetallic hydroxides with abundant unsaturated functional groups on the surface. They have the advantages of high porosity, large specific surface area, and strong anion exchange capacity. LDHs have been extensively applied in the extraction and enrichment of toxic substances such as OPPs [53,54]. Based on the template of core-shell polymerization structure, Du et al. [55] synthesized a three-layered $NiFe_2O_4$@polydopamine (PDA)@Mg/Al-LDHs nanocomposite by coating Mg/Al LDHs on the outer layer of $NiFe_2O_4$@PDA. The results showed that the average extraction rate for methamidophos, parathion, and phoxim reached 84.9%, approximately 30% and 19% higher than those with $NiFe_2O_4$ and $NiFe_2O_4$@PDA, respectively. The extraction capacity was greatly increased.

3.3 Polymer materials

Polymer-modified MNPs have larger specific surface areas, better stability, and biocompatibility and are rich in functional groups, which thus provide abundant adsorption sites to widen their functions as well as application fields. In recent years, OPPs' extraction studies with MNPs modified with polymer materials mainly focus on natural and synthetic polymers. The former focuses on humic acid and the latter focuses on hyperbranched and molecularly imprinted polymers (MIPs).

Humic acid is a macromolecular organic substance formed by microbial degradation of animal and plant debris. Humic acid contains a large number of functional groups (carboxyl, hydroxyl, amino, quinone, etc.) and hydrophobic aromatic rings [56]. Janoš et al. [57] prepared versatile magnetic humic-acid adsorbents by bonding humic acid with MNPs. The hydrophobic humic acid provided adsorption sites for weakly polar OPPs, and the acidic functional groups in humic acid could interact with ionized groups in OPPs. After separation in a magnetic field, methyl parathion, parathion, and chlorpyrifos in water could be removed, and heavy metals and phosphates in water could be also removed via similar methods.

Hyperbranched polymers, a kind of polymer materials with a highly branched three-dimensional dendrite structure, have controllable molecular weight and can be potentially applied in many fields [58,59]. Among hyperbranched polymers, polyamide-amine hyperbranched macromolecules contain various types of amino groups and many organic branched chains, thus a variety of OPPs can be effectively adsorbed on these macromolecules. Wang et al. [60] successfully prepared a magnetic hyperbranched polyamide with Fe_3O_4 MNPs as the core. This magnetic material was taken as the adsorbent for detection of OPPs in orange juice by gas chromatography coupled with mass spectrometry. Compared with traditional amino-containing and C_{18} materials, the magnetic hyperbranched polyamide was fast and convenient to operate (the structures of these three materials are shown in Figure 4). Additionally, its detection performance for 11 OPPs was better.

MIPs are copolymers composed of target molecules (templates) and functional and cross-linked monomers containing vinyl or acrylic groups. During copolymerization, the monomers can interact with the functional groups in templates through covalent or non-covalent bonds [61,62]. When the templates are removed, binding sites that match with spatial configurations of the templates are formed within MIPs, and these binding sites can specifically recognize these templates and their analogues. The MIPs possess functions similar to those of natural receptors, such as enzymes or antibodies [63,64]. Masoumi et al. [65] fabricated magnetic molecularly imprinted polymers (MMIPs) by molecular imprinting technology with aminated Fe_3O_4 MNPs as the carrier, three OPPs as the template, copolymer of methyl methacrylate and maleic anhydride as the functional monomer, and triethylenetetramine as the cross-linking agent. The procedures of preparation and adsorption are shown in Figure 5. Phoxim, chlorpyrifos, and diazinon could be specifically adsorbed on this material. Kumar et al. [66] prepared MMIPs by a precipitation method with acrylic acid as the monomer and ethylene glycol dimethacrylate as the cross-linking agent. This material has strong specific adsorption capacity for chlorpyrifos in the presence of quinclofos and triazophos with similar structures to the target. The procedures of preparation of MMIPs and selective extraction of chlorpyrifos are illustrated in Figure 6. Although MMIPs showed high selectivity, the performance of regenerated material was not sufficient. After reusing more than 3–4 times, the recovery rates decreased significantly, so the material is not commercially favorable.

3.4 Metal organic framework materials

Metal organic frameworks (MOFs) are hybrid porous crystal materials formed by the self-assembly between metal ions or clusters (center) and organic ligands through coordination bonds [67–70]. With features of unique pore structures, large specific surface areas, and adjustable pore sizes, MOFs have become ideal adsorption and separation materials for various substances [71,72].

Zhang et al. [73] prepared a magnetic MOF composite material with an *in situ* growth method. Six OPPs, such as dichlorvos, dimethoate, and methyl parathion, can be extracted from biological samples with this material. In detail, Fe_3O_4 MNPs were synthesized by a coprecipitation method, and then the MNPs were reacted with $FeCl_3{\cdot}6H_2O$ and terephthalic acid to yield the Fe_3O_4/MIL-101(Fe) composite, in which the Fe_3O_4 MNPs uniformly encapsulated. The images of scanning electron microscopy and transmission electron microscopy are shown in Figure 7. In this study, magnetic nanomaterials were applied to extract OPPs from complex biological samples such as hair and urine for the first time. The results showed that this material could resist the interferences with matrix, which is

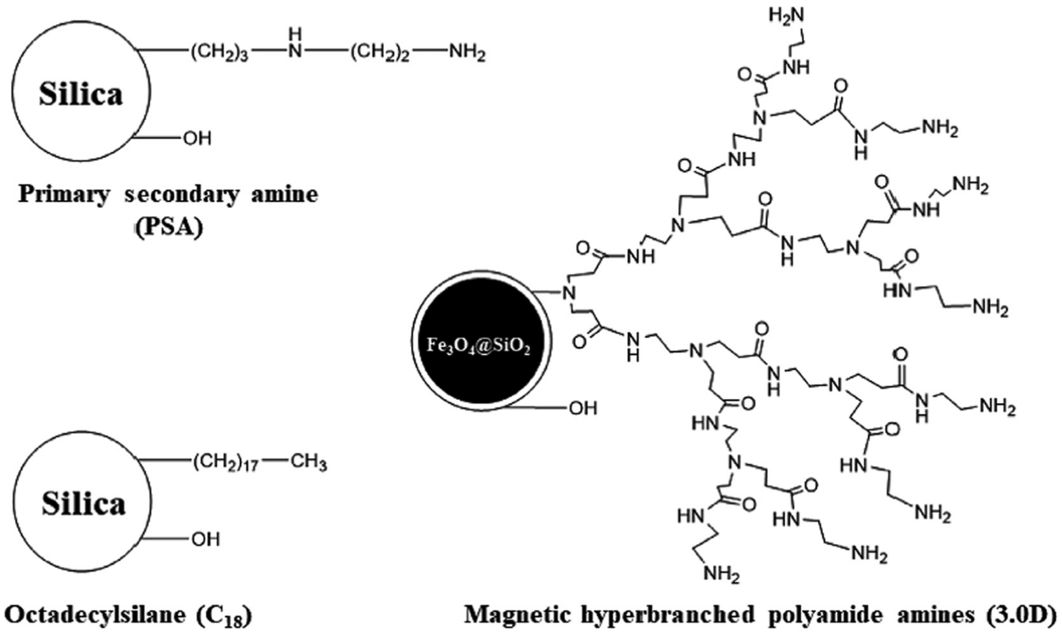

Figure 4: Structures of amino, C_{18}, and magnetic hyperbranched polyamide materials [60].

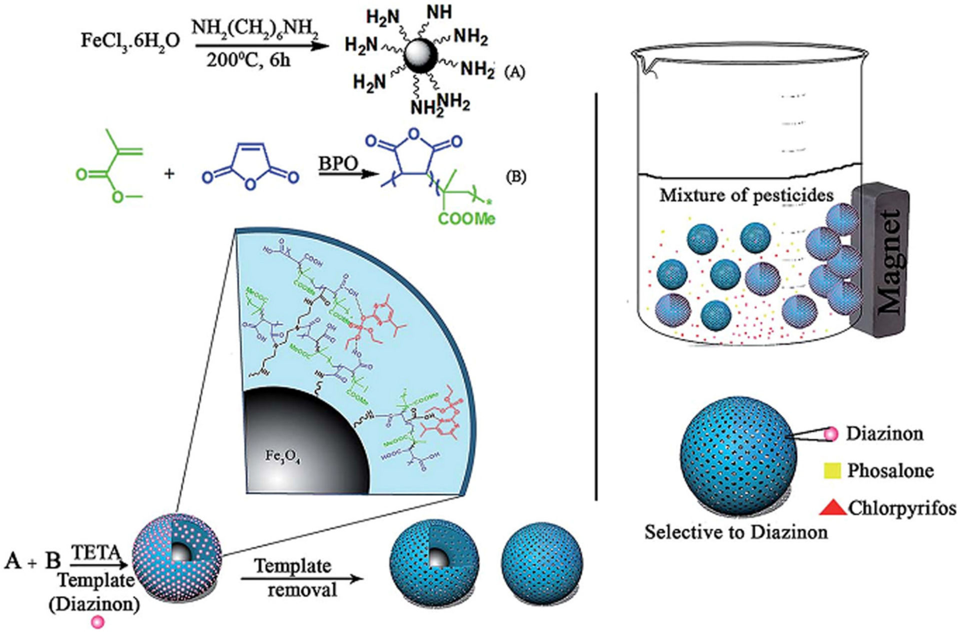

Figure 5: Schematic illustration of the preparation of magnetic MIPs and adsorption procedure [65].

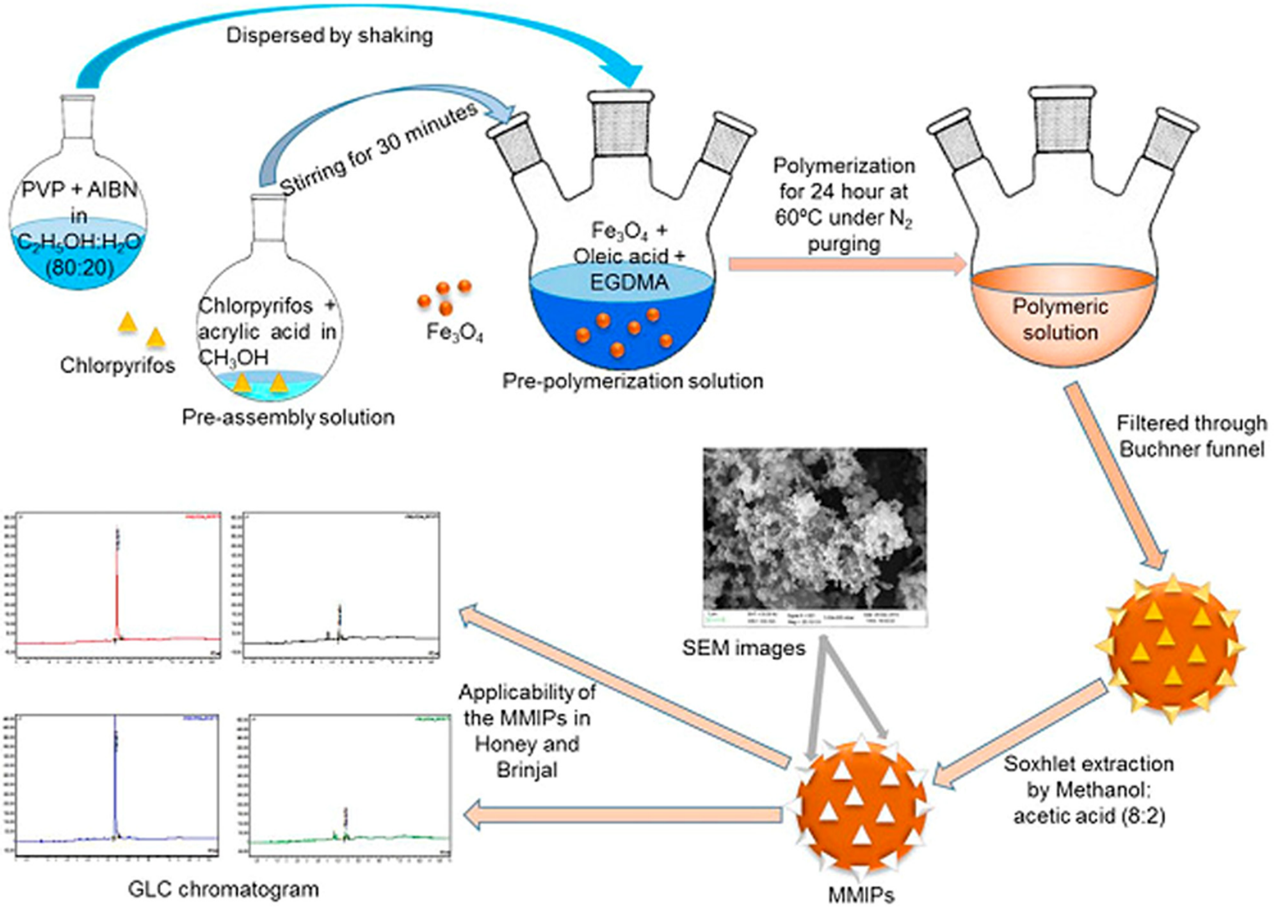

Figure 6: Schematic illustration of the preparation of MMIPs and selective extraction of chlorpyrifos [66].

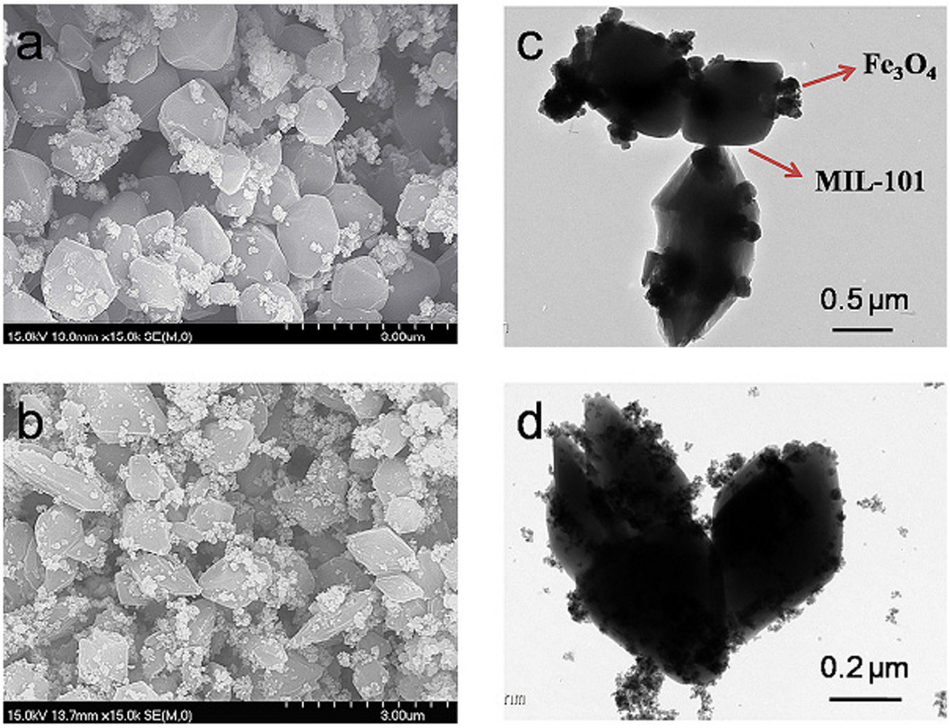

Figure 7: SEM images of Fe_3O_4/MIL-101 composites with Fe_3O_4 loading amounts of 50 mg (a) and 250 mg (b); TEM images of Fe_3O_4/MIL-101 composites with Fe_3O_4 loading amounts of 50 mg (c) and 250 mg (d).

beneficial for the extension of its application scope. Li et al. [74] prepared a magnetic nanoporous carbon material with Zn/Co-MOFs as the precursor by a simple one-step carbonization method. OPPs could be effectively extracted with this material through π–π and hydrophobic interactions. Building on this material, a magnetic solid-phase extraction technique coupled with gas chromatography and flame photometry was established for the quantitative analysis of OPPs in fruits. The extraction and total detection time were short, effectively simplifying the operation procedures and reducing the cost for reagent consumption and preparation.

3.5 Mixed micelles

A micelle structure refers to the shape of aggregates formed by a surfactant and spatial distribution of molecules when the concentration of surfactant exceeds the critical value [75]. It was reported that ionic surfactants could be adsorbed on the surfaces of MNPs via electrostatic interactions [76]. When the concentration of surfactant reaches a certain value, a proportion of surfactant, in the form of monolayer molecules, combines with MNPs to form hydrophobic semi micelles, and nonionic organic compounds can be captured through hydrophobic interactions. The other proportion, in the form of bilayer molecules, combines with MNPs to form ionic micelles, and the target substances can be captured through electrostatic interactions, thus forming MNPs modified with mixed micelles. Based on this material, the magnetic mixed-micelle solid-phase extraction technology has promising application prospects in the separation and extraction of organic matter and metal ions and purification of biological products [77–79].

Li et al. [80] prepared $Fe_3O_4@TiO_2$ NPs by mixing Fe_3O_4 MNPs with $TiCl_4$ following a hydrothermal synthesis method. Further, the $Fe_3O_4@TiO_2$ NPs were modified with surfactant cetyltrimethylammonium bromide (CTAB) under pH neutral conditions to prepare mixed-micelle-modified MNPs. Chlorpyrifos, dimethoate, and trichlorfon could be captured with this material. Under the preferable condition, the ratio between water dosage, $Fe_3O_4@TiO_2$ dosage, and CTAB dosage was 5,000:1:1, in which the adsorption capacity of mixed-micelle-modified MNPs reached a maximum. In practical applications, trace amounts of OPPs can be detected by this method, and water samples with a large volume can be also analyzed. Similarly, Moliner-Martinez et al. [81] modified $Fe_3O_4@SiO_2$ with CTAB to prepare mixed-micelle-modified MNPs, which served as the adsorption phase to establish intraductal online magnetic solid-phase microextraction coupled

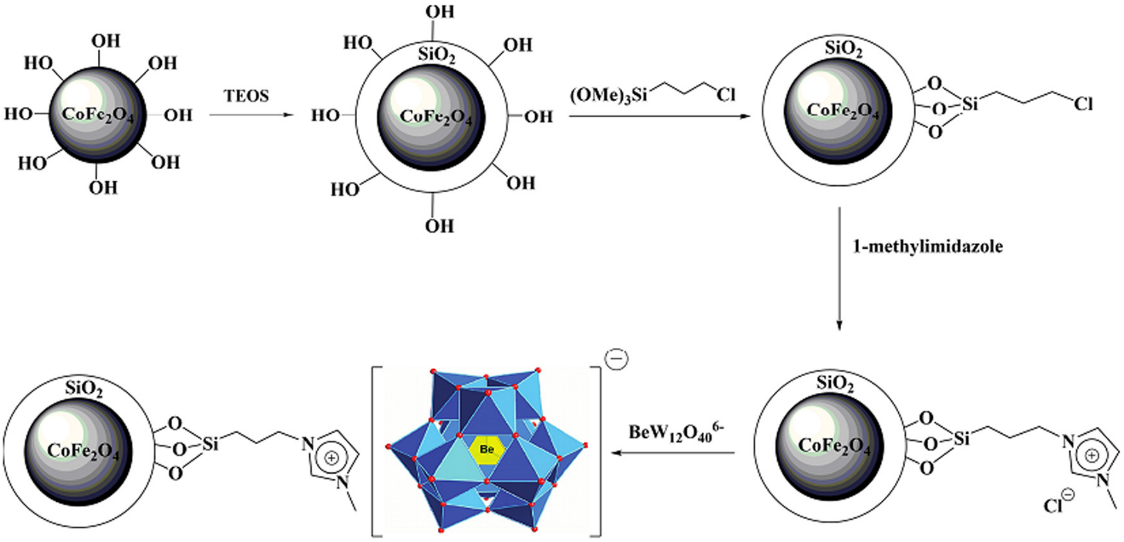

Figure 8: Schematic illustration of the synthesis of $BeW_{12}O_{40}$-ILSCCFNPs [87].

with capillary liquid chromatography and diode array detection. With this method, the detection of trace amounts of chlorfenvinphos and chlorpyrifos in wastewater samples was achieved. This method breaks the limitations of complicated traditional solid-phase extraction, and the recovery rate was greatly improved compared to other intraductal solid-phase microextraction techniques. Hamedi et al. [82] synthesized magnetic-core micelles as the adsorbents by encapsulating aminated Fe_3O_4 MNPs with sodium dodecyl sulfate, and the adsorbents were used in the corresponding ultrasound-assisted dispersion solid-phase extraction technology to rapidly extract and enrich three OPPs. The extraction performance was better than those of other pretreatment technologies such as supramolecular solvent microextraction and ultrasound-assisted dispersion liquid-liquid microextraction.

3.6 Ionic liquids

ILs, composed of organic cations and organic (inorganic) anions, are a kind of organic and soluble salt at room temperature. Most of ILs have good chemical stability, thermal stability, and electrical conductivity. By adjusting the composition of anions and cations in ILs, the adsorption performance can be changed for bonding with specific target substances [83]. Polymeric ionic liquids (PILs) possess the characteristics of ILs monomer and polymer and thus have larger surface areas and rich binding sites, effectively enhancing the adsorption performance. Additionally, high viscosity of ILs prohibits their leaching, thus improving their reusability [84].

Zheng et al. [85] performed the reaction between 1-vinylimidazole and bromohexane at equal molar ratio in isopropanol for 16 h in N_2 atmosphere at 60°C. Then, the mixture was cooled to room temperature, and isopropanol was removed by vacuum evaporation to yield the product 1-vinyl-3-hexylimidazolium bromide ionic liquid. This ionic liquid was used as a functional material to combine with vinyl-modified $Fe_3O_4@SiO_2$ through copolymerization to prepare PILs-functionalized MNPs. With this material, parathion, phoxim, fenthion, and temephos in tea drinks could be extracted and enriched, and the recovery rates declined by only 10% after 20 reuses. The regenerated material showed good performance. Yang [86] synthesized hydrophilic IL-immobilized MNPs with 3-chloropropyltrimethoxysilane as the coupling agent and *N*-methylimidazole as the ligand under microwave irradiation. Then, the Cl^- ions in this IL were replaced by lithium salt of bis(trifluoromethanesulfonate)imine to improve hydrophobicity of this IL. With this material, methyl parathion, parathion, and phoxim in water samples could be adsorbed. Amiri et al. [87] synthesized imidazole-functionalized silicon-cobalt-coated ferrite MNPs ($BeW_{12}O_{40}$-ILSCCFNPs) following the procedures shown in Figure 8. Because $BeW_{12}O_{40}$ contained many functional groups, the number of active adsorption sites increased. In combination with GC-FID, the OPPs in water and juice samples could be detected accurately. The enrichment factor for profenofos reached 2,676, showing the optimum extraction performance among all the results reported. From the perspective of sensitivity, the lower detection limit of this method was relatively low with the same detector.

Table 1: Different modified MNPs along with their absorption capacities used for OPPs

Type	Absorbent	Kinds of OPPs	Matrix	EF	LOD	Recovery (%)	Ref.
Carbon materials	Fe_3O_4@Glc	3	Water	174–205	97–124 (pg/mL)	60–92	[25]
	Fe_3O_4@TEOS@C_{18}	2	Water	172–184	14–19 (pg/mL)	85–92	[26]
	Fe_3O_4@VPA@C_{18}	4	Tea	420–455	10–50 (pg/mL)	81.7–92.8	[27]
	Fe_3O_4@G-CNPrTEOS	4	Milk	2,400	10–600 (pg/mL)	82–94	[30]
	Fe_3O_4@G-TEOS-MTMOS	4	Water	109–1,247	1.4–23.7 (pg/mL)	83–105	[31]
	3D-G/Fe_3O_4	8	Juices	473–510	1.2–5.1 (pg/mL)	86.6–107.5	[32]
	Fe_3O_4@SiO_2@GO-PEA	5	Water, fruits, vegetables	483–512	20–100 (pg/mL)	90.4–108	[33]
	Fe_3O_4@SiO_2@G	5	Water	—	16–33 (ng/mL)	90.2–102.9	[34]
Inorganic materials	KHA/Fe_3O_4	5	Water, juices	—	30–220 (pg/mL)	89–99.7	[37]
	$NiFe_2O_4$@PDA@Mg/Al-LDHs	3	Juices	—	60–130 (pg/mL)	81.8–94.4	[40]
Polymer materials	Fe_3O_4@SiO_2@PAMAM	11	Juices	—	0.74–8.16 (ng/g)	75.2–116.2	[45]
	Fe_3O_4@ poly(MMA-*co*-MA)	3	Water	172–196	—	—	[50]
	Fe_3O_4@AA/EGDMA	1	Honey, brinjal	—	10,000 (pg/mL)	86.2–102.3	[51]
Metal organic framework	MIL-101(Fe)/Fe_3O_4	6	Hair, urine	6–65	210–2,280 (pg/mL)	74.9–94.5	[54]
	Zn/Co-MOFs/Fe_3O_4	5	Fruits, water	56.2–77.9	18–45 (pg/mL)	84–116	[55]
Mixed micelles	Fe_3O_4@TiO_2@CTAB	3	Water	1,000	26–30 (pg/mL)	88.5–96.7	[61]
	Fe_3O_4@SiO_2@CTAB	2	Water	—	10–50 (pg/mL)	89–103	[62]
	Fe_3O_4@SiO_2@SDS	3	Water, juices	134–155	80–130 (pg/mL)	84–97	[63]
Ionic liquids	Fe_3O_4@SiO_2@PILs	4	Tea	84–161	10 (pg/mL)	81.4–112.6	[66]
	Fe_3O_4@SiO_2@ILs	3	Water	—	543–945 (ng/mL)	81.2–94.9	[67]
	$CoFe_2O_4$@SiO_2@ILs-$BeW_{12}O_{40}$	5	Water, juices	2,100–2,676	20–60 (pg/mL)	70–89.2	[68]

EF: enrichment factor, LOD: limit of detection, Glc: Glucose, TEOS: tetraethyl orthosilicate, VPA: vinyl phosphonic acid, G: graphene, CNPrTEOS: cyanopropyltriethoxysilane, MTMOS: methyltrimethoxysilane, 3D: three-dimensional, GO: graphene oxide, KHA: potassium-substituted hydroxyapatite, PDA: polydopamine, LDHs: hydrotalcites, PAMAM: hyperbranched polyamide amine, MMA: methyl methacrylate, MA: maleic anhydride, AA: acrylic acid, EGDMA: ethylene glycol dimethacrylate, MOFs: metal organic frameworks, CTAB: cetyltrimethylammonium bromide, SDS: sodium dodecyl sulfonate, PILs: polymeric ionic liquids, ILs: ionic liquids.

4 Performances of different functionalized MNPs for the extraction of OPPs

For comparison, the studies on the extraction of OPPs with different functionalized MNPs in recent years are listed in Table 1. The different functionalized materials and MNPs modification methods have great influence on the target substances extraction, enrichment factor, detection limit, and extraction recovery rate. As shown in Table 1, the modification principally includes core-shell methods, which are prevalent, and hybrid methods. Furthermore, under the condition of the same modifier, the MNPs synthesized by the core-shell methods exhibit higher enrichment factors for OPPs. Density of functional groups on the surface of an MNP modified with a hyperbranched polymer (Fe_3O_4@SiO_2@PAMAM) is high, and most of OPPs types can be adsorbed. Therefore, this MNP can be used for broad-spectrum screening of OPPs. Moreover, due to the large number of amino groups on this material, the electrostatic adsorption interaction is strong, thus reducing the specific adsorption capacity. Molecular imprinting can improve the specific adsorption capacities of MNPs and reduce the influence of matrix, but the development and application of this technique are restricted by difficult preparation of template and functional monomers complex, heterogeneous binding sites, and easy loss of template molecules. Although the recoveries of OPPs in practical samples extracted with functionalized MNPs are qualified, most of the samples studied are tap water, fruit juice, tea, and other water samples as well as some fruit samples. These substrates are relatively simple. OPPs can be extracted from hair, urine, and other biological samples with complex composition with MIL-101(Fe)/Fe_3O_4, but the enrichment factor, detection limit, and recovery rate should be further enhanced. G-modified MNPs exhibited better extraction performance with higher EF values and lower detection limits, compared to other modifiers. Thus, G-modified MNPs can be used in the detection of trace amounts of OPPs and have commercial application prospects in food safety control, water quality monitoring, environmental safety monitoring, and other fields. With a new Keggin-type anionic polyoxometalate $[BeW_{12}O_{40}]^{6-}$, the enrichment factor of ionic liquid-modified MNPs can be significantly improved and should be further investigated.

5 Conclusion and prospects

As a novel superparamagnetic nanomaterial, functionalized MNPs have attracted extensive attention from researchers. As an adsorbent in the pretreatment of samples containing OPPs, functionalized MNPs can overcome difficulties in extraction time, operation process, and enrichment efficiency compared to traditional extraction technologies and possess many unique advantages. In this paper, the related literature from the last decade was reviewed. Based on the overview of the characteristics, types, and synthesis methods of MNPs, the applications of MNPs modified with different functional materials for the pretreatment of samples containing OPPs were summarized. It is demonstrated in the literature that the extraction performance of MNPs mainly depends on the type of surface modification, which improves the specific surface area, stability, and compatibility of MNPs and provides abundant functional groups. Therefore, functionalized MNPs have high adsorption capacity for one or more OPPs through hydrophobic, electrostatic, π–π conjugation, hydrogen bonding, and other interactions.

To date, the research on pretreatment of samples containing OPPs with functionalized MNPs has just begun. With the continuous development and use of new pesticides, increased attention on food, and environmental safety, as well as more and more complexed substrates, the requirements on detection techniques of OPPs and other poisons and drugs will be more stringent. Therefore, for the exploration of pretreatment methods with MNPs with higher sensitivity and accuracy, better applicability, greater convenience, and higher throughput, the following points should be further investigated: (1) to develop new functional materials to improve stability of physical and chemical properties of MNPs, anti-interference ability toward the substrate, and specific adsorption capacity for target compounds; (2) to develop new synthesis methods to achieve standardized mass production, environmental friendliness, and recycling; (3) to study the adsorption mechanisms via theoretical simulations and physical-chemical characterizations to explore influence of the microstructures of functionalized MNPs on the overall properties of composite materials for effective improvement of the comprehensive performance; (4) to develop technologies combining magnetic pretreatment technologies with other detection instruments and establish miniaturized, automated, multichannel analysis methods.

In the situation of ultra-low concentrations of pollutants, highly complex sample matrix, and varying onsite detection environment, efficient and reliable sample pretreatment technologies are required. We believe that the combinations of innovative functional magnetic nanomaterials and fast detection technologies will promote the development of intelligent sensors with good adsorption performance, which will be greatly applicable in the fields of environmental monitoring, food safety, public safety, biomedicine, and so on.

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