Synthesis of Fe₃O₄-based Magnetic Nanocomposites and Application in Pesticide Residue Detection

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Abstract. Magnetic nanomaterials are a new kind of nanomaterials with great potential application value. Recently, there have been many reports about the combination of magnetic nanomaterials and agricultural residue detection technology to establish a new detection method. Due to the special super paramagnetic, the large number of surface active sites, easy separation and recovery, the Fe₃O₄ magnetic nanocomposite material is commonly used in complex sample pretreatment on extraction and enrichment of the target compounds. By combining with the target substance in complex sample matrix and under the action of external magnetic field, the material can quickly, simply and efficiently enrich and extract trace substances in the sample. This paper mainly introduces the application of Fe₃O₄-based magnetic nanocomposites in the detection of pesticides and the main preparation methods of Fe₃O₄-based magnetic nanocomposites, including coprecipitation, microemulsion, photothermal chemistry and ultrasonic decomposition, hydrothermal reaction and sol-gel method.

1. Introduction

Sample pretreatment is a very important process in pesticide residue detection. It not only affects the selection of subsequent detection methods, but also determines the reliability and accuracy of the test results, as well as the time and cost of analysis. Appropriate sample pretreatment can also effectively prevent the damage of analytical instruments. In recent years, magnetic solid phase extraction (MSPE) has attracted much interest. It has been widely used in the separation and enrichment of samples in environmental, food, biological, pharmaceutical and other fields. Comparing with traditional solid phase extraction technology, MSPE can avoid many problems in separation processing, including complicated operation and adsorption column blockage[1]. It makes the separation processing easier and faster. Among them, due to the special magnetic properties, Fe₃O₄-based nanomaterials have attracted much attention. It can be more stable and widely used in the matrix by functionalized modification with other materials. Surface-modified magnetic core-shell nanoparticles have some excellent physicochemical properties, such as good superparamagnetism, large specific surface area and a large number of exposed surface active sites. These properties make the Fe₃O₄-based magnetic nanomaterials have high adsorption efficiency, easy recycling and high separation efficiency. Through external magnetic field
separation, the trace analyte can be easily extracted from the the multi-component matrix and the particles are easy to recycle and reuse, which would substantially reduce the treatment cost[2]. In this paper, we want to summarize recent studies that address the main synthesis methods of Fe₃O₄-based magnetic nanocomposites and their applications in the detection of pesticides.

2. Synthesis of Fe₃O₄-based Magnetic Nanocomposites

2.1. Chemical coprecipitation
Coprecipitation is a simple method to synthesize magnetic nanomaterials. Metal oxides and ferrites are most commonly synthesized by this method. Fe₃O₄ magnetic nanomaterials is usually synthesized by adding alkali to Fe²⁺/Fe³⁺ aqueous solution at room temperature or high temperature in inert atmosphere. The size, shape and composition of magnetic nanoparticles can be controlled by different salts (such as chloride, nitrate, sulfate), the ratio of Fe²⁺ to Fe³⁺, reaction temperature, ionic strength and pH value etc. Ferroferric oxide is usually prepared by coprecipitation in aqueous media. The chemical equation is as follows:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$$

Er, EO[3] and others have successfully synthesized Fe₃O₄/reduced graphene oxide nanocomposites by one-step chemical coprecipitation method[4]. The magnetic nanomaterial can be used as magnetic sorbent in dispersive solid phase extraction process for preconcentration of 4-tert octylphenol and atrazine before gas chromatography-mass spectrometry system. In addition they have been characterized the magnetic nanoparticle and optimized adsorption conditions. The experimental results show that the limits of detection under the optimum conditions were found to be 1.23 to 4.10 ng.mL⁻¹ for 4-tert octylphenol and 6.81 to 22.71 ng.mL⁻¹ for atrazine, respectively. The low relative standard deviation (<= 6.2%) indicated good repeatability and satisfactory percent recovery values (96.3-112.6%) demonstrated the applicability of proposed method to tap water, river water and waste water samples. Chaoran[5]et al, successfully synthesized Fe₃O₄-hyperbranched polyester magnetic composite by coprecipitation as adsorbent to extract benzoylurea pesticides from tea. And they established a new method for the detection of benzoylurea pesticides in tea by liquid chromatography. Under the final experimental conditions, the detection limit of pesticides was 0.15-0.3 ugL⁻¹, and the recovery rate was more than 90.7%. This method has been successfully applied to the quantitative determination of benzoyl urea pesticide residues in practical samples. In addition, Weixuan[6] et al, synthesized Fe₃O₄/AMWNTs(acid multi-walled carbon nanotubes)magnetic composite carbon nanotubes hybrid material by chemical coprecipitation method, which was used for magnetic solid phase extraction combined with gas chromatography to develop quantitative detection of six pyrethroid pesticides in water and honey samples.

It can be seen that coprecipitation method has been widely used in the synthesis of Fe₃O₄ magnetic composite nanomaterials. Most of the solvents used in coprecipitation are water, and the reaction yield is high. Compared with other methods, the synthesis conditions of coprecipitation are milder and the time is shorter. However, the narrow size distribution and uncontrolled shape of the synthesized materials are the defects in coprecipitation method.

2.2. microemulsion
The main principles of microemulsion synthesis of composite magnetic nanomaterials are as follows: two kinds of mutually insoluble solvents form emulsion under the action of surfactants, and nanoparticles are obtained after nucleation, coalescence, agglomeration and heat treatment in microbubbles. Ming Zhou[7] et al, synthesized the magnetic nanocomposites using the mixture of styrene and dispersed Fe₃O₄ particles as monomer, potassium persulfate as initiator, twelve alkyl benzene sulfonate as emulsifier, and propyl alcohol as assistant emulsifier,by microemulsion polymerization. The synthesis conditions were optimized through orthogonal experiments of factors, including the concentration of iron salt, the concentration of precipitant and the reaction temperature. The morphology
and function of the composite were characterized and analyzed. The results show that the particles have uniform spherical shape. Good thermal stability and superparamagnetism will be widely used in sample preparation technology. The magnetic nanocomposites with superparamagnetism and biocompatibility have great application prospects in the field of rapid detection of pesticides. Recently, Hongying et al. have developed a magnetic dextran nanoscale gel for the synthesis of loaded Fe₃O₄ nanoparticles (Fe₃O₄@Dex) by microemulsion method as a simple method for magnetic resonance imaging (MRI) probes.

At present, although many types of magnetic nanocomposites have been synthesized by microemulsion method, the particle size and shape range are relatively wide. It has been reported that the size and dispersion of nanoparticles are affected by many factors, such as solvent type, surfactant or cosurfactant type, electrolyte additive, reagent concentration and molar ratio. And the synthetic yield is also at a low level. In addition, this method needs more organic solvents, which is not conducive to environmental protection. Comparing with other methods, it is difficult to expand the scale of production.

2.3. Thermal, photochemical, and ultrasonic decomposition

One of the simplest methods to prepare nanoparticles is to decompose organic metal precursors in the presence of organic surfactants by thermal, optical or ultrasonic methods. Surfactants are usually used to protect space particles so that they do not coalesce. Surfactants can be used to restrict the growth of particles and improve the stability of particles.

The thermal decomposition of organometallic precursors and zero valent metals initially led to the formation of metal nanoparticles, which could be further oxidized into high quality monodisperse metal oxides such as Fe₃O₄. The size and morphology of composite magnetic nanomaterials synthesized by this method depend on many factors, including the proportion of organic metal compounds, surfactants and solvents, reaction temperature and time. Maiyong et al., prepared NS-Fe₃O₄@N-PC (the hybrid nanostructure with N, S-codoped Fe₃O₄ supported/embedded on/in N-doped porous carbon nanococoon) nanocomposites by direct thermal decomposition of core@shell β-FeOOH@Polypyrrole composites. The material has excellent electrical conductivity and mechanical stability. When it is used as the electrode material of supercapacitors, the performance of supercapacitors remains unchanged after 5000 cycles of cyclic tests, and the specific capacitance is also larger than that of ordinary materials.

Singh et al., synthesized a new type of Fe₃O₄-Cr₂O₃ composite magnetic nano-materials under ultrasound irradiation by wet chemical method as photocatalyst, which effectively decomposed 4-chlorophenol in water under ultraviolet (UV) irradiation.

2.4. Hydrothermal

Hydrothermal reactions, also known as solvothermal reactions, are carried out in aqueous media in the reactor or autoclave, where the pressure can be higher than 1 GPa and the temperature is higher than 200°C. Hydrothermal method has the advantages of low reaction temperature, no further calcination, low cost and environmental friendliness. In recent years, polyethylene glycol (PEG) with uniform and ordered chain structure has been widely used as surfactant to assist hydrothermal synthesis of nanomaterials for size and morphology control. Lei et al. successfully synthesized cubic Fe₃O₄@SiO₂@Ag (FSA) composite nanomaterials with high SERS activity by layer-by-layer method. Cubic core-shell structure of Fe₃O₄@SiO₂ was prepared by a new method, and Ag nanoparticles were introduced into its surface by one-pot hydrothermal reaction. The coverage of Ag on the surface of FSA can be adjusted by controlling the reaction time. Then a series of FSA composites are obtained. The results show that the FSA composites with reaction time of 6 h have the best SERS performance. The obtained substrates have high SERS activity, stability and strong magnetic response. In practical application, FSA composite material can be used to detect Fumeishuang, a dithiocarbamate fungicide widely used as agricultural insecticide, the detection limit is as low as 0.24 ppm, which is lower than the maximum residue limit of 7 ppm in fruits stipulated by the U.S. Environmental Protection Agency. In addition, Heidari et al. synthesized carbon-coated Fe₃O₄/C magnetic nanoparticles by simple hydrothermal reaction, and characterized the obtained materials. MSPE-HPLC-UV method has been
successfully applied to the determination of organophosphorus pesticides (Opps) in water samples with a correlation coefficient of $R^2 > 0.9949$. The detection limit is as low as 4.3-47.4 pg.mL$^{-1}$ and the concentration factor is 330-1200. This method has great reference value for the establishment of a new fast and efficient pre-treatment enrichment method.

The main disadvantage of conventional hydrothermal method is that the reaction kinetics is slow at any given temperature. Microwave heating can be used in hydrothermal synthesis, which can accelerate crystallization. This combination is called microwave hydrothermal method \[16\]. Compared with the traditional hydrothermal method, the microwave hydrothermal method has a higher reaction rate and yield in a shorter time.

2.5. Sol–gel method
Sol–gel method is also known as chemical solution deposition. Its principle is to use compounds containing high chemical active components as precursors and to mix these raw materials evenly in liquid phase. Then, the compounds in solution produce hydrolysis and condensation reactions to form a stable transparent sol system. The sol slowly polymerizes between the aged rubber particles to form a three-dimensional network structure gel. The gel network is filled with a solvent that loses fluidity, and then dried and sintered to prepare a material of molecular or nano-substructure. Chahkandi\[17\] et al., synthesized hydroxyapatite nanoparticles by simple alkyl-sol-gel technology, and combined them with Fe$_3$O$_4$. A new magnetic potassium substituted hydroxyapatite (KHA/Fe$_3$O$_4$) was developed for the extraction of Opps from water samples, and their structures were characterized. KHA/Fe$_3$O$_4$ magnetic solid phase extraction coupled with gas chromatography flame ionization detector (GC-FID) was established. A new method for the determination of organophosphorus pesticide residues in water samples and fruit juices.

Under the optimum conditions, all the analytes have good linearity in the concentration range of 0.1-200 ng.ml$^{-1}$. This method has good application prospects in the detection of organophosphorus pesticides. The detection limit is less than 0.03ng.ml$^{-1}$, the recovery of standard addition is more than 89.0%, and the relative standard deviation is between 5.5% to 10.8%. In recent years, the combination of molecularly imprinted polymers and magnetic nanoparticles has also been reported for sample pretreatment. Mengxing \[18\] et al., synthesized core-shell mimetic magnetic molecularly imprinted polymers (Fe$_3$O$_4$ @ DMIPs) using ethyl paraoxon as template for the extraction and enrichment of organophosphorus pesticides in red wine. A new method for the determination of organophosphorus pesticides in red wine was established by combining high performance liquid chromatography with ultraviolet detector.

3. Application and Prospect
Recently, magnetic solid phase extraction (MSPE) has been widely used in the separation and enrichment of samples in environmental, food, biological, pharmaceutical and other fields. For example, removal of toxic metal ions and radioactive elements to capture microbial pathogens and organic dyes, acceleration of sewage condensation and remediation of contaminated soil, as biosensors, targeted slow release of drugs\[19-23\]. At present, the most widely used magnetic nanoparticles for residue analysis are the core-shell C$_{18}$-Fe$_3$O$_4$ magnetic composite nanomaterials. They are suitable for preconcentration or purification of non-polar and moderately polar pesticides. They have been widely used as adsorbents because of their good separation ability, excellent stability and easy operation. Compared with the traditional extraction technology, MPSE has higher enrichment factor (EF), so the detection limit of pesticides is lower. It can be predicted that this new material will be more widely used in the future. Now the main problems are that the preparation process of magnetic nanoparticles is cumbersome and time-consuming. In addition, the particle size is not uniform, easy to agglomerate. These problems will affect the adsorption efficiency and the recovery rate of magnetic nanocomposites. Therefore, further exploring the combination of Fe$_3$O$_4$ magnetic nanomaterials with other compounds or metal materials, and synthesizing Fe$_3$O$_4$ magnetic nanocomposites is a valuable research.
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