Application of a magnetic graphene nanocomposite for organophosphorus pesticide extraction in environmental water samples

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ABSTRACT

A novel magnetic nanocomposite was prepared and applied for the extraction of organophosphorus pesticide residue (malathion, chlorpyrifos, isocarbophos, fenamiphos, profenofos) in environmental water by magnetic solid phase extraction. The magnetic nanocomposite was synthesized by coating Fe_3O_4 with silicon dioxide and then bonding with graphene oxide under the catalytic action of hydrazine hydrate. A residue analysis method for the determination of organophosphorus pesticides in environmental water was established via magnetic solid phase extraction with the nanocomposite as the sorbent, followed by gas chromatography with flame photometric detection (GC-FPD). Various experimental parameters affect extraction efficiency and must be optimized, such as the sorbent amount, the type and volume of desorption solvent, desorption time, desorption step, salt concentration and pH. Under the optimum conditions, a linear response was achieved for malathion and chlorpyrifos in the concentration range of $0.05\,mg\,L^{-1}$–$5\,mg\,L^{-1}$. Other organophosphorus pesticides were quantified in a concentration range of $0.1\,mg\,L^{-1}$–$5\,mg\,L^{-1}$, and the coefficient of correlations were between 0.996 and 1 for this method. The method was used to determine organophosphorus pesticides in river water and groundwater. The average recoveries ranged from 90.2% to 102.9%, with low relative standard deviations (RSD), and the limits of detection (LOD) were between $0.016\,mg\,L^{-1}$ to $0.033\,mg\,L^{-1}$ at a signal to noise ratio of 3. The method was efficient for the residue analysis of organophosphorus pesticides in water with easy operation, high sensitivity, and good precision.

1. Introduction

Organophosphorus pesticides (OPPs), which are mostly phosphate or phosphorothioate compounds, have been widely used worldwide as agrochemicals. Some are highly toxic to human and other non-target organisms without selectivity. Due to their broad applications in agriculture or insect control in public spaces, OPPs and their metabolites have been frequently detected in vegetables, fruits, water, soil and other environmental matrices [1]. Pesticide pollution is a serious concern, and severe restrictions have been set for residue levels. It is necessary to establish fast, environmentally friendly and effective methods of OPP detection in order to ensure food quality and environmental safety.

At present, pretreatment methods for the analysis of OPPs commonly include liquid-liquid extraction (LLE), solid phase extraction (SPE), solid phase microextraction (SPME), QuEChERS and magnetic solid-phase extraction (MSPE). In recent years, the development of fast, simple, environmentally friendly and efficient residue analysis methods for trace amounts of pesticides in environmental matrices has received much attention. LLE is a very old and classic extraction method. Despite its longevity, it is laborious and time-consuming with low extraction selectivity. Moreover, analytes may be lost in this complex procedure, and LLE requires large amounts of organic solvents, which can be harmful to the environment [2,3]. SPE is a very popular pretreatment method for pesticide residue analysis. Compared with LLE, it offers cleanup and enrichment of organic compounds in water samples. It also has the advantage of extracting a wide range of analytes with diverse polarities. However the most

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important drawback is its outstanding lack of selectivity. The compounds with similar polarities or hydrophile/hydrophobe could be co-extracted by traditional SPE sorbents. This co-extraction effect not only decreases the absorption capacity for target analytes, but also increases the interference effect. Thus, the SPE usually has low recoveries and high standard deviations during the extraction of some analytes from complex matrix [2–4]. SPME, which uses a silica fiber coated with a proper sorbent phase, has the advantages of simple operation, short operation time, less solvent consumption, and is suitable for the extraction of polar and non-polar compounds in gas, liquid, and solid samples [5,6]. In practice, however, it takes a long time to achieve equilibrium between the sample solution and the fiber with many rigorous extraction conditions. It may not efficiently achieve the extraction of target analytes and quantitative results with this technique in a short time. Moreover, due to the limitation of coating types, the selectivity of SPME may be unsatisfactory as well. Therefore, this method has not been widely used [3]. QuEChERS, which stands for quick, easy, cheap, effective, rugged and safe, is a ubiquitous sample preparation method in pesticide residue analysis [3,7]. The sorbent can bind matrix interferences, avoiding interaction with target analytes, this method is widely used in analysis of pesticides of diverse polarities [2]. Magnetic solid-phase extraction (MSPE) is a pretreatment method based on the use of inexpensive magnetic or magnetizable sorbents [8]. The suspended magnetic sorbents can be recovered by a magnetic field, making the operation simple. There is no need to filter or centrifuge samples, making the procedure easier and faster. Therefore, this method saves time as well as cost. In recent years, some magnetic materials have been used in MSPE such as silica-coated magnetic material ($SiO_2@Fe_3O_4$), alumina-coated magnetic material (Fe_3O_4/Al_2O_3), zirconium-coated magnetic material ($Fe_3O_4@ZrO_2$), ferrites ($MnFe_2O_4$), metal oxide coated magnetic material (Mn_3O_4/Fe_3O_4) and organic-coated magnetic material (chitosan/Fe_3O_4) [9]. Graphene@Fe_3O_4 was used to extract phthalates and polycyclic aromatic hydrocarbons (PAH) in water samples [10,11]. X. Wang et al. synthesized Fe_3O_4-PSA and used it in combination with commercial C_{18} in MSPE for the simultaneous determination of 50 pesticides and 8 related metabolites in rice [12]. H. Razmi et al. investigated the application of carbon-coated Fe_3O_4 (Fe_3O_4/C) magnetic nanoparticles, which were used as a sorbent for the detection of trace amounts of OPPs from environmental water samples [13].

Graphene, a honeycomb plane film of sp^2 hybrid carbon atoms, is highly conductive, very strong, ultra-thin, and has a high theoretical specific surface area [14,15]. It has been used for the adsorption of heavy metals such as Cu^{2+} [16] and Co^{2+} [17] and organic compounds such as tyrosine [18] and glucose [19]. By simple physical adsorption, Luo et al. combined graphene with $Fe_3O_4@SiO_2$ to extract sulfonamide antibiotics in environmental water samples [20]. The advantage of this approach is that the synthesis steps are simple, but the physical combination between graphene and $Fe_3O_4@SiO_2$ may be less stable than chemical bonding. The stability of the material may be enhanced by covalent bonding.

A novel magnetic nanocomposite, graphene@$SiO_2@Fe_3O_4$, was designed and synthesized in this work. Fe_3O_4 was first coated with silicon dioxide, and the synthesized material was then bonded with graphene oxide under the catalytic action of hydrazine hydrate, resulting the nanocomposite graphene@$SiO_2@Fe_3O_4$. Graphene and silica were covalently bonded, enhancing the stability of this material compared with physical coating. Through the combination of graphene@$SiO_2@Fe_3O_4$ and MSPE, a method for the detection of OPPs residues in water was established. The experimental conditions, including sorbent amount, desorption agent, desorption agent amount, desorption time, number of desorption steps, the salt concentration and the pH in aqueous solution were optimized. Under the optimum experimental conditions, the method was verified and successfully applied for the analysis of OPP residues in real environmental water.

2. Experimental

2.1. Reagents and materials

Sodium citrate, sodium hydroxide, ferrous sulfate, anhydrous ethanol, ammonia, hydrochloric acid, sodium chloride, anhydrous methanol, acetonitrile, acetone, ethyl acetate were analytical grade and purchased from Beijing Chemical Works (Beijing, China). Sodium nitrate was analytical grade and purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD (Shanghai, China). Tetramethoxysilane (TEOS), $4\,mg\,mL^{-1}$ graphene oxide and 98% hydrate hydrazine were analytical grade and purchased from J&K Scientific LTD. Malathion, chlorpyrifos, isocarbophos, fenamiphos, profenofos, acephate were provided by the Institute for the Control of Agrochemicals (ICAMA) with purity over 98%. The standard solutions were prepared in acetone at a concentration of $5000\,mg\,L^{-1}$ and stored at $4\,^\circ C$. The river water was taken from Qinghe river (Beijing), and the underground water was taken from China Agricultural University.

2.2. Synthesis of magnetic nanocomposite

2.2.1. Preparation of Fe_3O_4 nanoparticle
First, 95 mL of de-ionized water with 5 mmol of sodium citrate, 20 mmol of NaOH, and 1 mol of $NaNO_3$ were heated to $100\,^\circ C$, forming a colorless and transparent solution. Then, 5 mL of $2\,mol\,L^{-1}$ ferrous sulfate aqueous solution was added to the mixture quickly, and the mixture was stirred for 1 h in an oil bath at $100\,^\circ C$ [21]. After the reaction, the product was collected by a magnet and washed with de-ionized water two times.

2.2.2. Preparation of $Fe_3O_4@SiO_2$
In a 500-mL flask, 1 g of the above product was added to 60 mL of de-ionized water, forming a homogeneous suspension with stirring. Then, 160 mL of anhydrous ethanol and 10 mL of ammonia were added in the suspension. The mixture was stirred in an oil bath at $50\,^\circ C$. Then, 4.5 mL of TEOS was added in the mixture slowly over the course of 1 h, and the mixture was stirred for 12 h in an oil bath at $35\,^\circ C$. [22] After the reaction, the product was collected by a magnet, washed with anhydrous ethanol several times, to remove all silicon compounds, and then washed with de-ionized water two times.

2.2.3. Synthesis of graphene@$SiO_2@Fe_3O_4$
The above $Fe_3O_4@SiO_2$ was acidized in 100 mL of $0.012\,mol\,L^{-1}$ hydrochloric acid for 12 h in order to expose hydroxyl groups on the silicon surface. Then, 1.5 g of acidified $Fe_3O_4@SiO_2$, 50 mL of $4\,mg\,mL^{-1}$ graphene oxide and 30 mL of 98% hydrazine hydrate were added to 50 mL of de-ionized water. After adjusting the pH of the mixture to 10 with ammonia, the mixture was stirred for 12 h in an oil bath at $80\,^\circ C$ [23]. After the reaction, the product was collected by a magnet and washed with de-ionized water several times. Finally, the product was freeze-dried and weighed.

2.2.4. Characterization of magnetic graphene nanocomposite
The composition and structure analysis of the nanocomposite ($Fe_3O_4@SiO_2$ and graphene@$SiO_2@Fe_3O_4$) was carried out by Fourier transform infrared (FTIR) spectrometer (IRTracer-100, SHIMADZU Corporation), using KBr discs with a ratio sample/KBr of 1:100 by mass. Transmission electron microscopy (TEM) images of the nanoparticle were obtained by a JEM-1200EX microscope (JEOL,