Preparation and application of Fe₃O₄ magnetic nanoparticles graphene sheet in the magnetic solid-phase extraction of organochlorine pesticides from water

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ABSTRACT

A novel magnetic solid phase extraction (SPE) analysis method was established by combining Fe₃O₄ magnetic nanoparticles modified grapheme as absorption material followed by GC/MS for detection of the organochiorine pesticide (OPs) in water. Magnetic nanoparticles modified grapheme (MNG) was prepared by graphene oxide (GO) and Fe²⁺ through redox reaction in one step. Then, cationic surfactant CTAB was added as micelle forming agent, in which MNG was carrier of mixed micelles extraction system. Mixed micelle modified MNG has higher loading capacity than pure Fe₃O₄ magnetic graphene. This method was applied to analysis of Ops in water source. The detection limit was in the range of 1.5-5.0 ng/L. The recovery was ranged from 67.2% to 95.6%. The RSD of repeatability was lower than 9.9%. As compared with ordinary SPE, the sensitivity of new method increased 50-109 times.

Keywords: Magnetic graphene; solid-phase extraction; organochiorine pesticides; detection; water source

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INTRODUCTION

Graphene is an atomic-scale honeycomb lattice made of graphite atoms. It has special mechanical, electrical, optical and thermal properties and other excellent performances, including large specific surface area (theoretical value is 2360 m^2/g), high mechanical strength (about 1000 GPa), fast electron transfer rate (200000 $cm^2 \cdot V^{-1} \cdot s^{-1}$) and high thermal conductivity (5000 $W \cdot m^{-1} \cdot K^{-1}$). Therefore, graphene has strong potential application in energy, electronics, biomedicine, composite and other fields [1,2]. In analytical chemistry, the two-dimensional structure of grapheme has more advantages than carbon nano-tubes (CNTs) which also belong to promising nanomaterial. Graphene provides more effective area for interaction with target molecule which demonstrates its promising utilization. Thus, graphene has been used in environmental analysis in recent years, which has shown a number of outstanding superiorities, especially in the analysis of organic pollutants. π electron conjugated structure and hydrophobicity of graphene offers additional affinity, thereby enhances its interaction with the organic pollutants in the environment, favors the realization of fast adsorption/desorption, which makes it as an excellent solid phase extraction (SPE) and solid-phase microextraction (SPME) material [3,4,5].

The adsorption capacity of graphene is powerful. However, the selectivity of adsorption is not very strong, so graphene is not suitable for directly using as SPE extraction materials due to the complex composition of environmental organic pollutants. Accordingly, the adsorption selectivity of graphene needs to be improved by chemical modification. Extensive carbon atomic edge and surface of one layer of graphene oxide contains carboxyl (-COOH), hydroxyl (-C-OH), and interlayer contains graphite oxide with oxygen groups including epoxy group (-C-O-C-) and carbonyl group (C=O, O-C=O), etc. The hydroxyl and epoxy groups are mainly located in the graphite surface, and the carbonyl is in the edge of the graphene. The micellar extraction technology is a new sample

preparation technology with high extraction rate, which takes micelles as adsorbent material with opposite charges of surfactant. Hydrocarbon chains of hydrophobic surfactant interact with analytes through hydrophobic carbon chains, while the polar group analytes produce the interaction through the electrostatic or hydrogen bonds. Hence the micellar extraction technology is suitable for applying in amphiphilic analytes. The micelle formation process plays a key role in the bearing capacity of the stationary phase carrier. At present, the most widely used micellar supported materials are metal oxides such as TiO_2, SiO_2 and $Fe(OH)_3$ [8,9,10]. However, the superficial area of these materials is relatively small, so the extraction efficiency is low. Graphene can be directly used as SPE adsorbent material, but graphene sheet is very thin and lightweight, which make it difficult to be completely separated from the solution by filtration or centrifugation. Meanwhile, Graphene is flexible, and prone to agglomeration that reduces the adsorption. This problem could be solved by external magnetic field.

OPs are highly effective insecticides that caused widespread pollution to the environment. The content of OPs in the water source is extremely low; it needs to be enriched before measurement. SPE can be employed to concentrate OPs in the water, while the existing adsorbents of SPE are poor in adsorption of polar OPs, which cause them unable to develop extraction. π-π interaction occurs due to hydrophobic interactions with graphene conjugated system. So, graphene shows excellent adsorption towards organic matter containing benzene rings. Therefore, graphene can be used for extraction and separation of hydrophobic OPs.

In this paper, a novel magnetic SPE method was proposed. Magnetic graphene (MG) is utilized as the stationary phase of the micelles. Flexible grapheme owing large specific surface area, which could form nano platform for the micelle formations, hence improves the extraction efficiency. For another hand, the graphene loads with micelles attracting and combining mutually with the analytes. For collection, magnetic material did not need centrifuging or filtration, which collects the MNG quickly by external magnetic field. This technique simplifies the extraction process greatly. MNG was charged by adjusting pH of the sample solution, and anionic surfactants CTAB was employed to modify the SPE materials. The effect of the adsorption of OPs on the properties of basal MG was investigated. The magnetic SPE-GC/MS detection method was utilized for detection eight OPs in the water source. The proposed method was also compared with the ordinary SPE. The methodology result showed this method was highly sensitive with high recovery rate.

EXPERIMENTAL SECTION

2.1. Chemicals and reagents
Hexadecyltrimethylammonium bromide (CTAB) was purchased from Sigma Aldrich. Standard solutions (100 µg/mL) of OPs were purchased from the Institute of Environmental Protection, China. $FeCl_2 \cdot 4H_2O$, $NH_3 \cdot H_2O$ and HCl were purchased from the Guoyao Chemical Reagent Co., Ltd. (Shanghai, China). All solvent used in GC/MS (GC/MS-QP 2010 Plus, Shimadzu, Japan) in this experiment were HPLC grade. Water used in the experiment was prepared from the Milli-Q ultrapure water system (Millipore). The stock solution of organic phosphorus (10 mg/L) was prepared with acetone, kept in a cool, dark refrigerator at 4 C.

2.2. Synthesis of MG sheets
Preparation of MNG based on the method of Hummers [11]. The flow chart was shown in Fig. 1. The MNG sheet was prepared by redox reaction using Fe^{2+} and GO in alkaline conditions. That is, 1.5 mol/L $NH_3 \cdot H_2O$ solution was dropped into 50 mL of graphene oxide solution (0.2 mg/mL) and adjusted pH value to 9. The solution was blown in nitrogen by Termovap Sample Concentrator (HP-5016SY, Shanghai, China) for 10 s to eliminate oxygen. Then, 5.0 mL $FeCl_2 \cdot 4H_2O$ solution (20 mg/mL) was added. The solution was stirred while blowing nitrogen, and adding $NH_3 \cdot H_2O$ to maintain the solution in pH9. The solution was stirred at room temperature for 1 hour. The color of the solution changed from yellow to black, who indicated that the MNG was successful prepared. MNG was collected by a magnet, and was washed repeatedly using deionized water. The concentration of MNG was 12.5mg/mL, and it was stored in the headspace sampling bottle filled with nitrogen.

2.3. Characterization of materials
High resolution electron microscopy (SEM), X-ray diffraction (XRD), Gas chromatography–mass spectrometry (GC-MS), vibrating sample magnetometer (VSM) were used for characterization of the morphology, structure and magnetic properties of MNG.
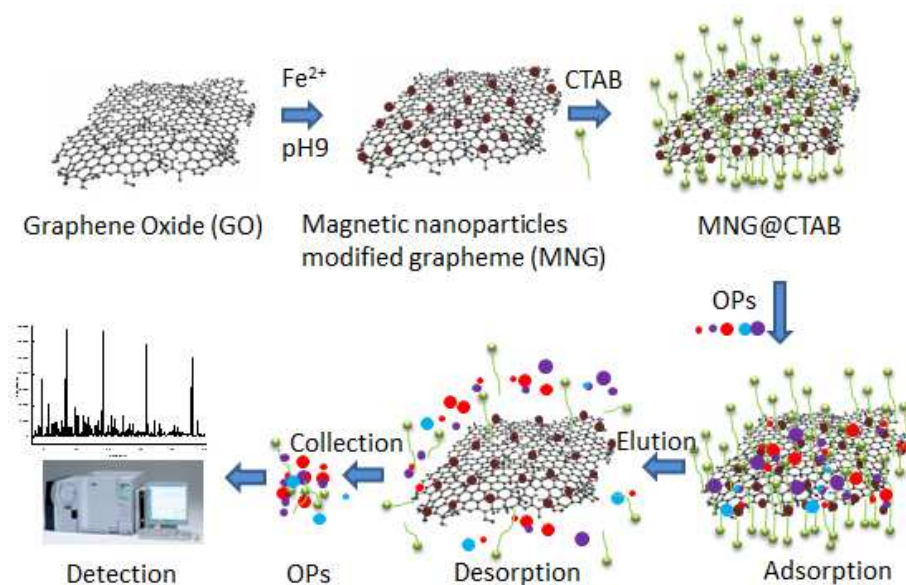
Fig. 1. Scheme of the MNG synthesis and SPE procedures

2.4. Extraction procedures

HCl was selected to adjust pH value to 3 of the sample solution (100 mL). MNG water dispersion 1.0 mL (1.0 mg/mL) and CTAB aqueous solution 0.75mL (1mg/mL) were added to the sample solution to extract for 20 min at room temperature. MNG sheet was collected by magnet. After desorption with 1.5 mL acetone, the acetone was analyzed on GC/MS.

2.5. Chromatographic conditions

OPs were detected by a DB-5 MS capillary column (30 m×0.25 mm×0.25 μm). The injection mode was splitless with volume of 1 μL. The carrier gas was helium, and the column flow was set at 26.2 cm/sec. MS ionization was EI mode, and electron impact mode was 70 eV. Ion source temperature was 260°C. GC/MS interface temperature was 280°C, and SIM mode was set for acquisition. The column temperature program was set at 90°C for 1 min, and then raised by 25°C/min to 180°C, held for 0 min, raised by 5°C per min to 300°C and held for 1 min.

RESULTS AND DISCUSSION

3.1. Synthesis and characterization of MG

With oxidation-reduction reaction between GO and Fe^{2+}, MNG sheet was prepared under alkaline conditions. At room temperature, the reaction could be accomplished in one step, and the method was convenient and simple. Fe_3O_4 magnetic nanoparticles (MNP) were formed on the surface of magnetic nanoparticles, and did not need other organic connections, consequently no organic pollutants was introduced to the adsorbent. After the reaction, MG could keep the morphology of graphene, so as to maintain the good ability of the stationary phase carrier. SEM characterization of MNG was shown in Fig. 2A, GO was an ultrathin and translucent slice, lateral dimensions ranged from tens of nanometers to a few microns. Fig. 2B showed the SEM image MNG. Fe_3O_4 particles are deposited on the surface of the nano film, the distribution of Fe_3O_4 MNP in the MNG sheets was uniform, and there were not many aggregates of MNP Fe_3O_4. The average particle diameter of Fe_3O_4 nanoparticles was 10 nm.
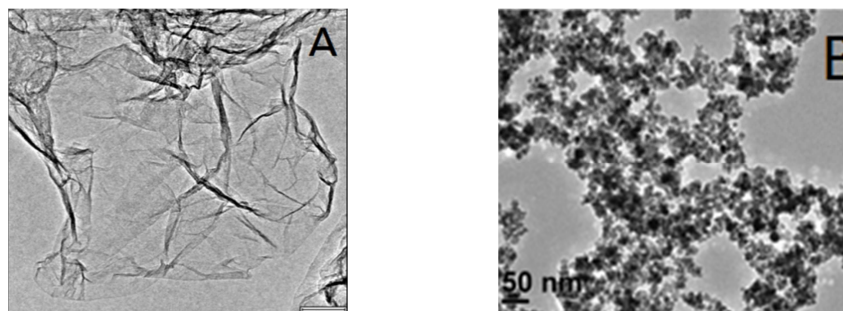
Fig. 2. (A) SEM image of grapheme oxide. (B) SEM image of magnetic nanoparticles modified grapheme (MNG)

Magnetic nanoparticles Fe_3O_4 were easily aggregate in water solution. In order to solve this problem, MNPs Fe_3O_4 is fixed onto MG. The magnetic properties of MG were determined by magnetometer (VSM). As shown in Fig. 3A, the maximum saturation magnetization of MG was 51 emu/g, which was adequate for the analysis of practical water samples. After exposure to the external magnetic field, all the graphene sheets modified by magnetic nanoparticles were rapidly dispersed. In addition, MNG sheets were of typical super paramagnetic magnetic behavior, which made them as good adsorbents for SPE. MNG also contained a number of polar functional groups, such as hydroxyl and carboxyl group, which not only contributed to abundant adsorption site for micelles, but also improved the dispersion of MNG in water. The dispersion system of MNG in water was stable that agglomeration was not found at room temperature for over a month, as well as magnetic effect of MNG was not decreased. Zeta potential of pH3-11 in MNG was shown in Fig. 3B. The Zeta potential of MNG equaled to 6.8 mV in pH3. When pH reached to 7, the Zeta potential was reduced to -15.0. As pH went even further, no significant change of Zeta potential appeared which indicated a saturation condition of negative charge. Isoelectric point (IEP) of MG was -3.7. In order to study interaction between graphene and MNPs Fe_3O_4 in MG, the Fe_3O_4 potential of pure graphene and MNP Zeta was compared. MNPs Fe_3O_4 was with positive charge under acidic conditions (<pH7), conversely, with negative charge in alkaline conditions (>pH7). While the Zeta potential of graphene was negatively charged with pH values ranged from 3 to 11. The Zeta potential of MNG was negatively charged in most pH conditions, which was closer to graphene than that of MNG. Therefore, when determining the zeta potential of MNG, graphene should play more significant role than MNP Fe_3O_4.
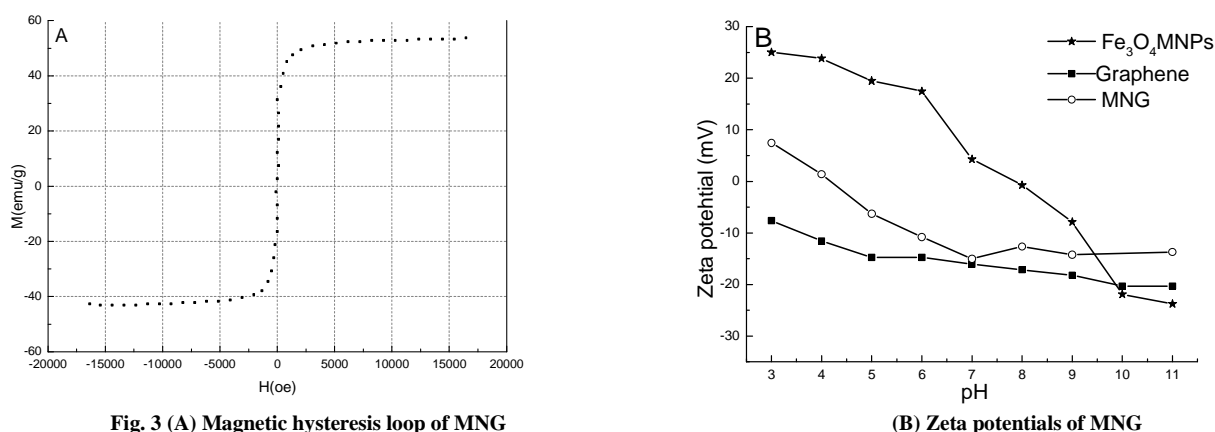

Fig. 3 (A) Magnetic hysteresis loop of MNG

(B) Zeta potentials of MNG

3.2. Formation of admicelles on MG sheets

In order to obtain higher micellar load capacity while using CTAB as a reagent for micelle formation. The MNG plates need to take as many negative charges as possible. The negative charge of the MNG reached the maximum when the pH value was higher than 6.8. In addition, the environmental water samples are generally in neutral pH, so pH 6.8 was selected in the SPE condition. The formation of CTAB micelles in MNG was studied by means of determination of Zeta potential. Fig. 4A shows Zeta potential of MNG while adding different amount of CTAB. Generally, Zeta potential of MNG increased with the increasing of CTAB. CTAB concentration ranged from 0-0.1 mg (1.0 mg MNG), zeta potential of the MNG changed from negative to zero. In this period, micelles formed on MNG plate surface. While CTAB increased from 0.1 to 1.0 mg of CTAB, zeta potential of MNG also increased positive, indicating that is the formation of mixed micelles. When CTAB concentration is higher than 1.0 mg CTAB, the zeta potential has little change on MNG, indicating that in MNG sheet surface micelles has reached saturation, CTAB to the beginning of the formation of free micelles in the bulk solution. CTAB coated MNG plate is expressed as MNG@CTAB. It was indicated from the above results that the maximum adsorption capacity of CTAB on the MNG is about 1.0 mg/mg. Therefore should provide greater adsorption capacity and penetration volume.

This method was applied to extract eight OPs in water samples. OPs are persistent organic pollutants in the environment, which has caused a wide attention. They are enriched in animals and amplified as accumulation through the food chain, which has manifested the toxicity to the immune and nervous system. The pKa values of these OPs were low, whose present form was ionic in the water environment, so as to carry out an intense adsorption through the electrostatic interaction of CTAB micelles. Furthermore, the carbon chain of OPs could be introduced into CTAB micelles by hydrophobic interaction. So, MNG@CTAB should be suitable for extraction of OPs.
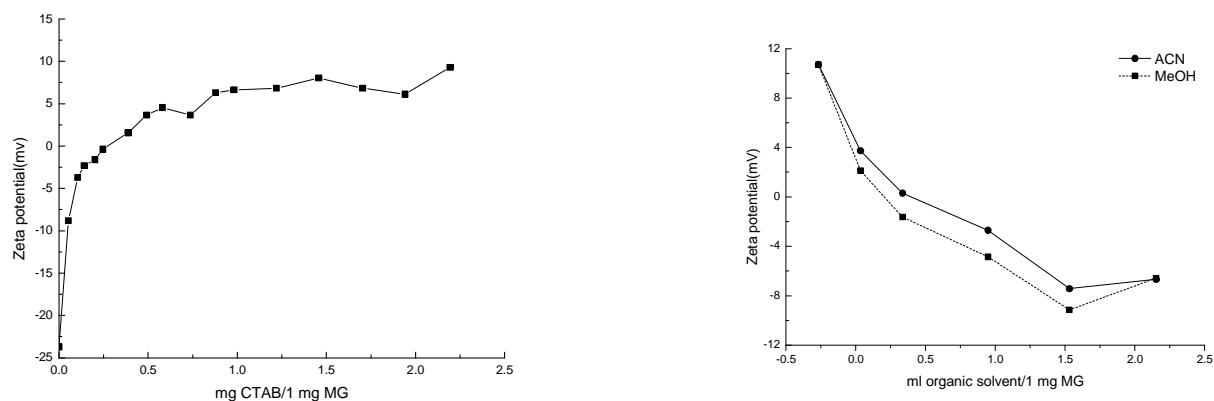
Fig. 4. (A) Effect of CTAB amount on the zeta potential of MNG   (B) Effect of eluent volume on the zeta potential of MNG@CTAB

3.3 Effect of the type and volume of eluent solvent

The effect of elution volume on MNG@CTAB was studied by measuring zeta potential. The purpose of the elution was to desorb CTAB micelles from the MNG plate, thereby released the analytes into the elution solution. Two organic solvents, methanol and acetonitrile, were tested. As shown in Fig. 4B, the Zeta potential of MNG@CTAB was changed from positive to negative by organic solvent elution, which indicated that CTAB micelles could be adsorb effectively. Using 1.5 mL acetonitrile to make negative ions to a maximum value, the Zeta potential of MNG was recovered to -7.8 mV. It was seen from Fig. 3A that the residual MNG of the CTAB plate was very low, which demonstrated that the elution was effective. Thus, 1.5mL per mg MNG cetonitrile was used as the elution solvent in the following experiments.

3.4. Comparison of MG with pure Fe_3O_4 MNPs

In order to compare effect the MNG as the solid phase carrier of micelle, pure MNP Fe_3O_4 was compared. We found that MNG provided more significant advantages than pure MNP Fe_3O_4. Firstly, MNG was more favorable for the environmental water sample pretreatment. As is known, environmental water samples are usually in alkaline pH condition. MNG allows the extraction of cationic patterns (pH 6.8), thus avoiding this problem. But for Fe_3O_4 MNP, they have no net charge at the neutral pH, so the obtained micelle carrying capacity is high, the extraction must be carried out under alkaline conditions. Secondly, the MNG by the hybrid micelles were more than MNP Fe_3O_4. We studied the formation of MNP micelles at pH 9.6 and found the maximum adsorption capacity (about 0.9 mg/mg) of CTAB was lower than that of MG. In addition, the extraction efficiency of MNP Fe_3O_4@CTAB at pH 9.6 was lower than that of MNG@CTAB at pH 6.8. These results suggest that graphene can provide the formation of more micelles, thus improving the extraction efficiency. Third, the dispersion of MNG in aqueous solution is more stable than Fe_3O_4 MNP. At room temperature for three days, the magnetic of MNP Fe_3O_4 decreased sharply. Thus, the reproducible results of the MNP Fe_3O_4 should be prepared. While the MNG was kept at room temperature for more than one month, no decrease was observed in the magnetic response. The results showed that graphene can be used as a good protective agent for Fe_3O_4 MNG.

3.5. Method validation

The proposed method was validated including linearity, limit of detection (LOD), limit of quantification (LOQ), precision and recovery. Linear relationship were good (R^2>0.98). The limits of detection (LOD) of MNG@CTAB SPE were in the range of 1.5-5.0 ng/L while the LOD of ordinary SPE were decreased to 0.75-5.45 mg/L. Therefore, the sensitivity of PAH analysis is increased by 50-113 times, which shows that MG@CTAB has a high adsorption efficiency. In the detection of real water samples, the sensitivity is higher than the previous report. The methodology validation was also tested. Select 0.5 ug/L OPs. The sensitivities of OPs were increased by 50-109 times. The blank recoveries were in the range of 67.2-95.6%, which indicated that the effect of sample matrix on the extraction efficiency was significant.

3.6. Application of the established method to the analysis of environmental water samples

In order to evaluate the potential impact of the sample, we studied the recovery of the water samples. Trace OPs (0.1-3.5 ng/L) was found in the samples. The sample recoveries were in the range of 64.3-94.2%. The recovery rate of pp'-DDD was lower than that of other OPs. Nonetheless, this result is in line with the quantitative analysis.

Table 1. Method validation of detection Ops from water source by MNP

Compound	Linear range (ng/L)	r^2	RSD (%)		Recovery (%)
			Run-to-run ($n=6$)	Day-to-day ($n=3$)	
α-666	5–500	0.9975	4.5	5.6	92.4
β-666	5–200	0.9893	7.8	8.8	84.6
γ-666	5–200	0.9850	7.9	9.6	86.5
δ-666	5–200	0.9952	4.2	5.6	84.5
pp'-DDE	5–200	0.9875	9.5	9.7	64.3
op'-DDT	5–200	0.9952	8.6	9.6	81.5
p'-DDD	5–200	0.9843	7.5	8.6	78.6
p'-DDT	5–200	0.9851	9.8	9.9	94.2

CONCLUSION

Graphene has great potential to be used as a support or substrate material as it has huge specific surface and unique morphology. In this work, micelle was used as support to develop a new type of SPE material MNG. Combining the universality of micelles and its good extraction ability, MNG is simply prepared, which has high load capacity. The MNG can be negative or positive charged according to the solution pH, thus can be supported as cationic and anionic micelle. In these conditions, the MNG showed higher carrying capacity than the conventional materials and MNP Fe_3O_4. The method was successfully applied to environmental water source samples. The extraction efficiency and the enrichment factor were high, and get good repeatability and recovery rate. We believe that this work not only presents a new method for the SPE of micelles, but also reveals the new role of graphene in the field of analysis.

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