Magnetic Graphene Oxide Based Solid Phase Extraction for Environmental Pollutants Analysis

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Abstract. Heavy metal ions and organic pollutants have aroused considerable concerns about their toxic effects on human body and the ecosystem. Thus it is of great significance to develop accurate and sensitive methods for the analysis of these pollutants in environmental matrices. Because of their trace levels and the complexity of sample matrices, sample preparation is necessary before their instrumental detection. As a new and prospective sample pretreatment technique, magnetic solid phase extraction (MSPE) has drawn much attention from the analysts, and has been widely used in various analytical fields. This review focuses on the current progress that has been achieved in MSPE based on graphene oxide for preconcentration and separation of heavy metal ions and organic pollutants in environmental water, with 61 references.

1. Introduction
Heavy metals have caused much concern, because they tend to be gradually gathered in human body and therefore result in serious health problems [1, 2]. Air, water and soil are being polluted by toxic heavy metal. Thus, it is required to develop accurate and sensitive methods for detection of heavy metal ions in environmental and food samples. Inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectrometry (ICP-OES) can carry out sensitive analysis of heavy metals [3-9]. However, they require expensive and complex instrumentation.

Besides heavy metals, organic pollutants have attracted much attention from the public and the researchers. Among organic pollutants, persistent organic pollutants (POPs), endocrine disrupting chemicals and emerging organic pollutants are focuses. For example, POPs are highly toxic, persistent, and bioaccumulate, and are now widely distributed in the environment [10, 11]. Typical POPs include polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), phthalate esters (PAEs), perfluorinated compounds (PFCs) and polybrominated diphenyl ethers (PBDEs). Pharmaceuticals and endocrine disruptors are emerging organic contaminants which interfere with hormones and reproductive systems [12-14].

Because environmental pollutants usually present in water samples at low concentrations, sample preparation steps are often required before their determination. Among a number of enrichment and separation approaches, solid phase extraction (SPE) is the most often used technique because of its advantages such as high ability for analytes enrichment and matrices removal, easy operation and low cost [15-25].

Magnetically separation technology allows easy and rapid route for isolation of magnetic particles from solution by using a magnet [26, 27]. Applying a magnetic field, magnetic sorbent can be easily separated from matrix solutions after sorption of target analytes. As a result, centrifugation or filtration was not needed. Thus, in magnetic graphene, high sorption ability of graphene is combined with the isolation
convenience of magnetic materials. Recently, magnetic solid phase extraction (MSPE) has been rapidly
developed. MSPE uses magnetic material as the solid phase sorbent, which can greatly simplify SPE
procedures and improve extraction efficiencies [28-31]. Up to now, MSPE absorbents are mainly based
on Fe₃O₄. Obviously, adsorbent is the key factor that influences the extraction recovery for the target
analytes.

Graphene oxide (GO), an oxidized form of graphene, contains abundant and highly reactive
oxygen-containing functional groups, including epoxy, carboxylic groups and hydroxyl, which makes
it hydrophilic and improves its dispersion in water. Thus, GO can be used as sorbent materials for solid
phase extraction [32-38]. Recently, magnetic GO has been widely and successfully used as the
adsorbent for MSPE [39-43]. In addition to hydrophobic and π-π interactions, the interaction between
adsorbate and GO also include electrostatic interactions.

In this paper, the applications of magnetic graphene oxide SPE for trace detection of heavy metal ions
and organic pollutants in environment water are reviewed.

2. MSPE for heavy metal ions

Arsenic is often investigated as a metal [44]. Industrial activities, agricultural activities and natural
phenomenon can cause arsenic pollution [45]. Because of their good dissolving ability for various
compounds and environmentally friendly property, the use of ion liquids (ILs) in developing functional
hybrid nanomaterials has been a focus [46]. Zhang et al [35] reported a new sorbent, MGO modified IL
(MGO-IL), and subsequently used it for highly efficient removal of As(III) and As(V) from solution.
The effects of solution pH, IL type, contact time, initial arsenic concentration, and sorbent amount on
arsenic removal were examined. It was found that the MGO-IL had good sorption performance for both
As(III) ion and As(V) ion.

Rofouei et al [47] prepared magnetic buky gel, with ionic IL and MGO (IL/MGO), and applied it for
extraction of six heavy metals(Cd, Co, Cr,Cu, Niand Zn) in water, following the complexation with
1-(2-pyridylazo)-2- naphthol (PAN), and determined with ICP-OES. Under the optimum extraction
conditions, LODs of 0.1-1 μg L⁻¹, and EF of 17-47 were obtained. Employment of Fe₃O₄/GO
nanocomposite [48] and other modified types with 1,6-hexadiamine, triethylenetetramine, and
diethylenetriamine for magnetic extraction/speciation of meal ions were also developed [49, 50].

Recently, a variety of magnetic GO nanocomposites has been used as sorbents for MSPE for heavy
metal ions, such as Fe₃O₄@grapheneoxide@polyimide (Fe₃O₄@GO@PI) nanocomposite for Pb(II)[51],
magnetic MGO/SiO2@copolymer polypyrrole–polythiophene (MGO/SiO2@coPPy-Th) for metal ions
[52], Fe₃O₄/GO@polythiophene (GO/Fe₃O₄@PT) nanocomposite for Hg(II) [53] and Fe₃O₄-graphene
moderated with 4-methyl-2(2-pyrazinyl)-1,3- thiazole-5-carboxy acid oxide (Fe₃O₄-GO@MPTC) as the
chelator for thallium [54].

3. MSPE for organic pollutants

3.1. Endocrine disrupting chemicals

Li et al [26] developed a novel method for trace detection of bisphenol A (BPA), applying magnetic
reduced graphene oxide based SPE coupled with dispersive liquid-liquid microextraction (DLLME) for
extraction of BPA, before determination by high performance liquid chromatographic. DLLME is a
simple, fast, sensitive, cheap and green microextraction way [55-58]. For BPA, the enrichment factor
was 5217 and the limit of detection was 0.01 μg L⁻¹. The good reusability of magnetic reduced graphene
oxide was demonstrated for 12adsorption-desorption cycles without obvious drop in the recovery of
BPA.

Wang et al [59] prepared octyl (C8)-modified magnetic graphene oxide (MGO-C8) as the sorbent for
MSPE of phthalate acid esters (di-(2-ethylhexyl) phthalate (DEHP), di-n-butyl phthalate (DBP) and
di-n-octyl phthalate (DNOP)), and detected the PAEs by gas chromatography–mass spectrometry. The
recoveries of the selected PAEs employing MGO-C8 as the sorbent were significantly higher those
achieved by MGO. The LODs and (RSDs) were in the range of 0.5-1.0 ng L⁻¹ and 4.8-7.5%,
respectively.
The presence of herbicides in environment has been an increasing attention. Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is one of the most often used herbicides for the control of broadleaf and grassy weed. Now, atrazine is listed as an environmental endocrine disruptor. Zhang et al [60] proposed an analytical method for ultra-trace atrazine detection in water, using MGO based SPE combined with DLLME, followed by gas chromatography- mass spectrometric determination. An enrichment factor as high as 1033 and a LOD as low as 0.6 ng L\(^{-1}\) for atrazine were obtained under the optimum conditions.

3.2. Persistent organic pollutants

PAEs are non–covalently bound to the polymeric chains, and exist at the freely mobile and leachable phase, thus can enter into the environment from a variety of plastic materials and cause water contamination [61]. Dibutyl phthalate (DBP), bis(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), dimethyl phthalate (DMP), di-n-octyl phthalate (DNOP) and butyl benzyl phthalate (BBP) are environmental priority pollutants listed by Environmental Protection Agency (EPA) of the United States. PAEs are often at very low concentrations or even at a trace levels in water. GO-based composites can act as the supporting materials for surface imprinting by using of their large surface areas. Moreover, GO sheets also show significantly improved physicochemical properties when coupled with compositized materials. Guo et al [62] synthesized dual-dummy-template molecularly imprinted polymers coated magnetic GO for isolation and preconcentration of PAEs in water, in which both dipropyl phthalate (DPRP) and diisononyl phthalate (DINP) were utilized as the dual-dummy templates, while (3-aminopropyl) triethoxysilane and phenyl trimethoxysilane used as the co-functional monomers, and tetraethyl orthosilicate as the cross-linker agent, respectively. The LODs for PAEs were of 0.01-0.05 µg L\(^{-1}\) and the recoveries for PAEs were higher than 92.9%, with the RSDs lower than 3.8%.

3.3. Emerging organic pollutants

Antibiotics are typical emerging organic pollutants. Among these antibiotics, sulfonamides antibiotics (SAs) were extensively used for diseases treatment of human and animals. But, most of them were migrated into the environment. Therefore, sulfadiazine (SDZ), sulfadoxine (SDM), sulfamethazine (SMM), sulfamerazine (SMZ), sulfathiazole (STZ) and sulfamethoxazole (SMX) and were frequently detected in surface water up to µg L\(^{-1}\) level. Fan et al [14] synthesized multi-templates (SDZ, STZ, SMZ, SMM, SMX and SDM) molecularly imprinted polymers using MGO as the carrier, for rapid detection of trace SDZ, STZ, SMZ, SMM, SMX and SDM in real water samples (well water, river water and lake water). The LODs for SDZ, STZ, SMZ, SMM, SMX and SDM were 0.014, 0.013, 0.012, 0.013, 0.012 and 0.010µg/L. The recoveries and RSDs of the six sulfonamides were 87.37–102.34%, and 3.18–6.49%, respectively.

In China, the application amount of tetracyclines has ranked the second among all the used antibiotics [63]. As the representatives of TCs, doxycycline (DC), tetracycline (TC), chlorotetracycline (CTC) and oxytetracycline (OTC) are widely adopted as feed additives for animal husbandry and veterinary drugs. Molecularly imprinted polymer can selectively identify target substances in complex systems. Zeng et al [43] prepared a multi-template molecularly imprinted polymer onto mesoporous silica modified magnetic graphene oxide using DC, TC, CTC and OTC as template molecules, N-[3-(Trimethoxysilyl)propyl]ethylenediamine (KH-792) and anilinomethyl triethoxysilane (KH-42) as co-functional monomers. The synthesized magnetical composite material was applied to enrichment and separation of TCs from aqueous solution via MSPE. The LODs of the tetracycline were 0.67-0.95 µg/L, and the spiked recoveries for the tetracycline were 82.7-103.3%, with RSDs of 1.03 -8.79%, respectively.

4. Conclusions

GO is an influential intermediate, can be carried out modification more conveniently, resulting in a number of functionalized GO composites. Magnetic graphene oxide (MGO) owns the high sorption capacity of graphene as well as the fast isolation ability of magnetic materials. MGO based SPE can greatly simplify the conventional SPE procedure and enhance extraction efficiency, and has been
successfully applied to enrichment and isolation of heavy metal ions and various types of organic environmental pollutants, and satisfactory analytical performances were achieved.

5. References
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