Recent advances in graphene-based magnetic composites for magnetic solid-phase extraction

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ABSTRACT

In recent years, graphene-based magnetic composites have attracted tremendous research interest owing to its exceptional properties, such as huge surface area, large delocalized π-electron system, strong magnetic responsiveness, and excellent mechanical/thermal stability. These promising properties together with the ease of processibility and functionalization render graphene-based magnetic composites to be ideal adsorbents in magnetic solid-phase extraction. In this review, we outline the state of the art on the preparation approaches for different graphene-based magnetic composites and its application as adsorbents in preconcentrating organic compounds, biological macromolecules, and metal ions. In addition, future research directions of this type of magnetic materials are identified as well.

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1. Introduction

Sample preparation is an essential step in the analysis of complex samples (such as environmental, biological, pharmaceutical, or food samples) especially when the analytes of interest exist in trace or ultra-trace levels. A proper sample pretreatment technique not just ensures satisfactory sensitivity through concentrating the analytes to the detectable limits of analytical instruments but also improves the selectivity of the methods via removing uninteresting and interfering substances present in the primary matrix. Moreover, proper sample pretreatment can prevent the occurrence of underlying damage to analytical instruments. Hitherto, various sample pretreatment techniques have been developed according to the analyte properties and matrix complexities. As an innovative type of solid-phase extraction (SPE), magnetic solid-phase extraction (MSPE) has garnered widespread recognition since the investigation on the technology in 1999 by Šafaříková and Šafařík [1—3]. In this technique, magnetic adsorbents are directly dispersed into sample solutions, and this dispersive extraction mode can enhance the contact area between adsorbents and analytes [4]. Hence, the extraction efficiency of MSPE is superior to that of conventional SPE. Meanwhile, typical SPE problems related with adsorbent packing, such as high pressure and packed bed clogging, can be avoided [5]. Notably, magnetic adsorbents can be separated from the sample solutions under an external magnetic field without the need of traditional centrifugation or filtration, thereby simplifying the extraction process. Furthermore, magnetic adsorbents can be recycled and reused easily, which is cost effective and environmentally friendly. Given all these findings, MSPE shows comprehensive advantages of simplicity, time and labor savings, and excellent extraction efficiency. Magnetic

adsorbents, commonly consisting of magnetic carriers and functionalities, play a vital role in the MSPE technique in that they directly affect extraction efficiency and simultaneously determine the sensitivity and selectivity of the method [5]. To date, a number of magnetic adsorbents for MSPE have been reported in the literature, involving the direct use of magnetic nanoparticles (MNPs) after surface functionalization (such as metal [6], metal oxide [7], silica [8], and surfactants [9]), or the use of composite/hybrid materials containing MNPs combined with molecularly imprinted polymers [10], carbon nanotubes [11], or graphene (G) [12]. Among the different materials used as MSPE adsorbents, G, a two-dimensional, single-/few-layer sheets composed of sp^2-hybridized carbon atoms, has become a rapidly rising star owing to its exceptional mechanical, thermal, and electronic properties and ultrahigh specific surface area (theoretical value 2630 $m^2 g^{-1}$) [13]. In general, G is a non-polar and hydrophobic adsorbent with the large delocalized π-electron system that can form a strong $\pi-\pi$ stacking interaction with the carbon-based ring structures [14]. Hence, this two-dimensional material is considered as a good candidate for the enrichment of carbon-based ring structures. In the last few years, various methods for the preparation of G-based magnetic composites have been developed, and G-based magnetic composites have demonstrated excellent efficiency in the isolation and enrichment of organic pollutions, biological macromolecules and metal ions. However, research on the advances in G-based magnetic composites focusing on their use as MSPE adsorbents is lacking.

In this work, different approaches to prepare G-based magnetic composites are described synoptically, and an overview of recently developed applications of these materials as MSPE adsorbents is discussed. In addition, future research directions of this type of magnetic materials are identified as well.

2. Fundamentals of graphene-based magnetic solid-phase extraction

G, an addition to carbon allotropes, is composed of sp^2-hybridized carbon atoms arranged in a honeycomb lattice. As the fundamental structural component of other carbon allotropes [15], this two-dimensional material surpasses all other allotropes in its usage in life and material sciences by virtue of its numerous intrinsic properties, such as ultrahigh theoretical specific surface area, high intrinsic mobility, high Young's modulus, thermal conductivity and good electrical conductivity [16,17]. Up to now, versatile strategies for the fabrication of G have been developed. The graphene oxide (GO)-production method (modified Hummers) is the most popular method; this strategy is based on the oxidation of graphite to GO followed by the reduction of GO to reduced graphene oxide (RGO) by using suitable reducing agents, such as hydrazine [18], sodium borohydride ($NaBH_4$) [19], sodium hydroxide [20], and ascorbic acid [21]. G is a double-sided polycyclic aromatic scaffold, and this special configuration confers huge surface area and large delocalized π-electron system. In particular, its large delocalized π-electron system can endue G with a strong affinity for carbon-based ring structures [22]. Thus, G is a wonderful adsorbent in sample pretreatment [23,24]. G is commonly considered as a non-polar and hydrophobic adsorbent, by contrast, GO is usually applied as a polar and hydrophilic adsorbent owing to its large quantities of polar moieties, e.g. hydroxy, epoxy, and carboxyl groups [25]. Nevertheless, when G or GO sheets are dispersed in the sample solution, it would be a daunting task to completely retrieve the analytes-adsorbed G or GO sheets from the well-dispersed solution even though centrifugation or filtration is used. In addition, although G or GO sheets can be employed as SPE adsorbents, there are still many tricky issues involving adsorbent packing, high back pressures, packed bed clogging and the irreversible aggregation of G or

GO sheets. To better address these problems, G-based magnetic composite comes into being and sparks exponential growth of research in scientific communities. Subsequently, different G-based magnetic composites are prepared in succession, which are discussed in detail in the next section.

After prepared, the G-based magnetic composites can be applied in the MSPE technique. The classic MSPE procedure is shown below:

Extraction: the magnetic adsorbents are added into the sample solution and evenly dispersed via ultrasonication or oscillation. Adequate system time was provided to reach the adsorption equilibrium.

Separation: the analyte-adsorbing magnetic adsorbents are retrieved with the aid of an external magnet, and the supernatant is discarded.

Desorption: a suitable desorption solvent is chosen and used to elute the analytes.

Separation: the magnetic adsorbents are magnetically retrieved, and the desorption solution is collected.

Reconstitution: the desorption solution is evaporated under a gentle nitrogen stream. The residue is reconstituted in an appropriate solvent and then used for subsequent analysis.

In order to find out the physicochemical properties of the adsorbents and improve their absorption capacity, it is an essential step to investigate the adsorption mechanism between the adsorbents and analytes. The adsorption mechanism between G-based magnetic composites and analytes mainly relies on the interaction between the functional groups of adsorbents and analytes. In general, G-based magnetic composites can exhibit excellent adsorption capacity toward numerous organic compounds and metal ions with the aid of $\pi-\pi$ stacking interactions, cation-π interactions, electrostatic interactions, hydrogen bonds, dative bonds, and hydrophobic interactions [26]. For G, its large delocalized π-electron system plays an important part in the formation of strong $\pi-\pi$ stacking interactions with the aromatic rings of several organic compounds. Different from G, GO can adsorb metal species and organic compounds, including oxygen- and nitrogen-functional groups, through dative bonds, cation-π interactions, electrostatic interactions or hydrogen bonds. Moreover, different kinds of organic functional groups, such as ionic surfactants [27], organic polymers (such as polydopamine [28], polythiophene [14], and polypyrrole [29]), supramolecules [30], ionic liquids [31], and metal-organic frameworks [32], are often introduced into the G-based magnetic composites to improve the adsorption selectivity of G-based magnetic composites via the change of interactions between adsorbents and analytes.

3. Preparation of graphene-based magnetic composites

Hitherto, an amount of G-based magnetic composites, composed of magnetic materials and G-based materials, have been reported in the scientific literature. As is known to all, there are many well-known magnetic materials involving iron (Fe), cobalt (Co), nickel (Ni), magnetite (Fe_3O_4), and maghemite (γ-Fe_2O_3), but iron oxides (Fe_3O_4 and γ-Fe_2O_3) are utilized most frequently in the MSPE technique on account of their ease of synthesis, controllable magnetization, superparamagnetism, and low toxicity [33,34]. In this article, we mainly outline and discuss the different approaches for the preparation of bare magnetic graphene composites (MGC), functionalized MGC and three-dimensional MGC (Fig. 1).

3.1. Preparation of bare magnetic graphene composites

Generally, the irreversible aggregation of G is inevitable because of strong van der Waals interactions between the G sheets and strong hydrophobicity, which hinder the improvement of its