Graphene Oxide for Organic Compounds Magnetic Solid-Phase Extraction

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Graphene oxide (GO) is a chemical compound with a form similar to graphene that consists of one-atom-thick two-dimensional layers of sp^2-bonded carbon. Graphene oxide exhibits high hydrophilicity and dispersibility. Thus, it is difficult to be separated from aqueous solutions. Therefore, functionalization with magnetic nanoparticles is performed in order to prepare a magnetic GO nanocomposite that combines the sufficient adsorption capacity of graphene oxide and the convenience of magnetic separation. Moreover, the magnetic material can be further functionalized with different groups to prevent aggregation and extends its potential application. A plethora of magnetic GO hybrid materials have been synthesized and successfully employed for the magnetic solid-phase extraction of organic compounds from environmental, agricultural, biological, and food samples. The developed GO nanocomposites exhibit satisfactory stability in aqueous solutions, as well as sufficient surface area.

Graphene oxide | magnetic solid-phase extraction | MSPE | organic pollutants | food samples | environmental samples | biological samples

1. Introduction

Solid-phase extraction (SPE) and liquid-liquid extraction (LLE) are two widely used and well-established techniques for the extraction of organic compounds. However, these conventional techniques tend to have many fundamental drawbacks such as complicated and time-consuming steps, requirement for a large amount of organic solvents and sample, as well as difficulties in automation [1][2][3][4]. Recent trends in sample preparation are focused on the progressive replacement of those techniques by miniaturized and environment-friendly techniques, such as solid-phase microextraction (SPME) [5], dispersive liquid–liquid microextraction (DLLME) [6], fabric phase sorptive extraction (FPSE) [7] and dispersive solid-phase extraction (d-SPE) [8].

Magnetic solid-phase extraction (MSPE) is a form of dispersive solid-phase extraction in which a magnetic sorbent is added into an aqueous sample in order to adsorb the target analytes. The sorbent is easily separated by applying an external magnetic field [9]. Subsequently, the analytes are eluted with the addition of an appropriate solvent and magnetic separation is performed again to collect the liquid phase, which is further analyzed. Compared with traditional SPE procedure, with magnetic sorbents there is no need to be packed into SPE cartridges, thus minimizing problems of column blocking and high pressure that are often observed in SPE. Meanwhile, the phase separation with an external magnetic field is a simple and rapid process compared to centrifugation and filtration steps. Sample and organic solvent consumption are also significantly decreased compared to classical SPE and LLE techniques [9][10].

Because of the evolution of technology and nanotechnology, novel extraction sorbents with improved chemical and physical properties have been synthesized and successfully used for magnetic solid-phase extraction of target analytes. Moreover, with the use of these materials, high extraction efficiency, good reproducibility in combination with low detection and quantification limits can be achieved [1][2]. Typical examples of MSPE sorbents are magnetic nanoparticles with surface modification by octadecyl (C_{18}) [11], activated carbon [12], carbon-nanotubes [13], graphene [14], graphene oxide [15], metal-organic frameworks [16], covalent organic frameworks [17] and zeolitic imidazole frameworks [18].

Graphene oxide is the oxidized form of graphene that can be easily prepared from natural graphite powder with Hummer's method after reaction with an anhydrous mixture of sulfuric acid, sodium nitrate and potassium permanganate [19][20][21][22][23][24]. Due to its superior properties such as good thermal and mechanical stability as well as its high surface area, graphene oxide has been used in multiple scientific fields including heterogenous catalysis, gas sorption, storage and separation, sensors and drug delivery [25].

In analytical chemistry, GO has been successfully employed for the sample preparation of a wide variety of samples including biological, food and environmental matrices [26][27][28]. Graphene oxide consists of one-atom-thick two-dimensional layers of sp^2-bonded carbon and the material is rich in oxygen-containing groups including hydroxyl, carboxyl and epoxy groups, which assist the interaction between the sorbent and organic molecules through strong π-π stacking, hydrophobic interaction and hydrogen bonding [29][30][31].

Graphene oxide is an ultra-light material that poses high dispersibility in aqueous solutions as well as high hydrophilicity which makes its separation from this kind of solutions difficult. In order to improve the separation, GO can form magnetic nanocomposites with magnetite through electrostatic interaction between the negatively charged graphene oxide sheets and the positively charged surface of Fe_3O_4 [32].

2. Preparation and Applications of GO for the MSPE of Organic Compounds

2.1. Nanocomposites of GO with Fe_3O_4 Nanoparticles

Due to its high surface area and its superparamagnetic properties GO/Fe_3O_4 has been employed for the extraction of a wide variety of organic compounds from various samples. The surface of magnetic graphene oxide is rich in hydroxyl and carboxyl groups, which assist the interaction between the sorbent and the target analytes through strong π-π stacking, hydrophobic interaction as well as hydrogen bonding [26][27][28][29][30][31].

The one-step co-precipitation approach is the most common synthetic route for the preparation of magnetic GO. In this approach, graphene oxide is dispersed in water. Subsequently, salts of Fe^{2+} (e.g., ferrous chloride) and of Fe^{3+}

(e.g., ferric chloride) are added, the mixture is heated and ammonium hydroxide is slowly added and the magnetite nanoparticles are formed [26].

Another common synthetic procedure is the solvothermal approach, in which GO is added in a dispersion of a Fe^{3+} salt (e.g., ferric chloride hexahydrate) and sodium acetate, under vigorously stirring for 30 min at room temperature [33][34]. The dispersion is transferred in an autoclave and heated under reflux for a specific time span. The ferric salt is added as the iron source, while the sodium acetate assists both the electrostatic stabilization of the magnetic nanoparticles onto GO in order to prevent agglomeration of the particles and the reduction of Fe^{3+} to Fe_3O_4.

Magnetic GO can be prepared by mixing GO and Fe_3O_4 under ultrasonic irradiation, stirring or mechanical shaking. In this case, Fe_3O_4 nanoparticles are dispersed in nitric acid solution in an ultrasonic bath for 30 min in order to generate a positively charged surface. Graphene oxide is dispersed in deionized water in order to generate a negatively charged surface. Subsequently, the dispersions of Fe_3O_4 and GO are mixed, the pH of the mixture is adjusted to a desired value and the mixture is subjected to vigorous magnetic stirring, mechanical shaking or ultrasonic radiation for a certain time span (e.g., 5 h) [35]. Finally, the GO/Fe_3O_4 material can be prepared after hydroxylation of Fe_3O_4 nanoparticles by mixing with GO and dimethyl sulfoxide. After ultrasonic treatment of the mixture for a certain time at room temperature, the desired material is obtained [36].

2.2. Nanocomposites of Reduced GO with Fe_3O_4 Nanoparticles

Reduced graphene oxide (RGO) is a nanomaterial obtained by chemical reduction of graphene oxide that contains less oxygen groups and has properties closer to those of graphene [25][37]. RGO has various applications such as removal of metals and dyes [38][39], catalysts [40], electroanalytical sensors [41] etc. Magnetic nanocomposites of reduced graphene oxide have been successfully applied for the MSPE of various analytes from different sample matrices. Due to the combination of the magnetic Fe_3O_4 nanoparticles and the graphene sheets, the magnetic RGO sorbent shows distinguished properties including good dispersity, high surface area, high adsorption efficiency and good super-paramagnetism [42].

There are different synthetic procedures for the fabrication of RGO/Fe_3O_4 sorbents. The co-precipitation approach is a multi-step procedure in which GO/Fe_3O_4 previously prepared by precipitating Fe^{2+} and Fe^{3+} in the presence of GO is reduced with the addition of hydrazine hydrate [43][44]. For the solvothermal approach, graphite oxide is exfoliated in diethylene glycol under sonication to produce graphene oxide while ferric chloride with sodium acetate are also dissolved in diethylene glycol. In this case, diethylene glycol was both solvent and reducing agent. Accordingly, the GO dispersion is added into the second solution and the mixture was sonicated and heated at 190 °C in an autoclave [43][45]. The RGO/Fe_3O_4 can be also prepared through the hydrothermal method, which is similar to the solvothermal but instead of organic solvents that are used in the solvothermal method, water is used as a solvent in the hydrothermal approach. For this purpose, a salt of Fe^{3+} and sodium hydroxide is added to an aqueous solution of graphene oxide and the mixture is heated in an autoclave for a certain time span [43][46].

Sudan dyes have been extracted from tomato sauce and chili-containing foods with RGO/Fe_3O_4 prior to their determination by HPLC-DAD [47]. The developed MSPE procedure was simple, economic and provided satisfactory extraction recoveries and LOD values. Magnetic RGO/Fe_3O_4 has been also used for the MSPE of bisphenol A from water samples prior to its determination by HPLC-UV. The MSPE technique was coupled with dispersive liquid–liquid microextraction (DLLME) in order to utilize the benefits of both sample preparation techniques. The magnetic sorbent was separated conveniently and rapidly from the sample matrix and it was found to be reusable for at least 12 repeated cycles [48].

2.3. Functionalized Nanocomposites of GO with Fe_3O_4 Nanoparticles

The main disadvantage of graphene oxide-based adsorbents is the important π–π stacking interactions between graphene oxide nanosheets, which are responsible for serious aggregation and restacking of the nanosheets, resulting in a potential block of the active adsorption sites of the sorbent and a decrease of its specific surface area. In order to overcome this problem, functionalization of the sorbent with different molecules that can enter between the GO nanosheet and prevent them from aggregation and restacking can take place [49].

In order to overcome this limitation, Yilmaz et al. developed a magnetic nanodiamond/graphene oxide hybrid and used it for the MSPE of sildenafil from alleged herbal aphrodisiacs by HPLC-DAD system. Functionalization with nanodiamond successfully prevented the aggregation and restacking of GO nanosheets [49].

Functionalization of graphene oxide-based adsorbents can also take place to enhance the extraction efficiency of the material by introducing compatible chemical molecules with high surface area and abundant functional groups in the structure of GO.

Polyamidoamine (PAMAM) dendrimer has been used to develop amino-terminated hyper-branched PAMAM polymer grafted magnetic graphene oxide nanosheets for the MSPE of selective serotonin reuptake inhibitors from plasma samples [50]. Due to the large number of terminal groups of polyamidoamine dendrimer, the structural characteristics as well as the internal spaces between their branches, which can trap the target analyte, the functionalized GO/Fe_3O_4 sorbent exhibited higher extraction efficiency compared to the conventional GO/Fe_3O_4 nanocomposite.

Functionalization with soluble eggshell membrane protein (SEP) was found to increase the stability and adsorption performance as well as accuracy and recoveries of GO/Fe_3O_4 due to the high density of surface functional groups such as amines, amides and carboxylic groups of SEP [51].

Porphyrin has been also used for the functionalization of GO/Fe_3O_4 nanocomposite and the sorbent was used for the MSPE of sulfonamides from tap and river water samples [52]. Due to the π-π stacking and electrostatic attraction between the negatively charged functionalized nanocomposite and the positively charged sulfonamides, the extraction process was accelerated. The novel sorbent showed higher adsorption capacity than the conventional GO/Fe_3O_4.

A co-polymer of divinylbenzene (DVB) and glycidylmethacrylate (GMA) was used for the functionalization of GO/Fe_3O_4 in order to develop a sorbent for the MSPE of chlorophenols from environmental water prior to their determination by HPLC-MS/MS [53]. Due to π-π stacking and hydrogen-bonding interactions between the analytes and the functionalized adsorbent, good extraction efficiency was observed.

Polystyrene (PS) [54] and poly(pyrrole-co-aniline) [55] are two examples of functional groups that were employed to prepare magnetic graphene functionalized nanocomposites, which were used for the MSPE of PAHs from water samples. Polystyrene is rich in phenyl and alkyl groups. Therefore, functionalization with PS enhanced the extraction efficiency by increasing the active surface sites of the material. The sorbent exhibited sufficient surface area, excellent magnetic properties and resulted in good extraction efficiencies and low detection limits [54]. Similarly, the poly(pyrrole-co-aniline) functionalized graphene oxide nanocomposite combined the properties of the polypyrrole and polyaniline co-polymer, the GO, and the magnetic nanoparticles. As a result, the developed nanocomposite exhibited a significant enhancement of extraction efficiency due to the increased number of active surface sites on the sorbent as well as the protection of the Fe_3O_4 nanoparticles [55].

Polythionine was also employed for the functionalization of magnetic graphene oxide through an oxidative polymerization reaction of thionine on the surface of GO/Fe_3O_4 [56][57]. This surface modification significantly improved the merits of GO/Fe_3O_4, providing satisfactory extraction efficiency. The functionalized nanocomposite was used for the MSPE of chlorpheniramine [56] and duloxetine [57] from human plasma prior to their determination by HPLC-UV.

In order to enhance the dispersibility of magnetic GO in hydrophobic media, functionalization with phytic acid has been reported. Phytic acid-stabilized GO/Fe_3O_4 was applied for extraction of PAHs from vegetable oils. Due to the super-amphiphilicity of phytic acid, the dispersibility of the conventional GO/Fe_3O_4 sorbent increased. [58].

Functionalization of GO/Fe_3O_4 can also be performed for the enhancement of its selectivity towards the target analytes. In 2015, Abdolmohammad-Zadeh and Talleb synthesized a β-cyclodextrin (β-CD) grafted GO/Fe_3O_4 nano-hybrid and used it for the MSPE of gemfibrozil from human serum and pharmaceutical waste-water samples followed by determination using spectrofluorometry. This chemical compound can selectively bind with various organic, inorganic and biological guest molecules into its cavity to form stable host–guest inclusion complexes by a series of forces such as hydrophobic and van der Waals interactions. Therefore, due to the surface modification of graphene oxide with β-cyclodextrin, selective separation of the target analyte from complex sample matrices was achieved [59].

Other examples of chemical molecules that have been used for the functionalization of GO/Fe_3O_4 are triethylenetetramine [60], silica [61], sporopollenin [62] and phenylethyl amine [63]. The superior adsorption capacity of the functional groups resulted in functionalized magnetic GO nanocomposites with sufficient surface area, excellent extraction efficiency, good stability as well as ease in handling and separation.

2.4. Functionalized Nanocomposites of Magnetic GO with MIPs

Molecularly imprinted polymers (MIPs) are highly selective, tailor-made synthetic polymeric materials that exhibit high adsorption capacity. Moreover, they can be easily prepared with economic synthetic procedures. Therefore, MIPs have been applied for the extraction and preconcentration of trace analytes in diverse fields, including natural, agricultural, and food products and environmental samples [64][65][66]. The combination of graphene oxide and molecularly imprinted polymers can significantly enhance the selectivity of the extraction procedure [65][66].

Ning et al. developed a molecularly imprinted polymer on magnetic GO and used it for the extraction of 17β-estradiol from milk powder samples. For this purpose, GO/Fe_3O_4 nanoparticles were grafted with acrylic acid. Subsequently, the MIPs-GO/Fe_3O_4 sorbent was prepared from 17β-E2 (template molecule), acrylamide (functional monomer), ethylene glycol dimethacrylate (cross-linker), and 2,2′-azobis(isobutyronitrile) (initiator) in acetonitrile dispersion of the functionalized magnetic GO material. With the use of developed sorbent, specific recognition, as well as highly effective removal of 17β-E2 from complicated matrices, were achieved [67]. Barati et al. synthesized a molecular imprinted polymer based on magnetic chitosan/graphene oxide and used it for the selective extraction of fluoxetine from environmental and biological samples prior to its spectrophotometric determination. Due to the multi imprinting sites and high surface area of the magnetic chitosan/GO, high selectivity and adsorption efficiency was observed [68].

2.5. Functionalized Nanocomposites of Magnetic GO with MOFs

Metal-organic frameworks are mixed organic-inorganic supramolecular materials that became popular in 1995, when Yaghi and Li reported the synthesis of a MOF with large rectangular channels [69]. These materials are based on the coordination of metal ions or clusters with bi- or multidentate organic linkers [70][71]. Metal-organic frameworks exhibit various extraordinary properties including luminosity, tunable pore size, flexibility and thermal stability as well as high surface areas [72][73].

The combination of graphene oxide and metal organic frameworks enhances the merits of sorbent including its reusability, its pore volume, its dispersion capability, its extraction capacity, its mechanical strength as well as its surface area [74][75][76].

2.6. Functionalized Nanocomposites of Magnetic GO with MOPs

Microporous organic polymers (MOPs) represent a class of amorphous porous materials, composed of fully covalently bound organic building blocks. MOPs have lately gained much research interest, due to the combined superiority of porous materials and functional polymers [77][78][79]. MOPs exhibit well-defined porosity as well as high surface area. Because of their tunable surface chemistry, MOPs can be easily functionalized [77]. Depending on the choice of monomers, functionality and polymerization method, MOPs can be prepared both as solution processable or as insoluble networked materials [78]. Therefore, MOPs have various applications including gas storage [80], environmental remediation [81], catalysis [82], energy storage [83] etc. In analytical chemistry, MOPs have been used as sorbents for the extraction of different organic compounds including hydroxylated PAHs [84] and 5-nitroimidazoles [85].

By combining MOPs and magnetic GO it is possible to develop nanocomposites that combine the extraordinary properties of both MOPs and GO. Shahrebabak et al. synthesized a triazine-based polymeric network modified magnetic nanoparticles/GO nanocomposite and used it for the MSPE of basic and acidic pesticides from food (e.g., cucumber, tomato) and water samples by HPLC-UV. For the fabrication of the material, Fe_3O_4 nanopaticles were modified by triazine-based polymeric prepared from melamine and terephthaldehyde. Subsequently, the functionalized Fe_3O_4 nanoparticles were mixed with GO in THF and the mixture was sonicated. The novel sorbent showed well-defined porosity, high surface area, good chemical stability and tunable surface chemistry. Due to the different functional groups of the nanocomposite (i.e., amine and carboxylic groups), simultaneous extraction of basic and acidic pesticides was achieved [77].

2.7. Applications of Magnetic GO Nanocomposites Modified with Ionic Liquids (ILs) and Deep Eutectic Solvents (DESs)

Ionic liquids (ILs) and deep eutectic solvents (DESs) are an alternative to environmentally harmful ordinary organic solvents. ILs are generally composed of bulky, non-symmetrical organic cations (i.e., imidazolium, ammonium pyrrolidinium, pyridinium etc.) and different inorganic or organic anions [86][87][88]. DESs are systems formed from a eutectic mixture of Lewis or Brønsted acids and bases that contain a variety of anionic and/or cationic species [89][90]. ILs and DESs have a tunable nature and their properties can be optimized through the choice of their cationic and anionic constituents [87][88]. Although DESs and ILs have similar physical properties, their chemical properties differ resulting in different potential applications [91][92]. By combining ionic liquids and deep eutectic sorbents with magnetic graphene oxide it is possible to design and develop new extraction sorbents with extraordinary properties [86][92].

In 2016, Cai et al. synthesized a planar graphene oxide-based magnetic ionic liquid nanomaterial for extraction of chlorophenols from environmental water samples coupled with HPLC-MS/MS [92]. For this purpose, $Fe_3O_4@SiO_2$ magnetite microspheres functionalized with amino-groups (Fe_3O_4 $@SiO_2$-NH_2) and 1-carboxymethyl-3-methylimidazolium chloride were used to functionalize graphene oxide. The novel sorbent exhibited great adsorption capacity and was successfully used to extract both polar and non-polar chlorophenols from tap, river and well water. The sorbent was found to be reusable for at least six times.

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