Application of graphene and its compounds in pretreatment of environmental samples

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Abstract. Due to its large surface area, good mechanism strength and thermal stability, graphene is recognized as an ideal extractant of organic matters, especially aromatics and has been widely used in pretreatment of environmental samples, such as in solid-phase extraction (SPE), solid phase microextraction (SPME) and dispersive solid-phase extraction (d-SPE). Modifying the graphene with three-dimensional aerogel and compounds can improve its extraction performance. Graphene can extract organics because of the delocalized π bond, its hydrophobicity, electrostatic interaction and the hydrogen bond, and its extraction performance differs as the conditions vary. In particular, the pH value, the ionic strength, the extraction temperature and time, the eluant, the desorption temperature and time have significant impacts on the extraction results. In this paper, we analyzed the impacts of these factors from the mechanism perspective, with a vision to provide a theoretical basis for application of graphene and its compounds in pretreatment of environmental samples.

1. Introduction
Graphene, a novel carbon nanomaterial, boasts the following advantages in pretreatment of organic environmental samples. First, with good thermal and chemical stability, it is an ideal adsorbent; second, its high specific surface area and sides can serve as good adsorption sites of molecules; third, its 2D π-conjugated structure has good adsorption performance on aromatics; fourth, the raw materials for preparation of graphene are cheap and widely available; fifth, it is easy to modify the graphene, and intermediate oxidized graphene has rich hydrophilic groups, which can realize selective adsorption in specific modification, connect with different carriers and thereby achieve different extraction methods [1]. That being said, the graphene also has defects. For instance, due to its 2D structure, small size and weight, it is likely to cause hyper-pressure on the extraction device and makes it difficult to realize centrifugation and separation [2-4]. In these years, scholars have tried to improve the extraction performance of graphene and graphene oxide by preparing 3D aerogel, compounds or modifying the graphene, and applied the modified products to pretreatment of samples for SPE, SPME, d-SPE.

2. Solid-phase extraction
Solid-phase extraction (SPE) boasts high recovery rate, small time consumption, high enrichment efficiency and convenience for automation, and has been widely used in sample pretreatment. The extractant is the essence of SPE, deciding the selectiveness and sensitivity of the extraction. Thus, developing new extractant has become a new research hotspot.

Graphene has many defects; for instance, it is hard to control its size, it is prone to bonding, and small-size graphene sheets are prone to damages and are not suitable for high-pressure online SPE.
Many compounds of graphene and graphene oxides have been prepared so far, such as silica gel, molecularly imprinted polymer, biomolecules. Gao et al. \cite{5} have prepared chitosan/oxidized graphene that is widely available, with good biocompatibility, and reusable. Compared with graphene aerogel, the compounds perform significantly better in extraction, have higher recovery rate in the water phase and can be reused 80 times, incurring no significant changes in the Raman spectrum.

The 3D graphene compounds not only have the inherent features of 2D graphene materials, but have large surface area and rich pores, making the compounds a new research hotspot \cite{6-9}. Thesing et al. \cite{8} prepared the 3D graphene framework with graphene and L-cysteine to extract triclosan from lake water. The recovery rate reached 66% - 72%, the detection limit is 0.07 mg/L and the quantification limit is 0.22 mg/L. Sun et al. \cite{7} prepared 3D graphene/ multiwalled carbon nanotubes through chemical reduction and lyophilization; as the proportion of graphene oxides increases, the pore structure and aperture size of the composites are optimized; when used to extract four organophosphorus pesticides in water, the graphene achieves a detection limit of 0.28 µg/L, with a recovery rate of 94.8%~103.5%.

Aside from preparing graphene-based compounds, optimization of the sample’s pH value, the ionic strength, the extraction time and the eluant have significant effects on the extraction efficiency.

It is widely perceived that the graphene and graphene oxide cannot only have electrostatic interaction with the cation and anion analytes, but can absorb the aromatics through the six-membered ring delocalized π-conjugated structure, making them more suitable than ionic compounds in extraction of aromatics \cite{10}. The pH value of the sample affects not only the form of the analytes, but the interactions between the adsorbent and analytes \cite{11}. Jiang et al. \cite{12} found that when the pH of the sample stays between 3 and 9, the extraction efficiency of chlorophenol samples by graphene shows no changes, indicating the important role of the π–π non-electrostatic effect on interactions between the graphene and the chlorophenol. Sun et al. \cite{7} found that in strong acid, competitive adsorption occurs between H+ and organophosphorus pesticides, so the extraction efficiency of the 3D graphene/multiwalled carbon nanotube increases as the pH value rises, and when the pH exceeds 6, the extraction efficiency drops. Besides, when the analytes are neutral molecules, the changes in the pH value have no significant effects on the recovery rate\cite{13, 14}.

Han et al. \cite{14} argued that the extraction drive of organophosphorus pesticides by graphene is the π–π interaction effect and the hydrophobic interaction. Comparison of the extraction efficiency of different eluents reveals that the interaction between polyaromatic hydrocarbon and graphene is the π–π interaction, and the interaction increases as the condensed rings increase. The interaction between DDT and the graphene is the π–π interaction; the strong heteropolar solution is hard to destroy, while the weak heteropolar solution is easy to be eluted\cite{5, 14}. When the graphene is used to extract chlorophenol from water samples, due to the strong hydrogen-bond interaction between the chlorophenol and the unreduced hydroxide radicals on the surface of the graphene, the protic solvent methyl alcohol has higher elution efficiency than the non-protic solvent acetonitrile. The alkaline environment of the alkaline methanol can promote ionization of the chlorophenol, which reduces its interaction with the graphene and increases the recovery rate.

When the concentration of the sodium chloride is between 0 and 100 mM, the graphene solid-phase extraction tray is employed to extract the polyaromatic hydrocarbon and the organophosphorus pesticide. The result shows no significant changes in the recovery rate and no impacts on the ionic strength, which may be attributable to the low solubility of the analytes in water \cite{13, 14}.

3. Solid phase microextraction

Solid phase microextraction (SPME) \cite{10} packs preconcentration, extraction and purification into one step. It consumes little or no solvents, has fast extraction speed, is easy for operation, highly reproducible, and compatible with gas chromatography (GC) and liquid chromatography (LC). The sampling modes include the direct immersion (DI) and headspace (HS).

To solve the problems of using graphene as the direct extractant \cite{12-17}, researchers proposed the sol-gel method, the coprecipitation method, the solvothermal method, the organic cross-linking agent, and the microwave-assisted method\cite{18-20} to improve the durability of the extraction fiber. Zhang et al. \cite{19}
used the graphene-based quartz fiber to develop a HS-SPME-GC method for detection of polyaromatic hydrocarbons in soil and water samples. The fiber was used with stable performance for over 150 times, and the enrichment factor is 2-17 times higher than the commercial SPME column. The authors also find that the graphene-coated fiber shows higher extraction efficiency with the reduction of the graphene oxides, and its adsorption of polyaromatic hydrocarbons is higher than that achieved by other alternative-based aromatic compounds and fatty hydrocarbons, and the adsorption improves as the condensed rings increase. The adsorption relies mainly on the π-π interaction and, subsequently, the hydrophobic interaction; besides, the weak covalent bond (the hydrogen bond) also plays a role.

Factors like the sampling mode, the pH of the sample, the ionic strength, the extraction time and temperature, the desorption condition all have impacts on the extraction efficiency, but their impacts differ as the analytes and the extractants vary. Li et al. compared the extraction efficiency of benzenes by graphene in water samples under two sampling modes, the immersion mode and the headspace mode. As the benzenes are volatile, most benzenes will be released to the headspace of the sampling bottle when heated. During immersion sampling, the extraction probe contacts with the water sample, forming a film between the water sample and the coating material, which prevents the organic from spreading to the coating layer.

The pH value of the sample will influence the interaction between the extractant and the analytes by changing the surface charge. Sereshit et al. prepared PAN-DBSA-graphene oxide nanocompounds by in-situ chemical oxidative polymerization, and used the compounds to extract tetracycline antibiotics from water and milk. When the pH is 3.0, the analyte has positive charges, and the adsorbent has negative charges, which leads to high extraction efficiency. When the pH is below 3.0, the tetracycline antibiotics are converted into dehydrated tetracycline antibiotics due to the dehydration effect, which leads to lower extraction efficiency.

The ionic strength plays dual roles. On one hand, the presence of salt changes the activity coefficient of the analyte in the water phase and thereby improves the extraction efficiency due to the salting-out effect; on the other hand, salt increases the viscosity and density of the water phase, and meanwhile occupies the active sites of adsorption, thereby reducing the extraction efficiency. Moreover, the ionic strength relies also on the sampling mode, because addition of salt will reduce the solubility of the analyte in the water phase, which increases the content of headspace gas.

The extraction temperature influences the extraction efficiency in a kinetic and thermodynamic manner. In terms of kinetics, higher temperature increases the diffusion efficiency of the analyte and thereby increases the extraction efficiency. In terms of thermodynamics, as the adsorption process releases heat, the temperature rise reduces the volume of the absorbed analyte; and as the DI and HS extraction methods differ, the Henry’s constant changes the distribution coefficient of the analyte between the fiber and the sample solution. Different effects compete and influence the extraction efficiency in different manners. When the DI-SPME method is employed, due to the high volatility or semi-volatility of the sample under high temperatures, the analyte increases the proportion in the headspace and reduces the extraction efficiency.

The desorption method is determined by the sampling mode. DI sampling uses a small doze of solvent for elution, while HS sampling uses heat for desorption. Chen et al. prepared porous plicated graphene-coated HS extractant to extract pyrethroid insecticides; the analyte cannot be completely desorbed under low temperatures; when the temperature exceeds 270°C, the peak area no longer changes, which indicates complete desorption, though high temperature will damage the coating and the sample injector. Lee et al. used the 3D network graphene to extract polybrominated diphenyl ethers, and found that a short desorption incurs the carryover effect, while a long desorption cuts the service life of the column extractor.

4. Dispersive solid phase extraction
Dispersive solid phase extraction diffuses the extractants in the sample solution. The full contact increases the mass transfer rate, reduces the time to reach the adsorption equilibrium, cuts the time for
sample pretreatment, and thus draws broad research attention. Among d-SPE techniques, magnetic solid-phase extraction (MSPE) which have been extensively reported is a sample pretreatment method with great prospects.

Graphene-based magnetic compounds are prepared through physical blending, in-situ growth and bonding of covalent bonds. Ulusoy et al. prepared shell-structured GO/MWCNT/Fe₃O₄/SiO₂ by the solution deposit method. When the doze of the adsorbent reaches above 7. Mg, the recovery rate of paracetamol remains stable, but the caffeine decreases. That’s because as the adsorbent increases, it becomes harder to desorb the adsorbed analytes, which requires more eluent solution and therefore reduces the extraction efficiency and sensitivity.

Wang et al. improved the preparation methods of magnetic graphene, and synthesized the Fe₃O₄@SiO₂-G compounds through the reactions of amides between the graphene and the amino Fe₃O₄@SiO₂, and applied the compounds to pretreatment of polyaromatic hydrocarbon, carbamate and pyrethriods pesticides in different sample substrates. As previously reported, the residues of the Congo red were extracted from the water sample and when the pH value is smaller than the zero potential, the adsorbent carries positive charge on the surface; otherwise, it carries negative charges. Therefore, under acid pH values, the amino radicals undergo protonation, which reduces the electrostatic interactions and hydrogen-bond interaction. Wei et al. found that when the pH value is small and the sample is acid, due to the strong hydrophobicity, the hydrogen-bond interaction and π-π interaction, the magnetic nitrogen-mixed graphene reaches the best recovery rate in extraction of non-steroidal anti-inflammatory drugs. As the pH value increases, the analyte presents the ionic state and affects the recovery rate.

Senosy et al. prepared the Zeolite imidazole ester skeleton functional magnetic graphene oxide to extract triazole fungicides in water, honey and fruit juice samples. As their result shows, when the adsorbent doze exceeds 16 mg, the increased adsorbent is likely to concentrate and the contact area drops, which reduces the rise of the recovery rate. When the extraction time exceeds 15 min, the recovery rate remains unchanged, which means the large specific surface area of the adsorbent accelerates the adsorption process. When the concentration of sodium chloride is increased in the sample, the salting-out effect will reduce the solubility of the analytes in the water, increase the viscosity and density of the solution, which reduces the extraction efficiency during the mass transfer process.

The research result reveals that the graphene, with its large delocalized π-electron system, has strong affinity with most aromatic compounds, lacks selectivity in complex substrates and thus causes competitive adsorption. Besides, the magnetic particles will occupy active sits of adsorption and reduces the extraction efficiency. Functional processing of the compounds can improve their performance. Current modifying materials include anionic and cationic surfactants, polymers, carbon nano tubes, ionic liquids, and metal organic frameworks.

5. Conclusions and prospect
Pretreatment of samples is crucial for purifying environmental samples, extracting and pre-condensing the target analytes. The key of pretreatment is to develop extractants that have good performance and are environmentally friendly. As known to all, good extractants have the following features. First, a good extractant is selective of the target analyte, and shows physical and chemical inertia to substrate interferents; second, it can achieve a high recovery rate and enrichment factor; third, it is easy and cheap to prepare, and shows chemical and mechanical stability. Graphene, a 2D carbon nano-material, has large surface area and good stability. Due to its delocalized π-π interaction with the target material, the hydrophobicity and the hydrogen-bond interaction, it can achieve high enrichment of the target material and is compatible with different forms of extraction. As graphene is prone to agglomeration, functional modification of graphene-based compounds or 3D structures becomes a dominating research direction.

Optimizing the extraction conditions is important for improving the extraction performance of graphene-based compounds. The key parameters vary as the extraction techniques differ. In general
cases, the parameters include the pH value of the sample, the ionic strength, the extraction time and temperature, the desorption solvent and the desorption time (the desorption temperature and time in the case of HS-SPME). The pH value of the sample affects the extraction efficiency by affecting the surface charges of the analyte and the extractant. When the pH value is below the pKₐ of the analyte, the H⁺ in the solvent occupies the active site of the adsorbent, which reduces the electrostatic interaction between the analyte and the extractant. The ionic strength affects the extraction efficiency through kinetic and thermodynamic mechanisms. The salting-out effect will reduce the solubility of the analyte in the sample, the added ions will occupy the adsorption sites in the extractant and increase the viscosity of the solvent, which reduces the mass transfer efficiency. Moreover, due to the different physical and mechanical properties of the target analytes, their interactions with the adsorbent vary, but theoretical analysis can help obtain the optimal extraction conditions.

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