

EXTRACTION OF PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES (PFASs) FROM ENVIRONMENTAL WATER SAMPLES BY CETYLTRIMETHYLAMMONIUM BROMIDE-COATED MAGNETIC GRAPHENE SHEETS

Liu Q*, Jiang GB

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Email: gbjiang@rcees.ac.cn

Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are widespread environmental organic pollutants.¹ These PFASs have low pK_a values and are present in their ionized form in environmental water samples, and thereby can strongly interact with cetyltrimethylammonium bromide (CTAB) hemimicelles/admicelles via electrostatic interaction. Graphene is emerging as a promising sorbent material in sample preparation due to its large surface area, π -electron rich system, and unique nanosheet morphology.²⁻⁴ In this work, we developed a novel and highly efficient extraction method for PFASs in environmental water samples by using magnetic graphene (MG) sheets as support for hemimicelles/admicelles. The flexible graphene sheets with large surface area can provide an excellent nano-sized platform for hemimicelles/admicelles formation, leading to high extraction efficiency and high preconcentration factors for PFASs. Furthermore, the magnetic sorbents can be easily and rapidly collected by an external magnetic field without centrifugation or filtration, thus greatly simplifying the extraction process.

Materials and methods

PFASs, including perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoA), perfluorotetradecanoic acid (PFTA) were purchased from Sigma-Aldrich. Organic solvents used in this work were all from J. T. Baker (Phillipsburg, NJ) and of HPLC grade. Graphene oxide (GO) was synthesized by the Hummers method according to previous reports.⁵ The MG sheets were facilely prepared through the redox interaction of GO with Fe(II) ions under basic condition (pH 9),⁶ and dispersed in water at 1 mg/mL.

For the extraction, an aliquot of MG aqueous dispersion and CTAB aqueous solution were added to the sample solution. The mixture was shaken for 20 min. Then, the MG sheets were collected by a magnet and the supernatant was poured out. The analytes were eluted with acetonitrile (ACN) and analyzed by HPLC-ESI-MS/MS in negative ion mode.

Results and discussion

Graphene was usually directly used as the adsorbent in extraction methods. Due to its large surface area and flexible nanosheet morphology, we think that graphene can also be used as an excellent support or substrate for other sorbent materials. Therefore, in this work, we tried to use graphene as the support for hemimicelles/admicelles for extraction of PFASs from environmental waters. Considering that graphene sheets are very thin and light, we endowed the graphene sheets with magnetic properties. In this way, the sorbents can be easily collected by an external magnetic field without centrifugation or filtration. The MG sheets were prepared via the redox reaction between GO and Fe(II). This is a one-pot, one-step and room temperature reaction, and thereby is more facile and simple than other methods.

The as-prepared MG sheets were characterized by different techniques. The Fe_3O_4 magnetic nanoparticles were *in situ* formed on the graphene sheets without any organic linkers, and thus introduced less organic contaminants to the sorbents. Furthermore, the MG maintained the nanosheet morphology of graphene, and thus kept the capability to serve as an excellent support material. The MG sheets showed good magnetic response and typical superparamagnetic behaviors, which are favorable for the use as sorbent materials in the extraction.

The formation process of CTAB hemimicelles/admicelles on MG sheets was firstly studied via zeta potential measurement. Generally, the zeta potential of MG increased with the increase of CTAB amount in the dispersion solution. The profile can be divided into three stages: 0 – 0.1, 0.1 – 1.0, and above 1.0 mg CTAB/mg MG. These three stages corresponded the formation of hemimicelles, mixed hemimicelles/admicelles, and free micelles, respectively. The maximum adsorption amount of CTAB on MG sheets was ca. 1.0 mg/mg. The elution condition was also studied via zeta potential. The most efficient elution was achieved with 1.5 mL ACN per mg MG.

The extraction conditions were also optimized. Without using CTAB, i.e., direct extraction of PFASs using only MG, the extraction efficiency was very poor. Upon adding CTAB into the solution, the extraction efficiency was greatly improved. The highest extraction efficiency was achieved with 1.0 mg CTAB/mg MG, corresponding to the saturation point of CTAB on MG sheets. The effect of sample volume was also studied, and it was found that 200 mL was the most suitable sample volume.

Under the above mentioned optimized conditions, the method detection limits (MDLs) of PFASs were in the range of 0.15 – 0.50 ng/L. Compared with that without extraction, the analytical sensitivity was enhanced by 50 – 113-fold by this extraction method. The sensitivity is comparable to or better than that reported in previous reports^{7,8} and is also adequate for real water sample analysis.⁹ The run-to-run and day-to-day RSDs were less than 8.4 and 11.6%, respectively. With a river water samples spiked at a level of 50 ng/L, the recoveries ranged from 56.3 to 91.4%, indicating that the sample matrix caused no significant effect to the analytical results.

Conclusion

In summary, we have developed a novel ternary extraction system by using MG sheets as support for CTAB hemimicelles/admicelles for PFASs in environmental water samples. This system combines the good extraction capability of hemimicelles/admicelles, convenience of magnetic nanoparticles, and high loading capacity of graphene, thus yielding high extraction efficiency, good reproducibility and good recoveries. Therefore, we believe that it should be a promising sample preparation method for PFASs as well as other compounds having similar structures in environmental water samples.

Acknowledgements

We acknowledge the financial support from the National Basic Research Program of China (No. 2009CB421605) and the National Natural Science Foundation of China (No. 21107120, 20890111, 20921063, 20931160427).

References:

1. Goss K. (2008) *Environ. Sci. Technol.* 42: 456-458.
2. Liu Q, Shi J, Sun J, Wang T, Zeng L, Jiang G. (2011) *Angew. Chem. Int. Ed.* 50: 5913-5917.
3. Liu Q, Shi J, Sun J, Wang T, Zeng L, Zhu N, Jiang G. (2011) *Anal. Chim. Acta* 708: 61-68.
4. Liu Q, Shi J, Zeng L, Wang T, Cai Y, Jiang G. (2011) *J. Chromatogr. A* 1218: 197-204.
5. Hummers W, Offeman R. (1958) *J. Am. Chem. Soc.* 80: 1339.
6. Xue Y, Chen H, Yu D, Wang S, Yardeni M, Dai Q, Guo M, Liu Y, Lu F, Qu J, Dai L. (2011) *Chem. Commun.* 47: 11689-11691.
7. Zhao X, Li J, Shi Y, Cai Y, Mou S, Jiang G. (2007) *J. Chromatogr. A* 1154: 52-59.
8. Yu J, Hu J, Tanaka S, Fujii S. (2009) *Water Res.* 43: 2399-2408.
9. Boulanger B, Vargo J, Schnoor J, Hornbuckle K. (2004) *Environ. Sci. Technol.* 38: 4064-4070.