Preparation of micelle supported magnetic hydroxylated multi-walled carbon nanotubes based DSPE for determination of PAHs

Mingyu Wang¹,², Shaojun Zhang², *, Xiao Zhang¹, Deyu Li²
1Ocean School, Yantai University, 32 Qingquan Road, 264005 Yantai, China
2College of Naval architecture and Marine Engineering, Shandong Jiaotong University, 1508 Hexing Road, 264310, Weihai, China
*Corresponding author e-mail: 15163118785@163.com

Abstract. A micelle supported Fe₃O₄ magnetic nanoparticles decorated hydroxylated multi-walled carbon nanotubes material was synthesized. The material was facilely synthesized between carbon nanotubes and Fe²⁺. The synthesized nanomaterial served as an excellent support for micelles, exhibiting high loading capacity and selectivity. The prepared material used in dispersive solid-phase extraction (DSPE) for investigation of gaseous phase polycyclic aromatic hydrocarbons (PAHs) emitted from marine diesel engine for the first time. The application showed good response (R² > 0.9981) in the range of 0.02 – 1.0 µg/L, satisfactory reproducibility (variation less than ± 10%) and high precision. Limits of detection of sixteen PAHs ranged from 0.009 to 0.018 µg/L (S/N=3). The spiked recovery of proposed method (72.65-96.54 %) was 1.01 - 2.32 times higher than that of the conventional method. The enrichment factors reached to 39.65-121.32 that exhibited good enrichment ability.

1. Introduction
Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants that formed from both natural and anthropogenic sources with mutagenic and carcinogenic properties. Because of their hydrophobicity, PAHs and its metabolites tend to be interacted with DNA, causing malignancies and heritable genetic damage in humans [1]. Therefore, close attention has been paid to the research of PAHs, especially determination gaseous phase PAHs emitted from diesel engine for atmospheric pollutant control [2].

Directly determination of PAHs in environmental samples using analytical instrument is still challenging because of the extremely low concentrations and complex unknown interferences [3]. Therefore, pre-concentration is required. Modern pretreatment technique dispersive solid-phase extraction (DSPE) greatly simplified pre-concentration and cleaning process that overcomes the limitations of the classical techniques. Many researches focused on synthesis or modification of adsorbent nanomaterials such as nanofibers, graphene, glassy carbon, activated carbon, multi-walled carbon nanotubes (MWCNTs). Among them, MWCNTs is considered as a most widely used adsorbent materials [4].
There have no report for determination of PAHs using MWCNTs as adsorbent; the reason lies in that the selectivity of the MWCNTs is low for direct adsorption the PAHs from complex environmental samples. In order to selectively extract specific pollutants, MWCNTs can be covalently bonded with hydroxyl groups (-OH) and then packed into a cartridge as SPE mode. SPE mode overcomes the separation step of MWCNTs-OH from the solvent, but the entire process is still time consuming and using large amount of organic solvents that harmful to human body and environment. Thus, magnetite/MWCNTs-OH (MMWCNTs-OH) composite were prepared by electrostatic self-assembly so to be easily collected by magnet thus greatly simplify the extraction process [5]. Finally, the extraction efficiency of MMWCNTs-OH composite is still need to be improved, and this problem could solved by combining micelles extraction technique [6]. In the current study, a surfactant modified magnetic hydroxylated multi-walled carbon nanotubes (MMWCNTs-OH) adsorbent was prepared and used as a platform for the formation of micelle in DSPE. Extraction of MMWCNTs-OH was performed by applying an external magnetic field. This method used in determination of gaseous phase PAHs emitted from marine diesel engine for the first time that greatly simplifies the extraction process.

2. Experimental

2.1. Synthesis of MMWCNTs-OH

MWCNTs-OH and MMWCNTs-OH were prepared according to the method of Ling and Zhang with some modification [7]. The flow chart was shown in Fig. 1. FeCl₃·6H₂O (0.060 g) and FeCl₂·4H₂O (0.020 g) were dissolved in 40 mL of deionized water. The solution was constantly stirred in a 100 mL flask. Subsequently, MWCNTs-OH (0.100 g) was added into the mixed solution followed by the slow addition of 30 mL (5%, v/v) ammonium hydroxide solution at 80 °C, and the mixture was stirred for 60 min. The whole reaction process was performed under nitrogen gas protection. Thereafter, the black precipitates formed (MMWCNTs-OH) were separated from the reaction medium via centrifugation at 2000 r min⁻¹ and then washed with deionized water several times until the pH close to neutral. The MMWCNTs was collected by a magnet and dried under vacuum.

![Figure 1. Scheme diagram of MMWCNTs-OH synthesis and DSPE procedures.](image)

2.2. Sample preparation

PAHs emitted from diesel engine were collected from a RT-flex60c marine diesel engine (Qingdao Wartsila Corporation, China) according to MARPOL 73/78 annex VI. A stainless steel joint connecting tube was welded on the tail end of the exhaust pipe and connected with a brass tube. The diameter of
the diesel engine exhaust pipe was 54 mm, and the internal diameter of brass tube was 5.0 mm. Each brass tube connected with a 250 mL aqueous glass containers for collection of exhaust emissions without diluting with air. The optimized aqueous solution in the containers including, sodium chloride (0.01mol/L) and 5% ethanol: n-hexane (3:1, v/v). Aqueous capture was collected for 10 min. The same batches of samples were used in the experiment.

In the sample extraction process, a micelle supported nanomaterial MMWCNTs-OH was prepared. Adjust the sample solution to pH3 by hydrochloric acid (HCl) firstly. Then, measured 100 mL sample solution and adding 1.0 mL MMWCNTs-OH solution (concentration 1.0 mg/mL) containing CTAB (1.0 mg/mL) to it. Extraction time was twenty minutes. A magnet was used for collecting MMWCNTs-OH material. The desorption solution using acetone at the volume of 1.0 mL. Finally, the obtained effluent was detected in a GC/MS-QP 2010 Plus.

3. Results and discussion

3.1. Characterization of MMWCNTs-OH

The SEM image of MMWCNTs-OH was shown in Fig. 1. Fe3O4 nanoparticles were observed evenly depositing on the surface of MWCNTs. There was no obvious aggregation observed. The diameter of Fe3O4 magnetic particles was about 10 nm. The SEM morphology of MMWCNTs-OH@CTAB adsorbent confirmed well decorated on the platform. This synthesis used oxidation-reduction reaction, which could not introduce impurities into the adsorbent after the reaction.

VSM was used for determination of magnetic properties of MMWCNTs-OH. As shown in Fig. 2a, the saturation magnetization of MMWCNTs-OH reached to the maximum at the value of 12.58 emu/g. The highest value was sufficient for determination of the target object. MMWCNTs-OH was rapidly dispersed after exposure to the external magnetic field. MMWCNTs-OH showed super paramagnetic that made it a good adsorbent. This phenomenon was caused by MMWCNTs-OH has abundant functional groups hydroxyl ions (-OH). The hydroxyl ions improved the proposed material better dispersion in solution. Moreover, the hydroxyl ions were susceptible to provide platform for micelles. The experiment studied the magnetic properties of MMWCNTs-OH@CTAB. After loaded with CTAB, the highest saturation magnetization was at the value of 12.19 emu/g, which was a little lower than the value of MMWCNTs-OH. But 12.19 emu/g was still sufficient for determination of object compounds in the sample solution. We could deduce from the result that MMWCNTs-OH played a more important role than MWCNTs-OH in magnetic properties of MMWCNTs-OH@CTAB.

![Graph](image_url)
Zeta potential means the potential of shear plane, which is an important index to characterize the stability of colloidal dispersion system. As values of Zeta potential have relative with the stability of colloidal dispersion, Zeta potentials under pH 3-11 conditions were compared among MWCNTs-OH, MMWCNTs-OH and MMWCNTs-OH@CTAB (Fig. 2b). Zeta potential of MWCNTs-OH was 6.35 mV at pH3. Zeta potential reduced to -39.46 mV at pH7.0. Zeta potential did not show significant changes when solution conditions increased to pH11.0. This phenomenon indicated MWCNTs-OH dispersed well in alkaline conditions. MMWCNTs-OH was negatively charged in the solution at the range of pH5.0 to pH11.0. The highest Zeta potential of MMWCNTs-OH@CTAB solution only reached 24.52 under alkaline conditions, which indicated its unstable dispersed. But the solution was stable dispersed under acidic conditions with Zeta potential reached 48.42, Therefore, MMWCNTs-OH@CTAB in acidic conditions was used for DSPE.

Figure 2c showed the vibrational band assignments (cm\(^{-1}\)) of the MWCNTs-OH: 1118 cm\(^{-1}\) (C-O), 1260 cm\(^{-1}\) (=C-O-C-OH), 1625 cm\(^{-1}\) (=C-O-H), 1715 cm \(^{-1}\) (C=O), 3439 cm \(^{-1}\) (O-H). The comparison among MWCNTs, MWCNTs-OH and MMWCNTs-OH indicated that the MWCNTs can be successfully modified after the oxidation-reduction reaction, and the hydroxyl functional groups were introduced to MWCNTs-OH and MMWCNTs-OH.

Fig.2d showed the XRD patterns of MMWCNTs-OH@CTAB. Characteristic peak of MWCNTs was observed at 2\(\theta\) of 26.2\(^{\circ}\). Iron oxide mainly includes Fe\(_3\)O\(_4\)(Mn), \(\gamma\)-Fe\(_2\)O\(_3\)(Mh), \(\alpha\)-Fe\(_2\)O\(_3\)(H) and FeO(OH). Among them, only Fe\(_3\)O\(_4\) and \(\gamma\)-Fe\(_2\)O\(_3\) are magnetic. Four characteristic peaks at 2\(\theta\) of 30.5\(^{\circ}\), 35.5\(^{\circ}\), 42.4\(^{\circ}\), 57.5\(^{\circ}\) represented magnetic Fe\(_3\)O\(_4\) or \(\gamma\)-Fe\(_2\)O\(_3\). Peaks at 2\(\theta\) of 53.1\(^{\circ}\), 68.1\(^{\circ}\), which illustrated there still have \(\alpha\)-Fe\(_2\)O\(_3\) existed in MMWCNTs-OH@CTAB.

### 3.2. Method validation

The details of GC/MS mass spectrometry parameters for determination of PAHs were listed in Table 1. Table 1 summarized the results of method validation, which showed the proposed method achieved a high precision. Satisfactory correlation coefficient (R\(^2\) > 0.9981) was obtained when PAHs concentration at the range of 0.02 – 1.0 \(\mu\)g/L. Values for the limit of detection (LOD, S/N\(\geq\)3) and limit of quantitation (LOQ) of MMWCNTs-OH@CTAB DSPE method were in the ranges of 0.009 - 0.018 \(\mu\)g/L and 0.01 - 0.020 \(\mu\)g/L. The corresponding relative standard deviation (RSD) was in the range of 4.23-9.96%.
Table 1. Method validation of MMWCNTs-OH@CTAB as adsorbent for DSPE followed by GC/MS analysis

| PAHs | Linear range (µg/L) | R² | LOD (µg/L) | Recovery (%) | RSD (%) | Variability (µg/m³) |
|------|---------------------|----|------------|--------------|---------|--------------------|
| NAP  | 0.02-1.0            | 0.9981 | 0.018 | 72.65 | 6.98 | 12.86±2.4 |
| ACE  | 0.02-1.0            | 0.9995 | 0.016 | 75.36 | 8.26 | 2.78±1.2 |
| ACT  | 0.02-1.0            | 0.9990 | 0.018 | 74.23 | 8.26 | 4.85±1.8 |
| FLU  | 0.02-1.0            | 0.9990 | 0.015 | 80.29 | 4.65 | 11.14±2.5 |
| PHE  | 0.02-1.0            | 0.9994 | 0.013 | 82.12 | 9.96 | 4.71±1.5 |
| ANT  | 0.02-1.0            | 0.9992 | 0.016 | 83.54 | 6.54 | 1.51±0.9 |
| FLT  | 0.02-1.0            | 0.9998 | 0.010 | 81.06 | 7.58 | 2.56±0.8 |
| PYR  | 0.02-1.0            | 0.9997 | 0.012 | 79.93 | 8.69 | 0.21±0.1 |
| BaA  | 0.02-1.0            | 0.9994 | 0.014 | 84.56 | 5.64 | 9.69±2.1 |
| CHR  | 0.02-1.0            | 0.9991 | 0.010 | 86.11 | 4.56 | 1.48±0.3 |
| BbF  | 0.02-1.0            | 0.9995 | 0.009 | 96.54 | 6.36 | 0.55±0.2 |
| BkF  | 0.02-1.0            | 0.9994 | 0.010 | 89.63 | 5.25 | 2.03±0.4 |
| BaP  | 0.02-1.0            | 0.9991 | 0.009 | 89.20 | 6.24 | 0.95±0.4 |
| IcP  | 0.02-1.0            | 0.9998 | 0.10  | 94.99 | 4.23 | 2.36±0.5 |
| DaA  | 0.02-1.0            | 0.9994 | 0.10  | 90.64 | 4.26 | 1.60±0.1 |
| BgP  | 0.02-1.0            | 0.9993 | 0.10  | 91.57 | 3.58 | 0.65±0.2 |

Repeated measurements of a group of 3 times, a total of 3 days (9 groups), and the arithmetic mean value was taken as measurement results of the group. The measurement results in the difference between maximum and minimum values as the stability of the measuring instruments in this period of time. As is shown in Table 1, the inter-day precision for 3 days showed a variation of less than ± 10%. The enrichment factors of the PAHs were in the range of 39.65-121.32. The results showed that the MMWCNTs-OH@CTAB DSPE method was reliable for detection PAHs at very low concentrations.

3.3. Application of the method to the analysis of real samples

Aqueous-capture-collection, DSPE and GC/MS method under SIM mode for an exhaust emissions sample added 16 PAHs (10 µg/L) as spiked standard samples to evaluate recoveries. The spiked recoveries were 72.65-96.54 %, and the corresponding RSD was in the range of 4.23-9.96%. (Table 1). The analysis time was 40 minutes and there were no noticeable water effects in the chromatogram. Practical analysis of PAHs emitted from exhaust pipe included 16 main PAHs, and the total amount was 62.36 µg/m³. Analysis results showed that all target PAHs dissolved in aqueous solution, even the largest one. The proposed method also captured and detected the heaviest of PAHs such as chrysene and indeno(1,2,3-cd)pyrene with ideal recovery yields. A clean separation and good chromatogram were readily achieved without the presence of sample matrix interference. Quantitative analysis of PAHs cost less than 30 min from the sample collection to detection, and the detection limits reached to nanogram grade, which illustrated the method achieved a high precision. This optimized method was also compared with traditional methods. As the collection and pretreatment time was only 21 min, it was less than 10% of the traditional methods. This demonstrated that the proposed method was comparable for collection and concentration of PAHs.

4. Conclusion

In this work, MMWCNTs-OH was synthesized with a simple procedure, and the loading capacity was high. MMWCNTs-OH can be charged and supported as anionic micelle. The MMWCNTs-OH with micelles showed higher carrying capacity than Fe3O4 magnetic nanoparticles material. The recovery of target compounds increased about 1.01 - 2.32 times than SPE method. The method was suitable for analyzing PAHs emitted from marine diesel engine. A traditional method for collection and extraction of PAHs was also performed, and the results showed that in the traditional process lost 27.52%
compounds. As the sample collection time was short from sampling to analysis, which cost less than 10% time of the traditional method so as to decrease the PAHs losses to minimum.

Acknowledgments
This research was supported by the funds of Shandong Provincial Higher Educational Science and Technology Foundation, China (J14LD04; J16LA61), Shandong Provincial Natural Science Foundation, China (ZR2014JL038), National Natural Science Foundation of China (51609131).

References
[1] C. Gao, Z.N. He, J. Li et al. Specific long non-coding RNAs response to occupational PAHs exposure in coke oven workers. Toxicology Reports. (2016) 160-166.
[2] T.P. Hu, J.Q. Zhang, C. Ye et al. Status, source and health risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soil from the water-level-fluctuation zone of the Three Gorges Reservoir, China. Journal of Geochemical Exploration. 172 (2017) 20-28.
[3] Z. Nyiri, M. Novák, Z. Bodai et al. Determination of particulate phase polycyclic aromatic hydrocarbons and their nitrated and oxygenated derivatives using gas chromatography – mass spectrometry and liquid chromatography – tandem mass spectrometry. Journal of Chromatography A. 1472(2016) 88-98.
[4] M.H. Dehghani, Z.S. Niasar, M.R. Mehrnia et al. Optimizing the removal of organophosphorus pesticide malathion from water using multi-walled carbon nanotubes. Chemical Engineering Journal. 310 (2017) 22-32.
[5] C. Su. Environmental implications and applications of engineered nanoscale magnetite and its hybrid nanocomposites: A review of recent literature. Journal of Hazardous Materials, Part A, 2017, 322: 48-84.
[6] M. Hryniewicka, B. Starczewska, The usage of micellar extraction for analysis of fluvastatin in water and wastewater samples. J. Pharm. Biomed. Anal. 106 (2015) 129-135.
[7] H.F. Zhang, Y.P. Shia. Preparation of Fe3O4 nanoparticle enclosure hydroxylated multi-walled carbon nanotubes for the determination of aconitines in human serum samples. Analytica Chimica Acta. 724 (2012) 54–60.