



Rapid and effective sample cleanup based on graphene oxide-encapsulated core–shell magnetic microspheres for determination of fifteen trace environmental phenols in seafood by liquid chromatography–tandem mass spectrometry[☆]

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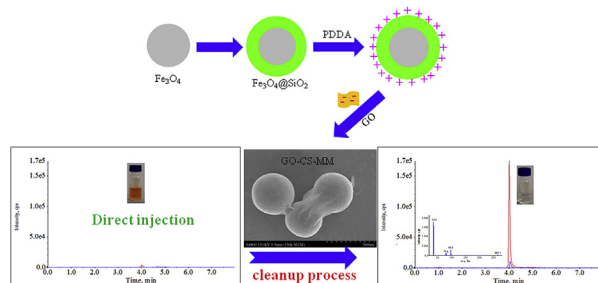
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HIGHLIGHTS

- Novel graphene oxide-encapsulated core-shell magnetic microspheres (GOE-CS-MM) were fabricated by a self-assemble approach.
- The as-prepared material GOE-CS-MM exhibited excellent cleanup efficiency and could availably reduce the matrix effect.
- The cleanup mechanisms refer to π – π stacking interaction and hydrogen bond.
- The developed MSPE–LC–MS/MS method was simple, fast, sensitive and accurate.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, graphene oxide-encapsulated core–shell magnetic microspheres (GOE-CS-MM) were fabricated by a self-assemble approach between positive charged poly(diallyldimethylammonium) chloride (PDDA)-modified $\text{Fe}_3\text{O}_4@SiO_2$ and negative charged GO sheets via electrostatic interaction. The as-prepared GOE-CS-MM was carefully characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), vibrating sample magnetometer analysis (VSM), and X-ray photoelectron spectroscopy (XPS), and was used as a cleanup adsorbent in magnetic solid-phase extraction (MSPE) for determination of 15 trace-level environmental phenols in seafood coupled to liquid chromatography–tandem mass spectrometry (LC–MS/MS). The obtained results showed that the GOE-CS-MM exhibited excellent cleanup efficiency and could availably reduce the matrix effect. The cleanup mechanisms were investigated and referred to π – π stacking interaction and hydrogen bond between GOE-CS-MM and impurities in the extracts. Moreover, the extraction and cleanup conditions of GOE-CS-MM toward phenols were optimized in detail. Under the optimized conditions, the limits of detection

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Cleanup mechanisms
Seafood samples

(LODs) were found to be 0.003–0.06 $\mu\text{g kg}^{-1}$, and satisfactory recovery values of 84.8–103.1% were obtained for the tested seafood samples. It was confirmed that the developed method is simple, fast, sensitive, and accurate for the determination of 15 trace environmental phenols in seafood samples.

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1. Introduction

Over the past few decades, there has been increasing concern on the environmental fate of a wide range of man-made chemicals due to their potential negative effects on the endocrine systems of humans and wildlife as endocrine disrupting chemicals (EDCs) [1–3]. Among them, environmental phenols, including 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), pentachlorophenol (PCP), bisphenol A (BPA), tetrabromobisphenol A (TBBPA), 4-(tert-octyl)phenol (4-tOP), and 4-nonylphenol (4-NP), are widely evaluated in rivers, lakes, groundwater, and sea water [4]. Therefore, many vivacious hydrophytes, fishes, mussels, and shrimps had been possibly contaminated by them, especially where grown in the polluted area. The determination of environmental phenols in various matrixes has been focused on.

Tandem mass spectrometry (MS/MS) is highly popular due to its high sensitivity and specificity compared to other analytic techniques [5–8]. The combination of MS/MS with liquid chromatography (LC–MS/MS) has gained a great popularity because of its effectiveness for the quantitative determination of medium- and high-polarity analytes at trace level [9]. The high selectivity and sensitivity of modern MS/MS systems have resulted in an increasing trend of high-throughput analyses that entail little or no sample preparation and a minimal chromatographic retention. Due to these important aspects, LC–MS/MS has been a well-established standard method in environmental science, forensic analysis, life science, and other areas where trace-level analytes in complex mixtures must be recognized [10–15]. However, in the recent few years, the general perception has been challenged because the presence of co-extracted matrix can severely impact the quantification process based on LC–MS/MS methods [16–20]. This phenomenon is called matrix effect, which is considered to be either a suppression or enhancement of the analytes response induced by the co-extracted matrix. Actually, matrix effect is becoming a main threat in the successful applications of LC–MS/MS, especially for the analysis of samples with complex matrix such as food samples. To overcome the matrix effect, the cleanup procedure of extracts to reduce or eliminate the influence of impurities in the matrix appears very important. The research of novel purification materials is considered to be of much popularity [21–24].

Graphene oxide (GO), the oxidation state of graphene (G), has attracted great attention of researchers in the field of the functionalized preparation and application because of its high surface area, excellent thermal and electric conductivity, and strong mechanical strength [25]. It holds great promise for potential applications in many technological fields such as drug delivery [26–28], sensor devices electronics [29], catalyst [30,31], water treatment [32], hydrogen storage [33,34], and solid-phase extraction [35,36], etc. Notably, the large delocalized π -electron system and ultrahigh specific surface area of GO make it promising candidate with strong affinity and high adsorption capacity for hydrophobic compounds and carbon-based ring structures. However, most of the reported GO-based composite materials were generally fabricated by introducing diverse nano- or micro-particles onto the surface of GO sheets [32,36–38]. In this manner, GO sheets were applied as support and the functional nano- or micro-particles were grown or

deposited as guest substances. However, there were some problems when these composites were used as adsorbent: firstly, a large number of adsorption sites of GO sheets were occupied by nano- or micro-particles and were not available for target molecules; secondly, aggregation of GO sheets could not be avoided, resulting in loss in the adsorption capacity of the adsorbent. By contrast, it is perhaps a good choice to fabricate tiny GO sheets onto bulk solid supports like silica or polymer surface so that the role of GO can perform to a maximal degree.

In this work, we prepared novel graphene oxide-encapsulated core-shell magnetic microspheres (GOE-CS-MM) via a self-assembly approach and used as MSPE adsorbent for the cleanup of seafood samples. The GO shell endows the adsorbent with highly efficient cleanup performance, while the SiO_2 shell protects the Fe_3O_4 core against oxidation and aggregation. The as-prepared GOE-CS-MM can effectively reduce even eliminate the matrix effect of determination of 15 trace environmental phenols in seafood samples by LC–MS/MS, and the cleanup mechanisms were investigated in detail, which refer to π - π stacking interaction and hydrogen bond. Moreover, the introduction of magnetic Fe_3O_4 makes it possible for rapid solid-liquid separation and effectively saves the pre-treatment time. It is proven that the developed method is simple, fast, sensitive, and accurate for the determination of 15 trace environmental phenols in seafood samples.

2. Experimental

2.1. Materials and reagents

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium acetate (NaAc), tetraethoxysilane (TEOS), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were analytical grade, and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Poly(dimethyldiallylammonium chloride) (PDDA) was purchased from J&K Chemical. GO sheets were supplied by Nanjing XFANO Materials Technology Corporation (Nanjing, China). Methanol and acetonitrile (LC/MS grade) were obtained from Thermo Fisher Scientific (USA). HPLC grade ammonium hydroxide and ethanol were purchased from ROE scientific (USA). Analytical grade of 2-chlorophenol (2-CP, purity > 99%), 2,4-dichlorophenol (2,4-DCP, purity > 99%), 2,4,6-trichlorophenol (2,4,6-TCP, purity > 99%), and 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP, purity > 98%) were supplied by Aladdin Chemical Reagent Co. (Shanghai, China). Bisphenol A (BPA, purity > 99%), bisphenol B (BPB, purity > 99%), tetrabromobisphenol A (TBBPA, purity > 99%), dienestrol (DE, purity > 99%), hexestrol (HEX, purity > 99%), diethylstilbestrol (DES, purity > 99%), o-phenylphenol (OPP, purity > 99%), 4-(tert-octyl)phenol (4-tOP, purity > 99%), 4-nonylphenol (4-NP, purity > 99%), pentachlorophenol (PCP, purity > 99%), 2,4-dibromophenol (2,4-DBP, purity > 99%), $^{13}\text{C}_6$ -PCP, D₄-2-CP, D₃-2,4-DCP, D₂-2,4,6-DCP, D₁₆-BPA, and D₈-4-NP were all supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany). Ultrapure water (18.2 M Ω -cm) was obtained directly from a Milli-Q Plus water purification system (Millipore Corporation, France). All other chemicals were analytical grade unless stated otherwise.

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