



# Magnetic polyethyleneimine functionalized reduced graphene oxide as a novel magnetic solid-phase extraction adsorbent for the determination of polar acidic herbicides in rice



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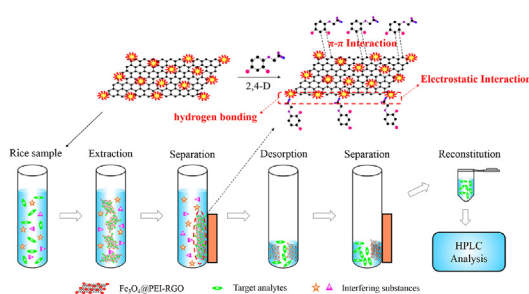
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## HIGHLIGHTS

- A novel Fe<sub>3</sub>O<sub>4</sub>@PEI-RGO was synthesized and applied for the analysis of polar acidic herbicides.
- PEI affected the surface property of RGO and changed the polarity of RGO.
- Fe<sub>3</sub>O<sub>4</sub>@PEI-RGO showed good extraction efficiency towards polar acidic herbicides.
- RSM was used to optimize parameters affecting the extraction efficiency.
- The adsorption mechanism was discussed in detail.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel magnetic polyethyleneimine modified reduced graphene oxide (Fe<sub>3</sub>O<sub>4</sub>@PEI-RGO) had been fabricated based on a self-assemble approach between positive charged magnetic polyethyleneimine (Fe<sub>3</sub>O<sub>4</sub>@PEI) and negative charged GO sheets via electrostatic interaction followed by chemical reduction of GO to RGO. The as-prepared Fe<sub>3</sub>O<sub>4</sub>@PEI-RGO was characterized by transmission electron microscopy (TEM), Fourier transform infrared spectrometry (FT-IR), X-ray diffraction (XRD), thermal gravimetric analyzer (TGA), vibrating sample magnetometer (VSM) and zeta potential analysis, and then was successfully applied to determine four phenoxy acid herbicides and dicamba in rice coupled with high performance liquid chromatography (HPLC). As a surface modifier of RGO, PEI not only effectually affected the surface property of RGO (e.g. zeta potential), but also changed the polarity of RGO and offered anion exchange groups to polar acidic herbicides, which would directly influence the type of adsorbed analytes. Compared with Fe<sub>3</sub>O<sub>4</sub>@PEI, Fe<sub>3</sub>O<sub>4</sub>/RGO and Fe<sub>3</sub>O<sub>4</sub>@PEI-GO, the as-prepared Fe<sub>3</sub>O<sub>4</sub>@PEI-RGO, integrating the superiority of PEI and RGO, showed higher extraction efficiency for polar acidic herbicides. Besides, the adsorption mechanism was investigated as well. It turned out that electrostatic interaction and  $\pi$ - $\pi$  interaction were considered to be two major driving force for the adsorption process. Response surface methodology (RSM), a multivariate experimental design technique, was used to optimize experimental parameters affecting the extraction efficiency in detail. Under the optimal conditions, a satisfactory performance was obtained. The calibration curves were linear over the concentration ranging from 2 to 300 ng g<sup>-1</sup> with correlation coefficients ( $r$ ) between 0.9985 and 0.9994. The limits of

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detection (LODs) were in the range of 0.67–2 ng g<sup>-1</sup>. The recoveries ranged from 87.41% to 102.52% with relative standard deviations (RSDs) less than 8.94%. Taken together, the proposed method was an efficient pretreatment and enrichment procedure and could be successfully applied for selective extraction and determination of polar acidic herbicides in complex matrices.

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## 1. Introduction

Phenoxy acid herbicides, as an important family of commercial herbicides, are widely employed to improve agricultural product yields via selective control of grass and broad-leaf weeds [1]. However, these acid herbicides are potentially teratogenic and carcinogenic, and even some of them are endocrine disruptors. To date, 2,4-dichlorophenoxy acetic acid (2,4-D), 4-chloro-methylphenoxy acetic acid (MCPA), 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP) and 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) have been included in the European list of priority pollutants [2]. The extensive use of these acid herbicides may eventually pose a serious threat to directed-seed planting systems and exert serious environmental effects on non-target organisms. Additionally, phenoxy acid herbicides can easily enter surface or ground water through natural drainage or infiltration due to their high polar and good solubility, and their degradation rates are relatively slow, which further exacerbates their influences on the environment [3]. Either direct contact or indirect exposure will be harmful to people's health. Consequently, many countries and unions have established legal directives to restrict the use and control the maximum residue levels of some phenoxy acid herbicides in cereals and environmental samples.

Various sample preparation methods have been developed for the extraction of phenoxy acid herbicides, including liquid-liquid extraction (LLE) [4], solid phase extraction (SPE) [5], dispersive liquid-liquid-liquid microextraction (DLLME) [6], solid phase microextraction (SPME) [7], solvent-bar microextraction (SBME) [8], supramolecular solvents (SUPRAS)-based microextraction [3], electromembrane extraction (EME) [9] and magnetic solid phase extraction (MSPE) [10]. Unlike the large number of studies concerning the analysis of residual polar acid herbicides in water, there are very limited methods applied for the detection of polar acid herbicides in cereals [11]. This may attribute to the following facts: The polar nature and good solubility of phenoxy acids herbicides make their specific extraction difficult; The matrices of cereals are very complicated including both polar (e.g. carbohydrate and sugar) and nonpolar (e.g. starch and macromolecule) compounds; Furthermore, the content of phenoxy acids herbicides is at trace level in cereals. Thereby, it can be an extremely challenging task to develop a sensitive and selective method for the determination of polar acid herbicides in cereals.

MSPE, combining extraction and separation, as well as clean-up and concentration of analytes into a single step, has attracted considerable attention in sample preparation. In MSPE, magnetic adsorbents are directly dispersed into sample solutions and the dispersive extraction mode is conducive to the increase of interfacial area between adsorbents and analytes [12]. As a result, the extraction efficiency of MSPE can be improved compared with the conventional SPE. Meanwhile, the problems of column blocking and high pressure often encountered in SPE can be avoided [13]. The utilization of magnetic adsorbents lets the phase separation process become much simpler and traditional centrifugation or filtration will not be needed. In addition, magnetic adsorbents can be easily recycled and reused, which is economical and eco-

friendly. Undoubtedly, MSPE shows a comprehensive advantage of simplicity, saving time and labor and excellent extraction efficiency. Proverbially, magnetic adsorbents play a vital role in the MSPE procedure for the reason that they not only directly affect extraction efficiency but also determine the sensitivity and selectivity of the method [13]. Therefore, it is impending to develop new magnetic adsorbents with high adsorption capacities and selectivity.

Graphene (G), a single atomic layer of sp<sup>2</sup>-hybridized carbon atoms arranged in a honeycomb lattice with dimensions ranging from a few hundred nanometers to tens of micrometers, has become a rapidly rising star on the horizon of materials science by means of a unique set of properties, that is, ultrahigh theoretical specific surface area, high intrinsic mobility, high Young's modulus, thermal conductivity and good electrical conductivity [14]. Although versatile methods have been developed for the fabrication of graphene, the most popular method is the chemical method on the basis of the oxidation of graphite to graphene oxide (GO) and subsequent chemical reduction of GO to reduced graphene oxide (RGO) using a suitable reducing agent [15]. In general, G is considered as a non-polar, hydrophobic adsorbent with the large delocalized  $\pi$ -electron system, which can make a strong affinity for hydrophobic compounds and carbon-based ring structures [16]. Nevertheless, G is hard to be separated from aqueous solution. Thus, magnetic graphene composite, which connects the high adsorption capacity of G with the convenient separation of magnetic materials (e.g. Fe<sub>3</sub>O<sub>4</sub> or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), quickly becomes a research hotspot and is extensively applied for the trace analysis of water, food, biological and environment samples. Since magnetic nanoparticles almost do not have significant adsorption capacity, the adsorption capacity of magnetic graphene mainly relies on the adsorption characteristics of graphene which lacks ability to interact with polar or ionic compounds. Thereby, it makes the extraction of polar or ionic compounds from environmental or biological sample difficult when magnetic graphene is used as the adsorbent alone, which limits its application in some extent [15]. Secondly, in most cases, magnetic graphene actually has lower adsorption capacity than that of G owing to the occupation of a large number of adsorption sites of G sheets by magnetic nanoparticles and the unavoidable agglomerations of G sheets in the modification process. Furthermore, water solubility of the magnetic graphene composite is always unfavorable, counting against the dispersion of adsorbents in sample solutions and resulting in the decrease of interfacial area between adsorbents and analytes in turn.

Polyethyleneimine (PEI) is a hydrophilic cationic polymer with numerous active amine groups both in the backbone and in branched chains [17]. At low pH, a high density of amino groups in PEI can be protonated and highly protonated PEI can easily adsorb negatively charged compounds via strong electrostatic interaction. What is more, a high density of amino groups can generate strong hydrogen bonding with organic compounds containing oxygen- or nitrogen-functional group and chelation with metal species. Certainly, the hydrophobic vinyl of PEI can interact with hydrophobic parts of organic compounds through hydrophobic

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