Journal of Chromatography A, 1443 (2016) 43–53

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Three-dimensional graphene aerogel-supported iron oxide nanoparticles as an efficient adsorbent for magnetic solid phase extraction of organophosphorus pesticide residues in fruit juices followed by gas chromatographic determination

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ARTICLE INFO

Article history:
Received 13 February 2016
Received in revised form 4 March 2016
Accepted 17 March 2016
Available online 19 March 2016

Keywords:
Magnetic three-dimensional graphene
Magnetic solid phase extraction
Organophosphorus pesticides
Gas chromatography
Fruit juice

ABSTRACT

In this research, a magnetic three dimensional-graphene nanocomposite (3D-G-Fe_3O_4) was prepared, characterized and used as an effective nanoadsorbent in magnetic solid-phase extraction (MSPE) of eight organophosphorus pesticides (OPPs) from juice samples prior to gas chromatography-nitrogen phosphorous detection (GC-NPD). The properties and morphology of 3D-G-Fe_3O_4 were characterized by scanning electron microscopy (SEM), Fourier transform-infrared spectroscopy (FT-IR) and vibrating sample magnetometry (VSM). The main experimental parameters affecting extraction recoveries including extraction time, amount of adsorbent, pH of sample solution, salt concentration and desorption conditions were carefully studied and optimized. The results showed wide linear concentration ranges with determination coefficients between 0.9973 and 0.9999. The limits of detection (S/N = 3) of the method and limits of quantification (S/N = 10) were from 1.2 to 5.1 ng L^{-1} and 3.4–17.0 ng L^{-1}, respectively. The intra-day and inter-day RSDs were 2.6–5.1% and 3.5–6.9%, respectively. The method was successfully applied to the analysis of OPPs in fruit juices (apple, orange, grape, sour-cherry and apricot) with recoveries in range of 86.6–107.5%. The GC-NPD results were confirmed by gas chromatography–mass spectrometry (GC–MS). The results demonstrated that with combination of highly interconnected 3D network structure and magnetism property of adsorbent, 3D-G-Fe_3O_4 aerogel exhibited exceptional extraction ability towards the OPPs.

1. Introduction

Carbon based nanomaterials are well known for their high adsorption capacity for various compounds and thus they have been widely used as adsorbents over the past decades [1]. Graphene (G) is a relatively new type of carbon nanomaterial which is made of a single-atom-thick, two-dimensional sp^2 carbon network in a honeycomb lattice [2]. In recent years, this material has attracted the attention of many researchers due to its extraordinary electrical and thermal conductivity, high specific surface area, and large mechanical strength [3]. In addition, large delocalized π-electron system of graphene can form a strong hydrophobic and π-stacking interactions with different molecules, so G and G-based materials are good candidates for use as adsorbent in sample preparation techniques [4–16].

However, recent studies have shown that the restacking and aggregation between individual graphene sheets caused by the strong π-π stacking, hydrophobic interactions, and van der Waals forces may greatly decrease the intrinsic high specific surface area of G, which is undesirable for its applications. In order to solve this problem, the reassembly of two-dimensional graphene (2D-G) sheets into three-dimensional graphene (3D-G) structures such as aerogels, sponges and foams has gained remarkable interest in the last few years [17–20]. Compared with 2D-G, the 3D structures provide materials with higher specific surface area, lower density, stronger mechanical strength, and faster mass and electron transport kinetics due to combination of 3D interconnected framework and excellent intrinsic properties of G [21].

These unusual properties of 3D-G provide it with great application potential in many fields. To date, 3D-G structures have been mainly used in super capacitors [22–24], sensors [25,26], batteries [27] and catalysis [28]. The ultrahigh surface area, porous and hollow structure of 3D-G, and fast mass transport kinetics, make it a promising candidate for an efficient adsorbent. However, the

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http://dx.doi.org/10.1016/j.chroma.2016.03.046
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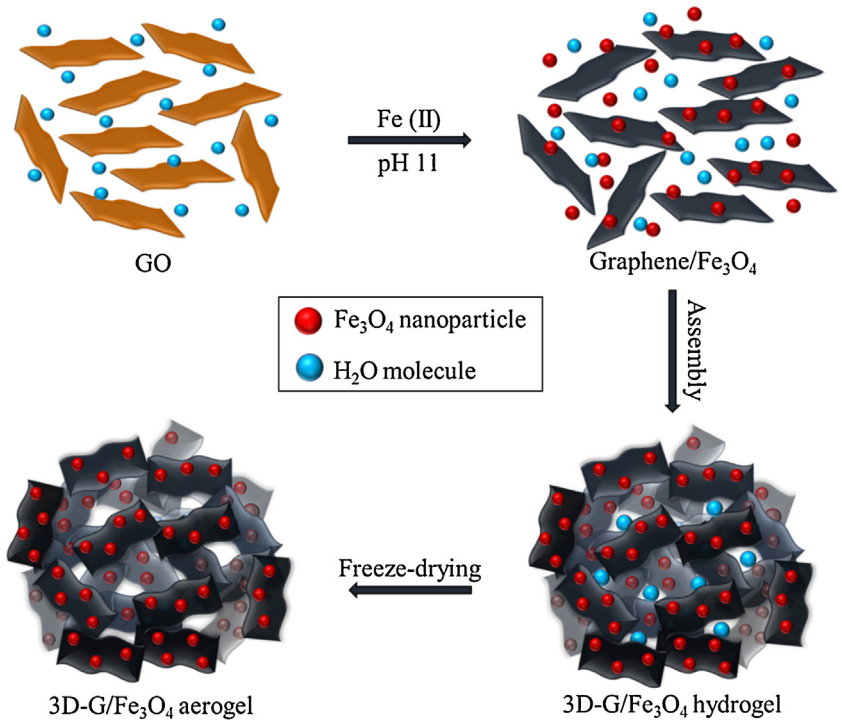

Fig. 1. Schematic illustration of the formation mechanism of the 3D-G-Fe_3O_4 aerogel.

application of 3D-G as an adsorbent for extraction or removal of chemical pollutants is still not deeply studied [21,29–32].

Within the past few years, much effort has been paid to the development of strategies for preparing 3D-G structures and compositions of graphene with other materials such as polymers, carbon nanotubes and metal oxides [18,33]. A simple approach for fabrication of a three-dimensional graphene-based magnetic nanocomposite (3D-G-Fe_3O_4) is the self-assembly of reduced graphene oxide nanosheets by ferrous ions and in situ simultaneous deposition of Fe_3O_4 nanoparticles [34]. The magnetic 3D-G combines the ultrahigh adsorption capacity of 3D-G and the separation convenience of magnetic materials, which makes it an ideal adsorbent for different compounds in sample preparation techniques especially magnetic solid phase extraction (MSPE) procedures. In MSPE, as a new mode of solid phase extraction (SPE), the magnetic adsorbent can be dispersed directly in the sample solution and the phase separation can occur simply by using an external magnet without any need to filter or centrifuge samples, making separation easier and faster [35].

Organophosphorus pesticides (OPPs) are some of the most common and most toxic insecticides widely used today for pest control in agriculture and public places [36]. They can easily leach or migrate into various environments during their usage [37]. Certain OPPs as well as their metabolites and degradation products can cause adverse effects on human health even at low levels of exposure [38]. Fruits and vegetables are among the foods most commonly contaminated with OPPs. The European Union has established maximum residue limits (MRL) for pesticide residues in many vegetables and fruits in the range of 0.01–0.3 mg kg^{-1} and 0.01 mg kg^{-1} for pesticide residues in processed foods [39]. Therefore. developing rapid, sensitive and simple analytical methods to detect OPPs residue in different matrices have become a major research focus.

The main aim of this work was to evaluate the performance of 3D-G-Fe_3O_4 as an efficient adsorbent for extraction of OPPs. Therefore, the as-fabricated adsorbent was used for the MSPE of eight OPPs (azinphos methyl, parathion methyl, fenitrothion, methidathion, ethion, phosalone, phorate and coumaphos) in different fruit juices. The OPPs residue levels were determined by GC-NPD, and the residues were verified by GC–MS. The factors affecting the extraction recoveries were carefully investigated and the related optimized values were obtained. This is the first report of application of magnetic 3D-G as an adsorbent for the extraction of OPPs in fruit juices.

2. Experimental

2.1. Reagents and materials

Acetonitrile, acetone, hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), ammonia solution (NH_3, 25%) and all other reagents were prepared from Merck Chemicals (Darmstadt, Germany). Methanol (MeOH) was obtained from Sigma Aldrich Ltd. (St Louis, USA). Pesticide standards (azinphos methyl, parathion methyl, fenitrothion, methidathion, ethion, phosalone, phorate and coumaphos) were purchased from Beijing Chemical Reagents Company (Beijing, China). A mixture stock standard solution containing each OPP at 50.0 mg L^{-1} was prepared in acetone and was stored at 4 °C in dark. Working solutions were prepared daily by appropriate dilutions with water.

2.2. Instrumentation

An Agilent technologies 7890 gas chromatograph (Santa Clara CA, USA) equipped with a nitrogen-phosphorus detector (NPD) and a split/splitless injector was applied for quantitative analysis of the extracted OPPs. All the separations were performed on a HP-5 capillary column (30 m × 0.32 mm i.d.; 0.25 μm, film thickness; 5% phenyl-95% methyl polysiloxane) (Agilent Scientific, USA) with helium (>99.999%) as carrier gas at the flow-rate of 1.0 mL min^{-1}. The GC chromatographic conditions were as follows: splitless mode; injector temperature, 250 °C; detector temperature,