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Review

Recent trends in the application of the newest carbonaceous materials for magnetic solid-phase extraction of environmental pollutants

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ABSTRACT

This paper provides a review of the latest applications of carbon-based materials for magnetic solid-phase extraction (MSPE), an advantageous sample pre-treatment increasingly adopted in analytical chemistry. In particular, this review focuses on the pre-concentration procedures developed for the determination of various classes of pollutants in environmental matrices. Beside the recent advances in the application of carbon nanotubes (CNTs), the newest carbonaceous materials have been considered, namely differently arranged nanocarbons (NCs), graphene (GN) and graphitic carbon nitride (g-C_3N_4). The analytical performance of the magnetic composites was critically discussed in relation to the physical–chemical properties resultant from the synthetic routes. The new sorbents generally afforded high extraction efficiency, good selectivity in complex matrices and durability for tens adsorption/desorption cycles, mainly due to high surface area, chemical stability, dispersibility in aqueous solution and, importantly, multi-type interaction. In particular, this was greatly enhanced by combining magnetic GN with other substrates or using derivatized GN, obtaining mixed-mode sorbents. The ease of preparation, durability and high enrichment factor make this new generation of MSPE carbon-based sorbents a valid alternative to the commercial solid phases.

Contents

1. Introduction

Since a variety of compounds are routinely used in household activities, and in industrial production processes as well, lots of synthetic chemicals are continuously released into the environment. Unfortunately, the widespread use of compounds not originally present in nature can involve serious threats and negative side effects on wildlife, and on the whole ecosystem in general [1]. The environmental monitoring of many chemicals considered hazardous for the biosphere (humans included) is thus becoming a priority task [2]. This means that is not just important to get information about the contamination levels, but also to

Abbreviations: ACN, acetonitrile; BFRs, brominated flame retardants; CNFs, carbon nanofibers; CNTs, carbon nanotubes; CPs, chlorophenols; DCM, dichloromethane; EF, enrichment factor; g-C_3N_4, graphitic carbon nitride; GN, graphene; GO, graphene oxide; ILs, ionic liquids; MeOH, methanol; MIP, molecularly imprinted polymer; MOF, metal organic framework; MSPE, magnetic solid-phase extraction; MWCNTs, multi-walled CNTs; NCs, nanocarbons; PAHs, polycyclic aromatic hydrocarbons; RGO, reduced graphene oxide; RSD, relative standard deviation; SPE, solid-phase extraction; SPME, solid-phase microextraction; SWCNTs, single-walled CNTs; UAMSPE, ultrasound-assisted MSPE.

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understand the fate of the pollutants once entered the environment [1,3]. Undoubtedly, interdisciplinary expertise is required, and of course analytical chemistry is directly involved. Since actual environmental matrices, e.g. surface waters, have complex composition, working strategies are necessary to develop robust, friendly, selective and accurate analytical methods. Additionally, sensitivity is mandatory for trace determination of pollutants, in most cases present at concentrations in the nanograms/micrograms per litre ranges [4]. Sample preparation, a very important step in the overall analytical method, becomes crucial at these low concentrations. It essentially requires the pre-concentration of the target analytes from the matrix onto suitable sorbents and their elution in the minimum solvent volume, before instrumental analysis. Solid phase extraction (SPE) is one of the most routinely used techniques for pre-concentration of a large number of compounds and elements from actual matrices, due to its advantages over traditional extraction, that are high enrichment factor (EF), good recovery, use of small volumes of organic solvents and possibility of automation (off- or on-line) of the whole process [5,6]. As a matter of fact, use of SPE has greatly increased in the recent decades, prompted by the development of a variety of advanced novel sorbents showing improved selectivity [5], with the new forms of carbons having a prominent role [7,8].

Unlike the conventional fixed-bed column SPE, magnetic solid-phase extraction (MSPE) entails use of magnetic sorbents for the in-batch pre-concentration of target analytes from large sample volumes. The magnetic sorbent is added to the sample solution promoting analyte adsorption by vortex or sonication; then the solid phase is easily separated from the sample by an external magnetic field and, successively, the analyte is eluted and quantified. This approach presents various advantages over traditional SPE, in primis avoiding of time-consuming and tedious on-column SPE procedures, and rapid and simple analyte separation with no need for centrifugation or filtration [6].

In the past few years a huge number of analytical methods based on MSPE have been undertaken, especially in view of the extraordinary properties of the novel carbon materials, i.e. carbon nanotubes (CNTs), and more recently graphene (GN) and graphitic carbon nitride (g-C_3N_4). Magnetic particles have been also combined with differently arranged nanocarbons (NCs) obtained by alternative carbon sources, e.g. glucose biomass. CNTs have been successfully applied as SPE sorbents and chromatographic stationary phase, as reviewed in previous papers [7,9], and considerable is also the application as MSPE sorbents for determination of organic and inorganic species in environmental, food and biological matrices, recently reviewed by Herrero-Latorre et al. [6]. CNTs, that can be sketched as sheets of graphite rolled into a cylinder, with a single wall (SWCNTs) or multiple walls (MWCNTs), showed indeed outstanding sorption properties compared to classic carbon-based materials as graphitized carbon, graphite, and octadecyl-silica. This is due to their unique physical–chemical properties, namely high length-to-diameter ratio combined with the π-delocalized curved surface, large surface area (theoretical value up to 1315 $m^2 g^{-1}$ [10]), multi-type interaction with target analytes, including electrostatic forces, π–π stacking, dispersion forces, dative bonds and hydrophobic effect [9]. Since CNTs applications are often limited by their insolubility in most solvents due to strong inter-tube Van der Waals forces, modification of their side walls is powerful to enlarge their potential [7]. Indeed, functionalization is effective for modulating retention and selectivity of pristine CNTs, hence obtaining mixed-mode materials with improved selectivity [11–14].

A new form of carbonaceous material nowadays attracting great interest is GN, whose impact in the scientific community seems to be even bigger than CNTs. Since the first experimental evidence of its unique electronic properties in 2004 [15], GN has become the most intensively studied material. GN consists of single-layer or few-layer thickness of sp^2-hybridized carbon atoms forming a honeycomb 2D structure with a very high specific surface area (theoretical value 2630 $m^2 g^{-1}$ [16]). Due to the high number of adsorption sites and amazing physical–chemical properties, GN is claimed to be the ideal candidate to prepare novel sorbent materials for (M)SPE, solid-phase microextraction (SPME), and also chromatographic stationary phases, as corroborated by the first very promising results gathered in previous reviews [8,17,18]. Either graphene oxide (GO), obtained by graphite exfoliation, or reduced graphene oxide (RGO) can be used. Due to the high density of epoxy, hydroxyl and carboxylic groups, GO is considered a polar material, while RGO shows the characteristics of reversed-phase with strong affinity for carbon-based ring structures. Nevertheless, differently from typical hydrophobic sorbents, the presence of residual polar groups even after reduction makes RGO a particular mixed-mode sorbent, combining hydrophilic and lipophilic interactions, thus can be applied for a wide polarity-range molecules [8]. Since GN materials exert various interplays with the target species, viz. π–π stacking, cation–π bonding, electron donor–acceptor interaction, hydrogen bond, hydrophobic interaction etc., they have been tested for SPE of metal ions and organic compounds, showing superior performance than CNTs, graphitic carbon, and commercial sorbents for pre-concentration of water contaminants [16,19,20]. This is attributable to the special morphology of GN, wherein, differently from CNTs, both sides of the planar sheets are easily accessible for molecular interaction, promoting fast adsorption equilibrium and analyte elution [21].

The carbon-based 2D material that is now emerging also in the analytical field is graphitic carbon nitride (g-C_3N_4), the most stable allotrope of carbon nitride mainly composed of carbon and nitrogen, and considered the most promising candidate to complement carbon materials. g-C_3N_4 is a new “graphene-like” material made of layered sheets of tri-*s*-triazine connected via tertiary amines, forming a defected-rich and N-bridged molecular structure. The synthesis is easy and inexpensive, entailing use of simple precursors under ambient conditions [22,23]. It can be easily swelled and exfoliated by aqueous sonication into nearly transparent ultrathin nanosheets, stable in both acidic and alkaline environments (pH 3–11) [24]. In the last years, g-C_3N_4 proved to have great potentiality in many fields, including photocatalysis, biosensing, bioimaging [25–27], and in principle could become a very efficient sorbent in analytical sample preparation. Indeed, the g-C_3N_4 double-sided polyaromatic scaffold shows both sides of the planar sheets available for molecules adsorption, similarly to GN. g-C_3N_4 exhibits a Lewis base behaviour, and the large π-electron system also endows a strong affinity for carbon-based ring structures, typical of many drugs, pollutants, and biomolecules [28].

Considering the actual state of the art, this review would focus on the recent applications of *carbon-based materials* for MSPE, the advantageous sample pre-treatment increasingly adopted in analytical chemistry. In particular, the manuscript was thought to cover pre-concentration procedures for determination of various classes of pollutants in *environmental matrices*. Beside the last advances related to the use of CNTs, the newest carbonaceous materials have been considered, namely differently arranged NCs, GN and g-C_3N_4, combined with magnetic nanoparticles. The analytical performance of these novel MSPE composites, prepared by different preparation schemes, was examined and critically commented in terms of sorption properties and selectivity in actual complex matrices, also looking for a correlation with their physical–chemical properties and morphology. Furthermore, the adsorption capacities of the carbon phases compared to the magnetic particles have been illustrated for some representative analytes in a summarizing figure. The behaviour of