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Nanomaterials as sorbents for food sample analysis

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ABSTRACT

The discovery of nanomaterials has bestowed a great impact in the improvement and development of many disciplines, including Analytical Chemistry, as a result of their particular properties that result highly adequate for an extensive variety of applications. Among them, metal-organic frameworks, magnetic and non-magnetic nanoparticles, carbon nanotubes and graphene, as well as their combinations, are the most important nanomaterials that have been used up to now, especially in sorbent-based extraction techniques. Many of them have been demonstrated to be highly appropriate for the extraction of a wide variety of analytes even from highly complex samples like foods. This review article is aimed at summarizing the most recent applications of such nanomaterials in food analysis. Particular attention has been paid to provide a general vision of the wide variety of sorbents that are currently being developed in this field.

Contents

Abbreviations: µdSPE, micro-dispersive solid-phase extraction; 17β-E2, 17β-estradiol; AAS, atomic absorption spectroscopy; AMT, 2-amino-5-mercapto-1,3,4-thiadiazole; BMA, butyl methacrylate; BP, buckypaper; BPA, bisphenolA; BSM, methyl α-(4,6-dimethoxypryrimidin-2-yl-carbamoyl sulfamoyl)-O-toluate; CAP, chloramphenicol; CE, capillary electrophoresis; CNTF, carbon nanotube film; CNTs, carbon nanotubes; DAD, diode array detector; DBP, dibutyl phthalate; DCBI, desorption corona beam ionization; DLLME, dispersive liquid-liquid microextraction; DVB, divinylbenzene; EAAS, electrothermal atomization atomic absorption spectroscopy; ECD, electron capture detector; ECLIA, electrochemiluminescent immunoassay; EDMA, ethylene dimethacrylate; FAAS, flame atomic absorption spectrometry; FD, fluorescence detection; FID, flame ionisation detector; GC, gas chromatography; GFAAS, graphite furnace atomic absorption spectrometry; GO, graphene oxide; HF, hollow fiber; HLB, Hydrophilic-lipophilic balance copolymer; HPLC, high performance liquid chromatography; HS-SPME, Head-space-SPME; ICP, inductively coupled plasma; IIP, ion imprinted polymer; ILs, ionic liquids; IS, internal standard; LODs, limits of detection; LPME, liquid-phase microextraction; MALDI, matrix-assisted laser desorption/ionization; m-dSPE, magnetic-dispersive solid-phase extraction; m-dSPIE, magnetic-dispersive solid-phase immunoextraction; MIL, Materials of Institute Lavoisier; MIP, molecularly imprinted polymer; MNC, magnetic nanoporous carbon; MOFs, metal-organic frameworks; MPPC, 3-(1-Methyl-1H-pyrrol-2-yl)-1H-pyrazole-5-carboxylic acid; MS, mass spectrometry; MSPD, matrix solid-phase dispersion; MWCNTs, multi-walled carbon nanotubes; MWCNTs-OH, hydroxyl functionalized multi-walled carbon nanotubes; nano-UHPLC, nano ultra-high performance liquid chromatography; NPs, nanoparticles; OCPs, organochlorine pesticides; OES, optical emission spectrometry; OMIM, 1-octyl-3-methylimidazole; OPPs, organophosphorous pesticides; PAMAM, polyamidoamine; PAN, 1-(2-pyridylazo)-2-naphthol; PANI, polyaniline; PAR, 4-(2-pyridylazo) resorcinol; PCBs, polychlorinated biphenyls; PDDA, poly(diallyldimethylammonium chloride); PEA, phenylethyl amine; PIL, polymeric ionic liquid; PNPEA, poly (N-phenylethanolamine); PPy, polypyrrole; PTES, propyltriethoxysilan; PVA, poly(vinyl alcohol); QDs, quantum dots; SBSE, stir bar sorptive extraction; SDS, sodium dodecyl sulphate; SDZ, sulfadiazine; SMO, sulfamethoxazole; SPE, solid-phase extraction; SPME, solid-phase microextraction; SWCNTs, single-walled carbon nanotubes; TBBPA, tetrabromobisphenol A; TCA, 2,4,6-trichloroanisole; TMSPT, 3-(trimethoxysilyl)-1-propantiol; TPP, triphenyl phosphate; UFLC, ultra-fast liquid chromatography; US-dSPE, ultrasound assisted-dispersive solid-phase extraction; UV, ultraviolet; VA-m-dSPE, vortex assisted-magnetic-dispersive solid-phase extraction; ZIF, zeolitic imidazolate framework.

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1. Introduction

Nanoscience is currently expanding to diverse areas where its application is continuously increasing due to the unique optical, electronic, magnetic, and catalytic characteristics that nanomaterials present [1]. Particularly in the field of Analytical Chemistry, the important advancements achieved in nanomaterial synthesis and characterization have allowed the development of new analytical methodologies [2,3], since their specific physical and chemical properties associated with their nano-size structure also provide numerous advantages in this field. In fact, there is a wide variety of applications which include their use as materials for the construction of electrochemical sensors or biosensors, supports, and sorbents for the analysis of different groups of analytes in a wide variety of matrices of environmental, biological and food nature [4,5].

The application of nanomaterials as sorbents has achieved a sharp increase in recent years since they can play an important role in sample and pre-concentration processes. In this sense, their low resistance to diffusion, large adsorptive capability and fast sorption kinetics are characteristics especially relevant in analyte concentration and interference removal, aspects of vital importance in the trace analysis of both organic and inorganic species in complex samples [1,3].

Due to the current globalized food production system, food safety and quality assessment are paramount concerns of national and international regulatory committees and, consequently, for the scientific community [6]. In this sense, numerous improvements have been developed in order to enhance the speed and reliability of analytical processes. However, food sample analysis constitutes one of the most important challenges in Analytical Chemistry due to the high complexity of these matrices which contain a large number of components with different nature and chemical properties. These aspects considerably hinder the selective extraction of the target analytes, that decrease the sensitivity of the methodology and that, in some cases, could even damage the separation method and determination systems as occurs with the presence of salts, lipids or proteins [7]. That is why the application of effective sample pre-treatment techniques that provide high extraction efficiency and offer an adequate clean-up of the samples is crucial. In this sense, the development of nanomaterials as sorbents has become an interesting alternative for such a purpose.

In this concern, diverse types of nano-sorbents have been evaluated in food analysis, such as carbon nanotubes (CNTs), graphene and graphene oxide (GO), nanoparticles (NPs) of different nature, metal-organic frameworks (MOFs) as well as diverse combinations of them using the synergy of their individual characteristics. Regarding their applications, those have been based on the development of diverse extraction processes including conventional solid-phase extraction (SPE), dispersive solid-phase extraction (dSPE) in the same way as its micro (μdSPE) and magnetic (m-dSPE) approaches, solid-phase microextraction (SPME), matrix solid-phase dispersion (MSPD), stir bar sorptive extraction (SBSE) or even in hollow fiber (HF) liquid-phase microextraction (LPME) techniques in which the pores of the fibre are filled with such nanomaterials together with an organic solvent.

The advantages that nanomaterials offer for food analysis have resulted in a large variety of applications and an important increase in the number of publications focused on their evaluation. In this article we review the principal nanosorbents used in this field, presenting their most relevant characteristics and paying special attention to the most novel studies and their applications for the extraction of both organic and inorganic analytes in food matrices.

2. Metal-organic frameworks

Metal-organic frameworks (MOFs) are an emerging class of porous materials constituted by the self-assembling of metal cations and organic electron donors through coordination bonds. The large variety of metallic ions and organic ligands available and the multiple ways in which they can be combined, allow obtaining different pore diameters and modifying the size of the cavities inside the three-dimensional structure. In fact, it is precisely this capacity to be modified, in addition to their large surface area, the possible functionalization of their internal surface as well as their thermal and chemical stability, which have upgraded the use of MOFs in diverse applications, attracting a special interest as sorbents in analytical applications.

In spite of their obvious advantages, it is noteworthy to mention that the application of MOFs as sorbents in food analysis has been quite limited, as can be deduced from the few papers found in the literature so far [8–14].

Attending to the information shown in Table 1, which compiles some examples of the application of MOFs for the extraction of different compounds from food matrices, it seems clear that one of the sample treatment techniques most commonly used has been dSPE for both analyte extraction [11,13] and sample clean-up [10], especially their μdSPE approach in which very low amounts of sorbent are applied. In these papers, the same MOF [MIL-101(Cr) (Materials of Institute Lavoisier)] was applied for the extraction of seven herbicides from soybean [10], corn, soybean, sunflower and peanut oil [11], as well as from peanuts [13].

Some other work has been published using MOFs as MSPD sorbents [12,14]. In these examples, two slightly different MOFs were employed. In one of them, $[(Nd_{0.9}Eu_{0.1})_2(DPA)_3(H_2O)_3]$ was used for the extraction of six pesticides from *Annona muricata* samples [12] while for the other, $[(La_{0.9}Eu_{0.1})_2(DPA)_3(H_2O)_3]$ was applied to extract other six pesticides from lettuce samples [14].

In most of these applications of MOFs as sorbents, high performance liquid chromatography (HPLC) coupled to diode array detectors (DAD) were employed [10–13], though in a few cases either gas chromatography (GC) with mass spectrometry (MS) detection [14] or nano ultra-high performance liquid chromatography (nano-UHPLC) with ultraviolet (UV) detection have also been used [9]. It is also noteworthy to mention that recovery values between 70 and 120% were obtained in all cases with limits of detection (LODs) in the order of a few μg/L or μg/kg independently of the MOF and technique used.

Besides the above-mentioned uses of MOFs, these nanomaterials have been applied in some different ways. The work of Lin et al. [8] is an example of this fact. In this paper, authors used MOF-5 to cover a stainless steel wire and to use it as a support to immobilize an aptamer capable of recognizing the target analytes (two polychlorinated biphenyls (PCBs)) on its surface. Thus, they created a highly selective sorbent to extract the analytes of interest from fish with a good extraction efficiency and low LODs.

Apart from the previous applications, MOFs may also be used as substrates to create other structures. This is the case of the work of Liu et al. in which the MOF (ZIF-67 (zeolitic imidazolate framework)) has been used as the base for building a magnetic nanoporous carbon by the calcination of the MOF three-dimensional structure [15]. This new sorbent was applied in magnetic dSPE (m-dSPE) for the extraction of four phenylurea herbicides from grape and bitter gourd samples, using HPLC-UV for their determination. In this way, it was possible to obtain recoveries between 89 and 105% with LODs in the range 0.17–0.46 μg/kg. Up to now, and to the best of our knowledge, this is the only paper that has been published regarding this issue.