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REVIEW ARTICLE

Carbon-based sorbents and their nanocomposites for the enrichment of heavy metal ions: a review

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Abstract

This review (with 168 refs) summarizes the progress that has been made on the field of microextraction of heavy metal ions using carbonaceous materials. Following an introduction into the features of such materials, we discuss the various kinds of sorption-based microextraction techniques (like solid phase extraction, micro solid phase extraction, solid phase microextraction, magnetic solid phase extraction, and dispersive solid phase extraction). The next section covers specific methods based on the use of carbon-based adsorbents (with subsections on uses of carbon nanotubes, graphene, fullerenes, activated carbon, carbon nanohorns, carbon nanofibers, graphitic carbon nitride, and their composites). The concluding section addresses current challenges, and gives an outlook on potential future trends.

Keywords Carbonaceous sorbents · Sorptive-based microextraction methods · Microextraction · Heavy metals · Graphene, graphene oxide, carbon nanotubes, activated carbon · Fullerenes · Carbon nanohorns · Graphitized carbon black

Abbreviations/acronyms

AFS	Hydride generation-atomic fluorescence spectrometer
AMP	2-((2-aminoethylamino)methyl)phenol
ANS	1-amino-2-naphthol-4-sulfonate
APDC	Ammonium pyrrolidine dithiocarbamate
ASV	Anodic stripping voltammetry
AuNPs	Gold nanoparticles
BMSAPD	Bis(4-methoxy salicylaldehyde)-1,2-phenylenediamine
CRM	Certified reference material
DCC	N,N-dicyclohexylcarbodiimide
DI-SPME	Direct immersion-solid phase microextraction
DMG	Dimethylglyoxime
DPASV	Differential pulse anodic stripping voltammetry
EAAS	Electrothermal atomic absorption spectrometry
EBB	Eriochrome blue black
EDA	Ethylenediamine
EDXRF	Energy-dispersive X-ray fluorescence spectrometry
ES	Emeraldine salt
EB	Emeraldine base
FI-CV-AAS	Flow injection-cold vapor-atomic absorption spectrometry
FI-SCGD-AES	Solution-cathode glow discharge-atomic emission spectrometry
g-C_3N_4	Graphitic carbon nitride
GFAAS	Graphite furnace atomic absorption spectrometry
GO-SBA-15	Silica-grafted graphene oxide
HF-SPME	Hollow fiber-solid phase microextraction
HG-AMPES	Hydride generation-microwave plasma atomic emission spectrometry
HG-DC-AFS	Hydride generation-double channel atomic fluorescence spectrometry
HPLC	High performance liquid chromatography
HQAB	4-(8-hydroxyquinoline-azo)benzamidine
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy

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IL	Ionic liquid
LIF	Laser-induced fluorescence
MPANI@GO	Fe_3O_4@SiO_2@polyaniline–graphene oxide
MSPE	Magnetic dispersive solid phase extraction
MS-FAAS	Micro sampling flame atomic absorption spectrometry
NaDDTC	Sodium diethyldithiocarbamate
PAN	1-(2-pyridylazo)-2-naphthol
PAN-imp-ACC	1-(2-Pyridylazo)-2-naphthol impregnated activated carbon cloth
PANI	Polyaniline
PEI	Polyethylenimine
Phen@GO	5-amino-1,10-phenanthroline
PPy	Polypyrrole
2-PTSC	Pyridinecarboxaldehyde thiosemicarbazone
REEs	Rare earth elements
SA-D-μSPE	Syringe-assisted dispersive micro solid phase extraction
SEP	Soluble eggshell membrane protein
TEOS	Tetraethoxysilane
TETA	Triethylenetetramine
TPED	N-[3-(trimethoxysilyl) propyl] ethylenediamine
TXRF	Total-reflection X-ray fluorescence spectrometry
USA-IL-LDMME	Ultrasound-assisted, ionic liquid linked, dual-magnetic multiwall carbon nanotube microextraction
WDXRF	Wavelength-dispersive X-ray fluorescence analysis
XRF	X-ray fluorescence spectrometry

Introduction

Heavy metal ions are released into the environment through different sources mainly including agricultural and industrial activities [1]. Some metal ions such as copper, zinc, and iron are vital for a healthy life at trace amounts; however, some other (e.g. Cd, Hg, As, and Pb) are considered very toxic and harmful even at trace levels of concentration [2]. Consequently, the development of promising techniques for the analysis of heavy metal ions is of great concern.

Various methods have been introduced and applied for the extraction of heavy metals from real matrices [3–6]. As conventional pretreatment techniques are time, reagents, and sample consuming, it has been tried to develop miniaturized analytical methods to minimize the consumption of reagents and energy. For instance, automation of pretreatment process, development of greener microextraction methods, and use of microwave and ultrasound radiation can be helpful to achieve this goal. Sorptive-based extraction methods are among the most successfull-employed methods for the enrichment of heavy metals from different complicated matrices.

As the type or nature of the sorbent is considered among the most critical factors that can influence the efficiency of the extraction procedure, it is important to use an appropriate material for the enrichment of the target metal ion [7, 8]. Lately, carbonaceous adsorbents and their hybrids with other nanoparticles have aroused considerable attraction in sorptive-based pre-concentration methods for the determination and analysis of hazardous metal ions. These sorbents show several notable properties including high sorption capacity, ease of surface modification, outstanding electrical/chemical and thermal properties [9, 10].

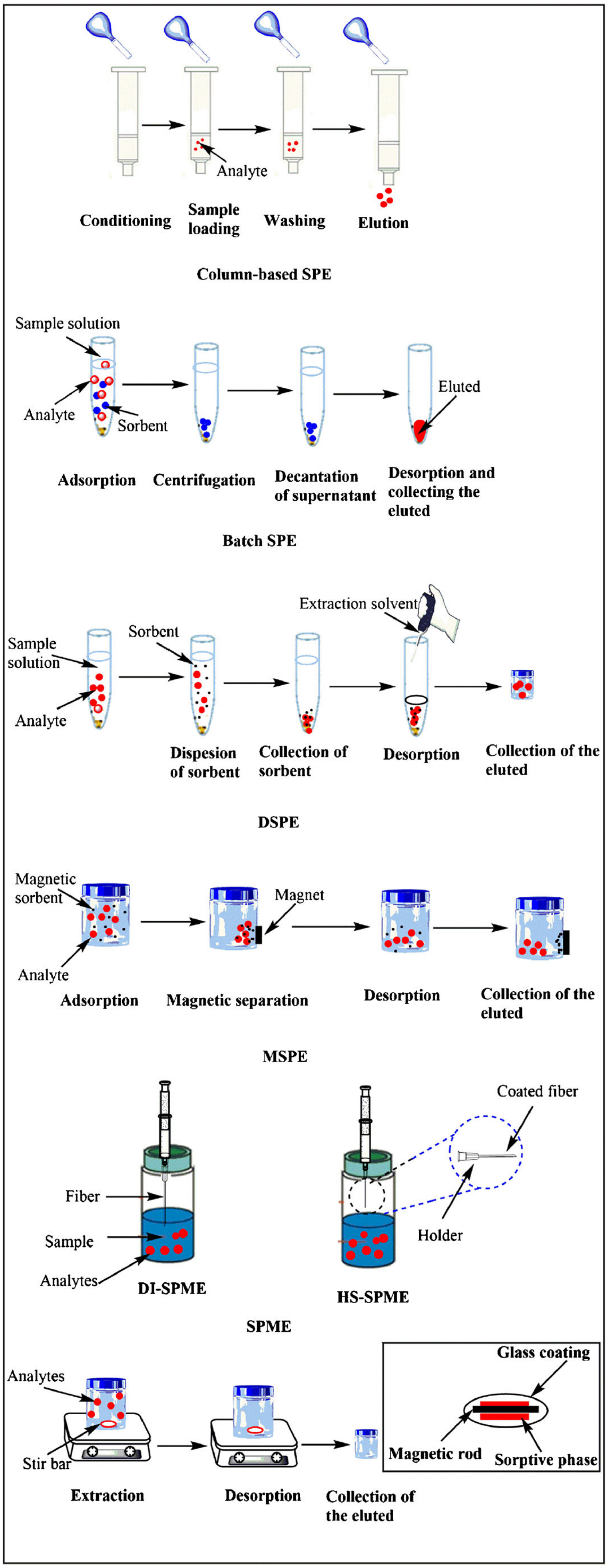
This review presents and highlights the recent applications (since 2010) of various classes of carbon-based compounds (namely activated carbon (AC), carbon nanotubes (CNTs), graphene (G), graphene oxide (GO), reduced graphene oxide (rGO), carbon nanohorns (CNHs), carbon nanofibers (CNFs), graphitic carbon nitride, and fullerenes) for the separation and pre-concentration of various heavy metals in the environmental, food, and biological samples. This review also emphasizes the current trends and developments in the synthesis and modification process of these sorbents in the sorptive-based techniques.

Different sorptive-based extraction techniques

Although a tremendous improvement has been occurred in modern analytical instruments, pretreatment methods are still commonly used to improve limits of detection (LODs) and reduce the matrix effect in the determination of heavy metals [11]. Normally, several factors like the type of analyte, the extraction procedure, and the extracting phase (either solvent or sorbent) should be taken into account before choosing a pretreatment technique [11]. Among numerous sampling methods, extraction and preconcentration of analytes using sorptive-based enrichment techniques have been widely utilized for the potential analysis of various chemicals from several complicated matrices [12, 13]. The general principle in sorptive-based pretreatment techniques is that analytes are interacted with the extraction phase or sorbent and separated from the sample media. Then the sorbent is isolated (using centrifugation, filtration or external magnet) from the sample solution and the retained analytes are eluted from the sorptive phase for further instrumental analysis (Fig. 1).

Solid phase extraction (SPE) was first introduced in the 1970s to lessen the consumption of a large amount of toxic organic solvents in liquid-liquid extraction (LLE). SPE is still utilized as one of the most profitable choices for analyte preconcentration in analytical chemistry [14]. In SPE, the solutes

Fig. 1 Schematic of different sorptive-based extraction techniques



are adsorbed onto the solid sorbent, isolated from the interferences and enriched. The type of the adsorbent depends on not only the analyte of interest but also the interaction of the sorbent and the analyte. Accordingly, an appropriate sorbent can enormously enhance the efficiency of the extraction process. Various benefits involving low-cost, simplicity, small volume of organic solvents, and compatibility with many analytical instruments are associated with the SPE [12, 14].

In 1990, the miniaturization in solid phase extraction resulted in the development of solid phase microextraction (SPME) [15] and it has continued to date. The fundamental aims of miniaturization include reduction of the consumption of samples, chemicals, solvents, sorbents, as well as the extraction and sampling tools [11]. In SPME, the analytes of interest are extracted into the sorptive phase, which is coated on the surface of fused silica fiber (and/or stainless steel wire) or placed inside the needle-like device [16, 17]. It is worth mentioning that the stability, nature as well as the thickness of the coating sorbent can affect the efficiency of the preconcentration procedure in SPME. The enriched target chemicals can be analyzed by either gas chromatography (GC) or liquid chromatography (LC) after thermal and solvent desorption, respectively. SPME is a cost-effective, and environmentally friendly pretreatment method.

In 1999, stir bar sorptive extraction (SBSE) was first applied as a new generation of miniaturized sorptive-based extraction technique [18]. An SBSE device is composed of a coated magnetic stir bar with a suitable sorbent (typically polydimethylsiloxane (PDMS)) which is placed inside the glass jacket. The magnetic bar is then exposed to the solution containing the analytes (either in the direct or headspace modes) for a certain duration. Afterward, the adsorbate is back-extracted from the sorptive phase using thermal desorption (TD) or solvent elution [19]. Depending on the nature of the target analyte and the sample matrix, different sorptive materials can be utilized in SBSE. For instance, metal-organic frameworks (MOFs), moleulary-imprinted polymers (MIPs), and carbonaceous material are among the most common sorptive phases in SBSE [20–22]. In comparison with SPME, the larger quantity of the sorptive phase in SBSE leads to lower limits of detection (LODs) and higher extraction recoveries [19].

Dispersive solid phase extraction (DSPE) is another form of SPE in which the adsorbent is exposed to the analytes via dispersion process to provide a large surface area and high sorption capacity. The following analysis of the analytes can be performed after isolation of the sorbent using centrifugation process [23]. DSPE possess several benefits including short equilibrium time, no need for conditioning stage, and high extraction recovery. Micro solid phase extraction (μSPE) and dispersive micro solid phase extraction (D-μSPE) are two other miniaturized forms of sorptive-based pretreatment methods. In both of these methods, the smaller quantity of sorbent is used compared to SPE and DSPE [23]. Until today, carbon-based sorbents have been continuously applied for the enrichment of heavy metals from diverse real samples using DSPE and D-μSPE [24–26].

Magnetic solid phase extraction (MSPE) is another alternative to general SPE in which an external magnet is used for the retrieval of the magnetic adsorbent from the aqueous sample. The extraction procedure can be performed by either functionalized magnetic nanoparticles (MNPs) or their composites with other materials such as CNTs, G, and GO [27]. The elimination of centrifugation and/or filtration step is the most notable superiority of this method that leads to the simplicity and rapidity of the enrichment process.

Carbon-based adsorbents and their characterization techniques

Contemporary trends in the development of sorptive-based enrichment methods have led to the synthesis and application of diverse range of solid materials (e.g. ion-imprinted polymers (IIPs), MOFs, CNTs, G, GO, metal, and metal oxide nanoparticles) for the enrichment of hazardous metals [28–31]. Several remarkable properties of carbonaceous sorbents mainly involving high sorption capacity, possibility for surface modification, reasonable extraction efficiency, and good conductivity make them be favorable among chemists and environmentalists for the isolation of harmful contaminants [32].

The elemental, structural, and chemical composition of carbon-based sorbents can be determined using diverse techniques including X-ray diffraction (XRD), scanning electron microscopy, energy dispersive X-ray spectroscopy (EDX), and Fourier transfers infrared spectroscopy. SEM allows the determination of the morphology of the prepared sorbent. In addition, SEM can confirm structural changes that may happen on the surface of the sorbent due to some phenomenon such as functionalization of the surface and adsorption/desorption of the analyte onto the surface of the adsorbent [33].

FT-IR is a proper technique to detect the present functionality of the prepared solid sorbent. For instance, the IR spectra can represent the incorporation of the diverse functional groups such as hydroxyl, amino, carboxyl, and carbonyl onto the surface of the modified carbonaceous materials.

In addition, the elemental analysis of the synthesized sorbent can be performed by EDX. Moreover, X-ray photoelectron spectroscopy (XPS) and XRD can confirm the chemical composition and crystal structure of the sorbent [33].

Moreover, the specific surface area of the applied sorbent is usually determined by the adsorption of N_2 on the surface of the sorbent at 77 K [33, 34]. The Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) theories aim to determine the surface area ($m^2\ g^{-1}$) and the adsorption cumulative pore volumes (cm^3 g^{-1}) of the adsorbent, respectively. This section focuses on the several categories of carbon-based substances, their physicochemical properties, preparation, and modification methods in sorptive-based pretreatment area.

Activated carbon

Activated carbon (AC) is classified as a carbon-based material composed of graphite crystallites possesses heterogeneous and irregular surface. Chemical treatment or pyrolysis of materials like nutshells, wood, and coal leads to the production of AC. Several factors such as synthesis procedure and the kind of materials used for synthesis were found to affect the surface structure of activated carbon. Various functional groups (e.g. quinone, carboxyl, hydroxyl, and carbonyl) can be attached to the surface of AC through gas and liquid phase oxidation. However, oxidation can decrease the surface of AC [35].

The presence of functional acidic molecules in the surface of activated carbon is beneficial for the extraction and removal of metal ions. However, the heterogeneous surface of AC may reduce the reproducibility of this sorbent. Moreover the hydrophobic structure of activated carbon restricts the interaction of inorganic analytes (metal ions) with this sorbent and results in the increase of the adsorption time. Therefore, the surface of AC can be modified using different chelating agents such as 8-Hydroxyquinoline, diarylazobisphenol, and pyrocatechol violet (Fig. 2). The modification can enhance not only the selectivity but also the adsorption ability of this sorbent toward target heavy metal ions [36]. The adsorption efficiency of AC depends on pH, temperature, salt concentration, as well as interferences concentration; therefore, these factors should be controlled to achieve reasonable sorption capacity [37].

In 2010, a column-based SPE was performed using modified AC with 2-((2-aminoethylamino)methyl)phenol (AMP) for the enrichment of three metal ions (Fe^{3+}, Cu^{2+}, and Pb^{2+}) followed by sensitive analysis using ICP-OES [36]. For this purpose, the adsorbed impurities on the surface of the AC were removed using HCl solution. Next, the COOH groups were added to the surface of the sorbent by interacting (at 60 °C for 5 h) with HNO_3 solution (5 mol L^{-1}). Then, 4.5 mg AC-COOH was interacted with 100 mL of ethylenediamine (EDA) under heating and stirring. The subsequent addition of N,N-dicyclohexylcarbodiimide (DCC) was lead to the production of AC-EDA. The AC-EDA was subsequently used for the preparation of AC-AMP using salicylaldehyde and sodium borohydride as the main precursors. Finally, an appropriate quantity of the synthesized sorbent was used to pack a polytetrafluoroethylene column. The influence of different parameters (e.g. pH, elution conditions, sorbent quantity, and flow rate) was then investigated to reach an optimum pre-concentration condition. High adsorption capacities (12.1–67.1 mg g^{-1}) and large pre-concentration factors (50–100) are obtained for the analysis of the target metal ions in both water and biological matrices. In the same research work, modified activated carbon with 4-(8-hydroxyquinoline-azo)benzamidine (HQAB) was used as a solid adsorbent for the analysis of lead ions in environmental water samples [38]. Chemical modification of the AC surface with HQAB can improve the sorption capacity (53.58 mg g^{-1}) and selectivity of the sorbent due to the presence of nitrogen and oxygen atoms in the structure of the ligand. The main advantages of these two reported methods are the reusability of the sorbents (up to 10 cycles for both) and large sorption capacity.

In 2012, a composite of gold nanoparticles (AuNPs) with AC and bis(4-methoxy salicylaldehyde)-1,2-phenylenediamine (BMSAPD) was reported [39] as a solid sorbent for the enrichment of Pb^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+} and Fe^{2+} from corundum sativa, olive, limon, and onion samples. The presence of AuNPs on the surface of AC allows the further modification of AC surface with the complexing agent. In addition, conjugation of AuNPs with AC leads to the enhancement of the sorbent selectivity toward the metal ions. The composite (AU-NP-AC-BMSAPD) provided trace analysis of the analytes (LODs: 1.4–2.6 μg L^{-1}) with large sorption capacity (31.5–37.4 mg g^{-1}) prior to FAAS analysis. The method combines the advantages of using AC and gold nanoparticles in the extraction procedure. However, desorption of heavy metals with a large volume of the eluent (6 mL of nitric acid 4 mol L^{-1}) from the surface of adsorbent can be considered as a demerit of the procedure.

Lately, Mogolodi Dimpe et al. [34] prepared a novel composite of activated carbon with magnetic nanoparticles and manganese oxide nanoparticles for the following dispersive magnetic solid phase extraction of several toxic heavy metals (e.g. Sn, Ti, Ta, Sb, Mo, Hf, Zr, W, Ge, Nb, Hf, Te). The presence of MnO_2 in the composite structure increases the affinity of the AC large surface area for the adsorption of target metals in water samples. The results were fitted into both Langmuir and Freundlich isotherm models; however, Langmuir model gave higher r^2 value (0.997). The main objective of miniaturization in separation science is to reduce the amount of reagents, time, and sample tools. However, adsorption of analytes with large amount of sorbent (125 mg) compared to the conventional SPE can be considered as a disadvantage of this research work. On the other hand, this microextraction method revealed good analytical figures of merit. The low LODs (0.0004–0.02 μg L^{-1}), high preconcentration factors (PF: 396–920) and reasonable precision (RSD < 5%) proved the applicability of the sorbent for analysis of metal ions in the environmental water samples. Recent applications of AC in sorptive-based extraction methods for the enrichment of heavy metal ions are presented in Table 1. According to the Table, modified AC with different chelating agents have been used for the efficient enrichment of a variety

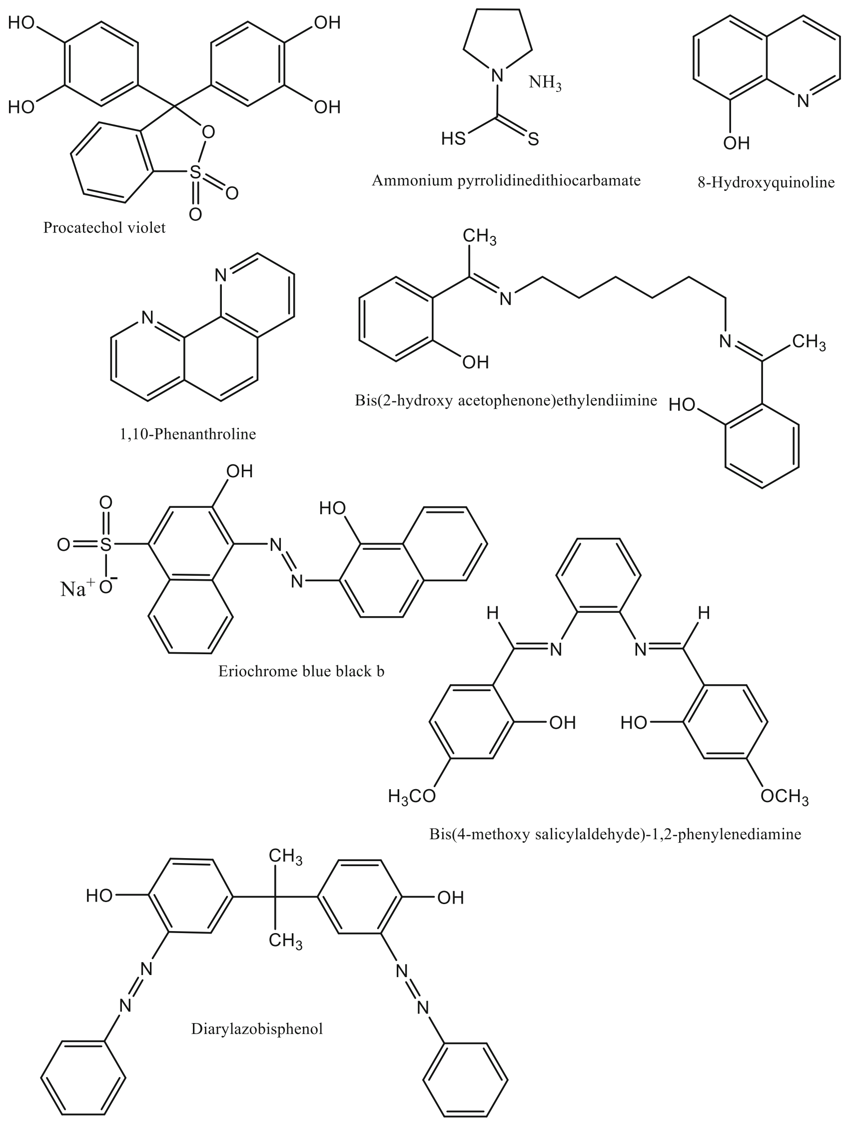


Fig. 2 Structure of general chelating agents for the modification of the surface of AC

of metal ions. This sorbent provides low limits of detection and high sorption capacity. Moreover, among diverse types of analytical instruments, FAAS and ICP have been the most common ones for determination of the target metals. Compared to other carbon-based sorbents, AC is cheap and more available. However, this adsorbent composed of larger carbon particles that are irregular in shape.

Graphitized carbon black

Graphitized carbon black (GCB) is a carbonaceous substance that has been used in SPE procedure for the first time in the 1980s. GCB can be produced by heating of carbon black at high temperature (about 2700–3000 °C) [40]. According to Corcia et al., [41] acidic compounds can be strongly adsorbed on the surface of graphitized carbon black due to the presence of some oxygenated groups such as quinones. The irreversible binding of target analytes onto the surface of the GCB can restrict the application of this sorbent in sorptive-based extraction techniques. To avoid this phenomenon, the sorbent can be treated by the solution of ascorbic acid in order to decrease the number of quinones groups on the surface of the GCB [40, 41].

Porous graphitized carbon (PGC) is another form of graphitized carbon possessing extremely homogeneous crystalline surface. The 2-D structure of PGC consists of sp^2-hybridized carbon atoms. The impregnation of silica with phenol-formaldehyde mixture followed by polymerization and carbonization at 1000 °C leads to the production of PGC. Then, the silica can be removed by the subsequent treatment in a concentrated solution of KOH or NaOH [40, 42]. Both GCB and PGC can be employed as sorbents for the isolation and enrichment of heavy metals in sorptive-based pretreatment methods, however, no research article has reported since 2010.

Table 1 Applications of AC-based solid phase extraction for the enrichment of heavy metal ions

No	Analyte	Sorbent	Method	Analytical instrument	Matrix	LOD (μg L^{-1})	Sorption capacity (mg g^{-1})	Ref.
1	Cu, Fe, and Pb	AC-AMP	SPE	ICP-OES	Water and tuckahoe	0.16–0.41	12.1–67.1	[36]
2	Cr, Fe, and Pb	AC-TETA	SPE	ICP-OES	River sediment	0.35–0.71	34.1–51.9	[80]
3	As(III)	AC-NaDDTC	SPE	GFAAS	Water	0.04	8.6	[81]
4	Hg	AC	SPE	XRF	Water	0.001	200	[82]
5	Cu, Co, Cd, Ni, Pb, Zn	AC	SPE	ICP-OES	Fruits	0.17–2.60	1.2–2.4	[83]
6	Cd, Pb, and Ni	PAN-imp-ACC	SPE	FAAS	Water, soil, and sewage sludge	0.1–2.8	43.2–45.0	[84]
7	Au	AC-ANS	SPE	ICP-OES	Water	0.26	32	[85]
8	Pb	AC	SPE	ICP-OES	Water	0.43	53.58	[38]
9	Pb	AC-EBB	SPE	ICP-OES	Water	–	127.89	[86]
10	Fe and Zn	AC	SPE	FAAS	Water	0.11–0.30	43.7–65.8	[87]
11	Cr, Cu, and Pb	AC- Ruthenium NPs	SPE	FAAS	Water, food, and plasma	0.02–0.09	31.3–39.8	[88]
12	Cu, Co, Ni, Fe, Zn, and Pb	AC-Au NPs	SPE	FAAS	Leek, radish, and banana	1–4-2.6	31.5–37.4	[39]
13	Cd, Pb, Ni, and Zn	AC@APDC	SPE	FAAS and GFAAS	Fish tissue	10.1–25.3 μg Kg^{-1}	–	[89]
14	Hg	AC-Fe_3O_4	MSPE	UV-Vis spectrophotometry	Water	–	714.3	[90]
15	Heavy metals	AC-Fe_3O_4-MnO_2	MDSPE	ICP-OES	Water	0.001–0.07	176–197	[34]

Carbon nanotubes

In 1991, Iijima discovered an allotrope of carbon named carbon nanotubes [43]. These substances are cylindrical in shape with a diameter of about several nanometers. Based on the number of graphene layers in the tubular structure of CNTs, these materials are classified into two groups: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [10].

Chemical vapor deposition, arc-discharge, and laser ablation are among the most typical synthesis procedures for the preparation of CNTs. Chemical vapor deposition is the most reliable method that leads to the high-scale production of pure CNTs. While laser ablation is frequently used for the synthesis of CNTs on a laboratory scale [35, 44].

Generally, non-covalent interactions including π-π interaction, van der Waals forces, and hydrophilic interactions are responsible for the adsorption of analytes onto the surface of CNTs. Carbon nanotubes can be oxidized through the interaction with several oxidizing agents (like sulfuric acid, nitric acid, and potassium permanganate) [10]. Oxidized CNTs are polar and can be easily dispersed into the aqueous media. The oxygenated functional groups on the surface of CNTs can interact with metal ions and lead to the efficient extraction of these analytes from complicated matrices [45].

Although SWCNTs have a larger surface area in comparison with MWCNTs, they have found lower applications in sorptive-based extraction techniques. The more complex synthesis process and resistance to functionalization and oxidation are the most important factors that confine the applications of SWCNTs in SPE methods [44].

In contrast to graphene-based sorbents, the inter walls of CNTs are not available for the analytes adsorption. Therefore, the main adsorption process is taken place on the outer surface of CNTs. In addition, the synthesis procedure for the preparation of graphene-based materials is easier than that one for the CNTs. In other words, no purification stages and complex instruments are needed for the production of graphene-based materials [45]. To date many toxic heavy metal ions have been separated and concentrated from different matrices (e.g. food, biological, and environmental samples) using CNTs as sorbent (Table 2).

In 2010, Ozcan et al. [46] packed an SPE column with MWCNTs for the subsequent enrichment of several heavy metals (Cu^{2+}, Fe^{3+}, Mn^{2+}, and Pb^{2+}) from the plant, water and food samples. The packed column was successfully applied for the extraction of the target metal ions with low LODs ranged from 3 to 8 μg L^{-1}.

In another example, a composite of MWCNTs and magnetic nanoparticles were prepared and employed as an efficient sorbent for the magnetic solid phase extraction of Mn(II) and Pb(II) after FAAS analysis [47]. To obtain the magnetic sorbent, an appropriate quantity of MWCNT was dispersed in the solution of Fe^{2+}/Fe^{3+} (1:2) under the inert atmosphere of argon. Then 20 mL of ammonium hydroxide solution was added gradually to the mixture and the reaction continued for 30 min at 50 °C. Finally, the synthesized composite was isolated using an external magnet and washed thoroughly with water and ethanol. The Fe_3O_4/CNT composite was used for the fast and convenient extraction of trace amounts of target metals (LODs: 0.6–1.0 $\mu g\ L^{-1}$) in rice, cosmetic, and urine samples. In addition, the reported results from the analysis of the certified reference material (CRM) was in good agreement with the actual values and proved the validity of the reported method. Compared to the pure CNTs, the magnetic composites has better dispersion ability that can lead to the easier isolation of the adsorbent from the sample solution. In addition, the surface of MCNTs is prone to more modification with other nanoparticles or functional groups. Moreover, the lower volume of elution solvent (200 μL) is used for desorption of metal ions from the surface of the MCNTs. According to the article, the synthesized composite was regenerated using the mixture of acid/ethanol and reused in the SPE process eight times.

A novel sorbent was prepared by the combination of magnetic nanoparticles coated with silica shell, MWCNTs, and 1-(2-pyridylazo)-2-naphthol (PAN) for the MSPE of cobalt and lead ions from water samples before FAAS analysis [48]. The ease of surface functionalization and stability of silica makes it be a suitable shell to protect the surface of MNPs from oxidation and corrosion in the presence of oxygen and acidic solutions, respectively. To prepare magnetic CNTs, an appropriate quantity of the synthesized MNPs through co-precipitation technique was mixed with 1 g of MWCNT and heated at 60 °C in EtOH solution. Then, a solution of tetraethoxysilane (TEOS) was added to the prepared magnetic CNT (at 80 °C) to obtain $SiO_2@Fe_3O_4@$MWCNT composite. After that, PAN (as chelating agent) was immobilized on the surface of the obtained composite to reach $SiO_2@Fe_3O_4@$MWCNT-PAN. This sorbent was then utilized in the vortex-assisted MSPE procedure. Low LODs (0.55–1.76 $\mu g\ L^{-1}$) and good precision (RSD%: 2.5–3.3) has proved the efficiency of this extraction method in the analysis of Pb and Co ions.

In one more case, modified MWCNTs with tricaprylmethylammonium chloride (Aliquat 336) was prepared as a solid material for the D-μSPE of Cr(VI) ions from water samples before total reflection X-ray fluorescence (TRXF) determination [49]. It is worth mentioning that the application of D-μSPE followed by TRXF analysis can provide the determination of the analyte of interest at trace levels of concentration. First, a solution containing 5% Aliquat 336 in methanol was interacted with MWCNTs (0.025 g) to obtain the modified CNTs with an anion exchanger. After the optimization of the extraction process, Cr^{6+} ions were enriched from the sample solution with high recoveries (101–108%) and low LOD (3.0 $\mu g\ L^{-1}$). It should be pointed out that lower amount of the adsorbent (5 mg) and the desorption solvent (300 μL) were used in the extraction procedure which can prove the superiority of D-μSPE over the conventional SPE. In recent research work, the adsorption efficiency of U(VI) ions using MWCNTs and modified MWCNTs with 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol (Br-PADAP) has been compared [50]. According to the results, Br-PADAP/MWCNTs revealed faster adsorption equilibrium and high adsorption capacity compared to pure MWCNTs. This can be attributed to the presence of the chelating agent on the surface of MWCNTs. In fact, modification of CNTs surface by metal complexing agents can improve the selectivity of these sorbents toward the adsorption of metal ions.

Based on the information of Table 2, since 2010, CNTs and their different composites have been used in diverse solid phase-based pretreatment methods for the analysis of metal ions. This group of carbonaceous materials can be easily modified to facilitate the adsorption process of analytes. However, the insolubility of CNTs can cause high pressure in column-based SPE. As CNTs can provide the trace analysis (at $\mu g\ L^{-1}$ and $ng\ L^{-1}$ levels) of toxic heavy metals in different complex matrices, their application can be more extended in separation science in the future. Therefore, there is still a great room to develop more convenient modification methods and produce novel composites from CNTs.

Graphene, graphene oxide, and reduced graphene oxide

The 2-dimensional structure of graphene is produced from a single layer arrangement of carbon atoms with sp^2 hybridization. Unlike other forms of carbonaceous materials (e.g. CNTs, and fullerenes), both sides of graphene planar sheets are available for analyte uptake in sample media [32, 51]. Compounds that contain aromatic rings (like pesticides, drugs, and polycyclic aromatic hydrocarbons) can be efficiently extracted using G, due to the interaction the π-electron system in the benzene ring of these substances with that one in graphene structure [32].

There are some synthesis methods for the production of graphene in both industrial and research scale. The micromechanical exfoliation of graphite can produce graphene. Although this method yields pure graphene, it is not applicable to large-scale production. Likewise, the exfoliation via ultrasonication process results in low-yield production of graphene [45]. The most promising scalable methods for preparation of G are the thermal decomposition of SiC and chemical vapor decomposition (CVD) of alcohols and hydrocarbons [45, 52]. In addition, the chemical reduction of graphene oxide using an appropriate reducing agent (e.g. hydrazine) is another typical method to produce graphene with high quality [53].

Table 2 Recent applications of CNTs as sorbent for the enrichment of heavy metal ions

No	Analyte	Sorbent	Method	Analytical Instrument	Matrix	LOD ($\mu g\ L^{-1}$)	Sorption Capacity ($mg\ g^{-1}$)	Ref.
1	Cd, Pb, and Ni	MWCNTs	SPE	FAAS	Water	0.04–0.32	1.0–9.3	[91]
2	Fe, Cu, Mn, and Pb	MWCNTs	SPE	FAAS	Water, sediment, plant, and food	3.5–8.0	–	[46]
3	Cr and Fe	SWCNTs	SPE	FAAS	Food and herbal plants	2.12–4.08	–	[92]
4	Cd and Pb	MnO_2/MWCNTs	SPE	ETAAS	Water	0.0015–0.0044	6.7–9.1	[93]
5	Cu, Ni, and Zn	MWCNTs	SPE	FAAS	Water	40–50	4.78–4.90	[94]
6	Pb	MWCNTs	SPE	ICP-OES	Water	0.27	60.3	[95]
7	Cu, Co, Cd, and Ni	MWCNTs	SPE	FAAS	Water	3.0–6.2	–	[96]
8	As and Sb	SWCNTs	SPE	HG-DC-AFS	Water	0.0021–0.0038	–	[97]
9	Pb	MWCNTs	SPE	AAS	Water	0.3	157.19	[98]
10	Cr	MWCNTs	SPE	XRF	Water	0.5	100	[99]
11	Cd, Ni, Pb, and Ni	MWCNTs	SPE	FAAS	Food samples	1.1–7.2	1–6.2	[100]
12	Cu, Fe, and Pb	MWCNTs	SPE	ICP-OES	Water	0.15–0.26	17.0–64.5	[101]
13	Cd	MWCNTs	SPE	FAAS	Water and food samples	0.05	86	[102]
14	Cd, Bi, Pb, As, Hg, and Ti	MWCNTs	SPE	ICP-AES	Skin whitening cosmetics	0.30–4.08	2.32–4.02	[103]
15	Cd	MWCNTs	SPE	FAAS	Water and lobster hepatopancreas	0.3	–	[104]
16	Hg	MWCNTs	SPE	FAAS	Water and fish	0.0125	11.58	[105]
17	Cd, Cu, Pb, Ni, and Zn	MWCNTs	SPE	FAAS	Food samples	1.7–6.0	–	[106]
18	Co, Ni, and Hg	MWCNTs	SPE	HPLC-UV	Water	0.04–0.9	–	[107]
19	Cd and Pb	MWCNTs	SPE	AAS	Water	0.09–0.7	101.2–175.2	[108]
20	Cd, Ni, and Pb	MWCNTs	SPE	FAAS	Water, sediment, soil, and fish	0.09–1.0	150–201	[109]
21	Au	MWCNTs	SPE	GFAAS	Water, human hair, and urine	0.000031	4.15	[110]
22	Co, Cu, and Hg	MWCNTs	SPE	HPLC-UV	Water	0.012–0.138	–	[111]
23	Cd, Cu, Pb, Ni, and Zn	MWCNTs	SPE	AAS	Water and food samples	0.7–2.6	4.0–6.4	[112]
24	Fe, Cr, Pb, and Mn	MWCNTs-GO	SPE	ICP-OES	Water	0.16–0.50	5.4–13.8	[113]
25	Cr	MWCNTs	SPE	LIF	Water	0.094 nM		[114]
26	As	MWCNTs	SPE	GFAAS	Water, rice and ash of rice straw	0.008	79.8	[81]
27	V	MWCNTs	SPE	GFAAS	Water and microwave digested food samples	0.012	9.6	[115]
28	Cr, Cu, Co, Zn, Fe, Ni, Pb, and Mn	MWCNTs	SPE	WDXRF	Water	0.6–1.9	–	[116]
29	Cr	SWCNTs	SPE	ICP-MS	Water	0.01	0.73	[117]
30	Pd	MWCNTs	SPE	FAAS	Water, fly ash, and road dust	0.3	15.7	[118]
31	Pb	MWCNTs-PPy	SPE	FAAS	Water	1.1	25	[119]
32	Ni and Pb	MWCNTs	SPE	ETAAS	Sludge and sediment	0.01–0.03	–	[120]
33	U (VI)	MWCNTs/Br-PADAP	SPE	ICP-AES	Water	0.14	83.4	[50]
34	Cd, Cu, Ni, Pb, and Zn	MWCNTs	SPE	FAAS	Water, food, and environmental samples	0.30–0.65	3.0–5.4	[121]
35	Co, Ni, Cu, and Pb	MWCNTs	D-µSPE	EDXRF	Water	0.11–0.46	–	[122]

Table 2 (continued)

No	Analyte	Sorbent	Method	Analytical Instrument	Matrix	LOD (µg L^{-1})	Sorption Capacity (mg g^{-1})	Ref.
36	Se	MWCNTs	D-µSPE	XRF	Water	0.06	–	[123]
37	Cd and Pb	MWCNTs	D-µSPE	TXRF	Water	1.0–2.1	–	[124]
38	Cd, Cr, Co, Ni, and Pb	MWCNTs	SA-D-µSPE	MS-FAAS	Water, fruit juice, saliva, and urine	0.3–2.0	–	[125]
39	Cr	MWCNTs	D-µSPE	TXRF	Water	3	–	[49]
40	As	MWCNTs	D-µSPE	ETAAS	Garlic	0.0071		[126]
41	Pb and Mn	MWCNTs	MSPE	FAAS	Lipstick and rice	0.6–1.0	–	[47]
42	Cd, Cu, Cr, Ni, and Pb	MWCNTs	MSPE		Water and black tea leaves	0.08–0.5	184–215	[127]
43	Co and Pb	MWCNTs	MSPE	FAAS	Water	0.55–1.76	–	[48]
44	Cd and As	USA-IL-LDMME	MSPE	ETAAS	Water and food	0.003–0.005	–	[128]
45	Cd	MWCNTs	MSPE	GFAAS	Water and urine	0.0012	3.67	[129]
46	Cd, Cu, and Pb	MWCNTs	HF-SPME	DPASV	Rice	0.0073–0.025	–	[130]
47	Cd and Pb	MWCNTs	HF-SPME	DPASV	Water	0.012–0.015	–	[131]
48	Ag, Cd, Pb and Zn	SWCNTs	DI-SPME	ICP-MS	Water	0.012–0.163	–	[132]

In 2012, Wang et al. [54] investigated the application of graphene as a sorbent in column-based SPE for the enrichment of the trace quantities of Pb^{2+} ions in different water (sea, tap, and river water) and vegetable (cucumber and tomato) samples. For this purpose, GO was synthesized through the Hummers method and then it was reduced with hydrazine to obtain graphene. An appropriate quantity of the synthesized sorbent (30 mg) was placed in an SPE column and utilized for the following enrichment of lead ions. The packed column was stable in more than 50 extraction/elution cycles and showed large sorption capacity (16.6 mg g^{-1}). The π-π interaction between graphene and the benzene rings in the structure of the chelating agent (dithizone) can enhance the affinity of the sorbent toward the adsorption of lead ions.

The hybrid of graphene and other nanomaterials can reduce the aggregation of this sorbent in aqueous samples and improve the efficiency of the extraction procedure in SPE. For example, Yavuz et al. [55] reported a novel composite of graphene and cobalt oxide (G@Co_3O_4) for the preconcentration of iron, lead, and copper ions from food and water samples. This composite showed high sorption capacity (58–78 mg g^{-1}) and low limits of detection (LODs≤0.81 µg L^{-1}). To prepare the composite, first cobalt oxide particles are chemically deposited onto the GO and then GO was reduced to G by adding the solution of sodium borohydride. This nano composite was applied in both batch and column-based solid phase extraction. According to the results, using low amount of G@Co_3O_4 (100 mg) is considered as the great advantage of the extraction process. However, based on the fast equilibrium time and large surface area of the sorbent, this amount of the composite is not low enough. Therefore, other analytical merits such as rapid kinetic (10 S), high sorption capacity and pre-concentration factor are considered among the most important characteristics of this sorbent.

In another case, Ezzodin et al., [56] found that the dispersion of magnetic graphene into the aqueous sample containing cadmium and lead ions offered an efficient extraction procedure for the enrichment of these ions prior to analysis by atomic absorption spectrometer. The conjugation of graphene with MNPs improved not only the dispersibility of the solid sorbent but also its sorption capacity. Extraction of the target analytes using 0.5 mg of magnetic graphene, which is much smaller than that in conventional SPE, is considered as the most notable feature of miniaturized SPE techniques.

Graphene oxide is a popular form of graphene-based substance among researchers in which many functional moieties containing an oxygen atom (hydroxyl, carboxyl, epoxide, and carbonyl) are incorporated. The addition of such groups make this sorbent be more hydrophilic in character [9]. In addition, the presence of functional groups in GO is responsible for electrical and hydrogen bonding interactions with metals and organic analytes. Likewise, modification of the GO surface is more possible due to the presence of polar oxygenated groups [9]. For instance, the aggregation of GO particles can be restricted by attachment of different nanomaterials such as SiO_2, MNPs, and TiO_2. On the other hand, the electrical and mechanical properties of GO is less than graphene due to the existence of many oxygen atoms in the structure of this sorbent [45, 57, 58].

The most typical procedure for the synthesis of GO is based on the oxidation of graphite via Hummers method. In this method, graphene oxide is produced by the gradual addition of potassium permanganate to the solution containing graphite, sodium nitrite, and sulfuric acid. The reaction is proceeded at 308 K for 2 h following the addition of hydrogen peroxide to produce the yellow product [59]. Despite the remarkable properties of graphene and graphene oxide in sorptive-based extraction methods, the softness of these sorbents can cause high pressure in column-based SPE and lead to the loss of the adsorbent [14]. In one case, the combination of GO with ethylenediamine (EDA) was utilized as a low-cost adsorbent for the simultaneous enrichment of several toxic heavy metals from water samples via D-μSPE [60]. Due to the presence of nitrogen heteroatoms in the structure of GO/EDA, no more chelating agent was used in the extraction process. According to the results, GO/EDA sorbent demonstrated the LODs in the range of 0.06–0.1 $\mu g\ L^{-1}$.

Magnetic graphene oxide is a composite of GO that can be prepared through co-precipitation procedure [61] and be utilized as an efficient sorbent with high sorption capacity in MSPE. As an example, Seidi et al., [62] investigated the magnetic DSPE through immobilization of polythiophene (PTh) on the surface of MGO for the determination of Hg in seafood samples. Similar to other previously published research articles, magnetic GO was synthesized through co-precipitation technique and then thiophene was polymerized on the surface of the MGO. As mercury is considered as a soft acid, it can interact with the sulfur atoms of PTh and consequently can be isolated from the sample media. In addition, the presence of PTh can improve not only the sorption capacity but also the stability of the sorbent against oxidative reagents. Regarding the optimum experimental conditions and using the experimental design methodology a concentration range of 1–85 $\mu g\ L^{-1}$ with LOD and RSD of 0.025 $\mu g\ L^{-1}$ and 4.0%, respectively, were reported. In the same case, a composite of MGO with polyaniline (MGO@PANI) was synthesized as a novel sorbent for the per-concentration of toxic Cr^{6+} ions at trace concentration levels [63]. GO was synthesized by the Hummers method with slight modification. To this end, graphite was added to the cold mixture of sulfuric and phosphoric acids followed by addition of $KMnO_4$ and hydrogen peroxide solutions. Next, MGO@PANI was prepared using several precursors including MGO, cetyltrimethylammonium bromide (CTAB), aniline, and $Na_2S_2O_8$. The conversion process between two forms of polyaniline (emeraldine salt (ES) and emeraldine base (EB)) and the available forms of chromium ion depend on the pH value. At a pH of 5.6, $Cr_2O_7^{2-}$ is the main form and it can interact with ES form of PANI and consequently can be extracted from the sample solution. Therefore, 5.6 was selected as an optimum pH to reach a maximum extraction efficiency. At more basic and acidic pHs, there is an adsorption competition between chromium ions with hydroxyl and anions of acids, respectively. The analytical performance of the extraction method for the analysis of Cr^{6+} included a wide linear range (0.015–0.3 $\mu g\ L^{-1}$), low LOD (0.005 $\mu g\ L^{-1}$), and high PF (40).

Reduced graphene oxide (rGO) is the third form of graphene, which can be synthesized via different methods including electrochemical, chemical, and thermal ones. Among these methods of preparation, chemical reduction of GO using common reducing agents (like ascorbic acid, lithium aluminum hydride, and hydrazine) is the most applicable one [52]. Like G and GO, reduced graphene oxide has been used as an extracting sorbent for the isolation and enrichment of metal ions in different samples. As an example, rGO was synthesized by heating the mixture containing GO, N_2H_4, and ammonia at 95 °C. Then, rGO was utilized as an adsorbent in a batch procedure for the determination of zinc ions in onion, potato, orange, and rock samples after FAAS analysis [64]. rGO was applied in 5 successive adsorption/desorption cycles by keeping it's analytical performance. In other example, rGO was added to the structure of a soluble eggshell membrane protein (SEP) (rGO-SEP) and used as a new bio sorbent for the anodic stripping voltammetry (ASV) determination of Hg^{2+} in the concentration range of 0.50 to 80 $\mu g\ L^{-1}$ [65]. rGO distributed uniformly into the porous structure of SEP and provided efficient adsorption and elution of mercury on the surface of the sorbent. To prove the adsorption ability of the prepared rGO-SEP in the SPE method, the efficiency of this composite was compared with SEP and rGO in the same experimental conditions. According to the reported results, the recovery of rGO-SEP was more than other two sorbents in the extraction process. It was attributed to the flexible structure of SEP that leads to more distribution and less aggregation of rGO. The column-based SPE revealed large sorption capacity (77 $mg\ g^{-1}$) and low LOD (0.14 $\mu g\ L^{-1}$) for the determination of mercury in water samples.

Moreover, a solid phase extraction method was reported by Aghagoli et al., [66] who employed a composite of molybdenum disulfide (MoS_2) and rGO for the separation and enrichment of two heavy metal ions (Ni^{2+} and Pb^{2+}) from both water and biological samples. The negatively charged surface of MoS_2 can interact with the π-electron system in the structure of rGO to form a composite (MoS_2@rGO) with high adsorption capacity. The composite was used in batch SPE and revealed high adsorption capacity (294–322 $mg\ g^{-1}$) and low

LODs (0.21–0.71 μg L^{-1}) in the proposed extraction procedure. These great analytical features can prove the benefit of modification of rGO with MoS_2 to reach an efficient extraction process. The applications of graphene-based sorbents for the extraction and enrichment of diverse heavy metals are covered in Table 3. Several notable merits including ease of modification, availability of both sides for the adsorption process, and simple synthesis process make graphene-based materials be superior sorbents in solid phase extraction. Low LODs and high sorption capacity obtained for the analysis of hazardous metal ions can prove these outstanding features of G, Go, and rGO. Compared to CNTs and AC, graphene-based materials are more applicable for metal extraction. It can be attributed to the larger surface area and the presence of oxygen containing groups on the surface of this class of sorbents.

Fullerenes

Fullerenes are buckyball carbon-based materials in which carbon atoms are attached to form penta- or hexagonal rings. Fullerenes consist of different isomers and homologous series from the most popular ones (e.g. C_{60} and C_{70}) to the larger ones (e.g. C_{240} and C_{540}) [44]. Fullerenes can be produced using several methods (such as laser ablation of carbon graphite, heating of carbon rods in vacuum and oxidative combustion of the mixture of benzene and argon) in laboratory. However, formation of some by-products like carbon-rich sot and poly aromatic hydrocarbons can decrease the purity of the main product. Therefore, separation techniques such as liquid chromatography or supercritical fluid chromatography should be applied to purify the produced fullerenes [67].

Fullerenes are known for their hydrophobic structure, large surface area, as well as ease of modification. The hydrophobicity of fullerenes makes them useful sorbents for the extraction of metal complexes with low polarity [1]. For instance, the low polar complexes of ammonium pyrolidine dithiocarbamate (APDC) and diethyldithiocarbamate (DDTC) with some heavy metal ions like Cd, Co, Cu, and Pb can be adsorbed onto the surface of fullerenes and be extracted from sample media [1]. In comparison with C18, C_{60} provides more selectivity toward the adsorption of metal ions due to the larger surface area and higher interstitial volume [67].

Several applications of fullerenes as sorbent for the isolation and pre-concentration of heavy metal ions have been reported before 2010 [68, 69]. The low aggregation tendency of fullerenes in both aqueous and organic solvents make them be potential sorbents in D-μSPE and DSPE. However, the low solubility of fullerenes can restrict their applications as coating materials in SPME [70].

Carbon nanofibers

Carbon nanofibers (CNFs) are cylindrical nanomaterials composed of graphene layers with a length of about 100 μm and diameters of around 600–200 nm [71]. The large surface area (up to 1877 m^2 g^{-1}) of CNFs makes them appropriate sorbents in solid phase-based extraction techniques. In addition, due to large dimensions, CNFs have lower tendency to aggregate in comparison to CNTs and G. Different functional moieties such as COOH, OH, and CO can be attached to the surface of CNFs to enhance their sorption capacity. CNFs can also be utilized as efficient coating layers in SPME due to the high chemical and thermal stability. Furthermore, high surface area of CNFs (up to 1870 m^2 g^{-1}) can provide the efficient enrichment of contaminants from real samples [72]. The fiber coated CNFs can be reused in several extraction cycles without losing its efficiency and morphology [73].

Among different techniques, (e.g. phase separation, drawing, and self-assembly) electrospinning is the most common technique for the fabrication of CNFs. In this method, nanofibers are produced from a viscoelastic solution (such as polyacrylonitrile (PAN)) via a repulsive electrostatic force [71]. The electrospun nanofibers can be used as a solid sorbent for the pre-concentration of different analytes from the sample solution.

Carbon nanohorns

Carbon nanohorns (CNHs) are another group of carbon-based nano materials that have been applied as a sorbent in sorptive-based enrichment methods. The carbon cage of these substances is made up of sp^2-hybridized carbon atoms [44, 71]. Compared to CNTs, CNHs can be prepared in large quantity at room temperature. In addition, no hazardous metal catalysts and acid treatment are needed for their synthesis process. Laser ablation, arc discharge, and Joule heating are among the typical preparation techniques that have been applied for the production of CNHs. The surface of CNHs can be modified through chemical modification. As an example, oxygen-containing groups and organic molecules can be attached to the surface and sidewalls of CNHs via covalent and non-covalent interactions. In addition, several functional moieties such as biomolecules, thiols, amines, and alcohols can be added to the oxidized surface of CNHs to produce more hybrid adsorbents [74]. Then modified CNHs can be successfully used in solid phase-based treatment procedures.

Although carbon nanohorns have been used less than graphene-based sorbents and CNTs in sorptive-based enrichment methods, the potential application of this group of carbonaceous materials can be enormously exploited in pretreatment methods.

Table 3 Applications of graphene-based sorbents in sorptive-based extraction of heavy metals

No.	Analyte	Sorbent	Method	Analytical Instrument	Matrix	LOD (μg L^{-1})	Sorption Capacity (mg g^{-1})	Ref.
1	Pb	G	SPE	FAAS	Water and vegetables	0.61	16.6	[54]
2	Cr (III)	G	SPE	FAAS	Water	0.5	24.8	[133]
3			SPE					
4	Co and Ni	G	SPE	FAAS	Water and vegetables	Co: 0.36 Ni: 0.51	Co: 25.8 Ni: 23.5	[134]
5	Pb, Cu, and Fe	G@Co_3O_4	SPE	FAAS	Water and food	0.15–0.81	58–78	[55]
6	Pb, Cd, Cu, Ni, and Zn	G	SPE	FAAS	Water and food	0.03–0.2	110–210	[135]
7	Co	G	SPE	FAAS	Water	0.36	20.6	[136]
8	Cd	G	SPE	FAAS	Seafood	0.16	392	[137]
9	Cd, Co, Ni, and Pb		SPE	WDXRF	Water	1.1–6.1	23.7–39.4	[138]
10	Pb and Cd	G@Fe_3O_4	DSPE	AAS	Water and dairy products	Pb: 0.50 Cd: 0.16	–	[56]
11	Pb and Cd	G-Zeolite clinoptilolite	DSPE	ETAAS	Water and serum	0.004–0.070	–	[139]
12	Pb, Cd, and Cr	G-Silica	D-μSPE	ETAAS	Human saliva and urine	0.004–0.089	125.8–146.3	[140]
13	As (V)	G	D-μSPE	AAS	Water, serum, and urine	0.0021	–	[141]
14	Hg, R-Hg	G	D-μSPE	FI-CV-AAS	Water and caprine blood samples	0.0098	10.7–13.7	[142]
15	Se	GO	D-μSPE	EDXRF	Water and biological samples	0.032	–	[143]
16	Pb, Cd, and Cr	GO	D-μSPE	EAAS	Water, human silva, and urine	0.005–0.035	–	[144]
17	Cr	GO	D-μSPE	EDXRF	Water	0.06	–	[145]
18	Cu, Ni, Fe, and Zn	GO	SPE	AAS	Water	0.11–0.63	6.0–6.7	[146]
19	Pb and Cd	GO	SPE	FAAS	Water, fish, and herbal samples	0.08–0.17	15.3–17.9	[147]
20	Pb and Cd	GO	SPE	FAAS	Water and vegetables	0.005–0.90	179–359	[148]
21	REEs and heavy metals	GO-TiO_2	SPE	ICP-OES	Water and sediment samples	0.21–2.64	–	[149]
22	Pb	GO-SBA-15	SPE	FI-SCGD-AES	Water	0.91	255.10	[150]
23	Cd	GO	SPE	FAAS	Water	0.47	–	[151]
24	As	GO-PEI	SPE	HG-MPAES	Water	0.0013–0.0018	125	[152]
25	Co, Cu, Ni, Pb, and Zn	GO	D-μSPE	EDXRF	Water	0.5–1.5	–	[153]
26	Co and Ni	GO	SPE	FAAS	Water, black tea, and tomato	0.18–0.25	6.8–7.0	[154]
27	As (V)	GO	SPE	HG-AFS	Water	0.029	45.7	[155]
28	Cu, Co, Fe, Ni, Pb, and Zn	GO-EDA	D-μSPE	EDXRF	Water	0.06–1.0	–	[60]
29	Cd, Co, Cu, Ni, Mn, and Pb	GO-Silica	HF-SPME	ICP-MS	Water	0.00039–0.028	4.6–25	[156]
30	REEs	MPANI@GO	MSPE	ICP-MS	Water and tea leaves	0.00004–0.00149	7.7–16.3	[157]
31	Pb	Phen@GO	D-μSPE	ICP-OES	Water and fish	0.0046	548	[158]
32	Cd	MGO	MDSPE	FAAS	Water, tobacco, and vegetables	0.12	33.7	[159]
33	Cr(VI)	MGO-PANI	MDSPE	GFAAS	Water	0.005	–	[63]
34	Pb and Cd	MGO	MSPE	FAAS	Water and vegetables	0.38–0.40	59.88–172.41	[160]

Table 3 (continued)

No.	Analyte	Sorbent	Method	Analytical Instrument	Matrix	LOD (μg L^{-1})	Sorption Capacity (mg g^{-1})	Ref.
35	Cd	MGO	MSPE	ICP-OES	Food samples	–	24.39	[161]
36	Cu	MGO	MSPE	FAAS	Food samples	0.9	–	[162]
37	Co, Cu, Cd, Ni, and Pb	MGO	MSPE	ICP-MS	Urine and plasma	0.016–0.395	1.28–9.71	[163]
38	Ni	DMG-IL-MGO	MSPE	FAAS	Water, cacao, spinach, and tea	0.16	129.87	[164]
39	Hg	MGO	MSPE	FI-CV-AAS	Seafood	0.025	1	[62]
40	Hg	MGO-2PTSC	MSPE	ICP-OES	Water and food	0.0079	–	[165]
41	As	MGO	MSPE	ICP-MS	Water	0.0079–0.028	–	[166]
42	Cr	MGO	MSPE	FAAS	Water	1.4–4.5	9.6–16.4	[167]
43	Ni and Pb	MoS_2-rGO	SPE	FAAS	Water, human silva, and urine	0.21–0.71	294–322	[66]
44	Hg	rGO	SPE	ASV	Water	0.14	77	[65]
45	Zn	rGO	SPE	FAAS	Rock and vegetables	0.14	3.2	[64]
46	Cr (VI)	rGO-Silica	SPE	UV-Vis spectrophotometry	Water	0.4	–	[168]

Graphitic carbon nitride

Graphitic carbon nitride (g-C_3N_4) is a stable form of carbon nitride materials with 2D structure composed of tri-s-triazine units that are linked by amine groups. g-C_3N_4 has unique properties including wonderful catalytic activity, chemical stability, ease of surface modification, and outstanding thermal and optical properties [75]. Among diverse synthetic methods (such as solvothermal method, chemical vapor deposition (CVD), thermal decomposition, and solid-state reaction), thermal decomposition is the most applied one for preparation of g-C_3N_4. In this technique, some nitrogen-rich substances (e.g. urea, cyanimide, thiourea, and melamine) are used in the synthesis process [76–78]. Several factors such as the type of nitrogen-containing reagents, pH of the sample solution, and temperature can influence the structure of the produced g-C_3N_4 via thermal decomposition technique [75].

The presence of nitrogen-containing groups (including –NH_2, -NH, and = N-) in the structure of g-C_3N_4 make this sorbent a suitable candidate for the enrichment of metal ions. In addition, the delocalized electron system of g-C_3N_4 can interact with either organic or inorganic analytes [75]. On the other hand, the polar carbon-nitrogen bonds in the structure of g-C_3N_4 can decrease the aromaticity of this sorbent compared to graphene. Moreover, the hydrogen bonds that are responsible for the connection of linear graphitic carbon nitride molecules are weaker than the covalent bonds in the structure of graphene. Consequently, g-C_3N_4 has better dispersibility in a sample solution. The surface of g-C_3N_4 can be modified using several techniques like a soft/hard template, oxidation, and protonation to improve the adsorption efficiency and enhance the surface area of this sorbent [75].

Lately, Fahimirad et al. [79] reported the application of a composite of g-C_3N_4 with MNPs and ethylenediamine in magnetic D-μSPE of Cd(II) and Pb(II) ions with recoveries more than 99%. To produce g-C_3N_4, melamine was heated up to 520 °C for about 4 h. Next, appropriate quantities of magnetic $SnFe_2O_4$ particles and g-C_3N_4 were mixed and calcinated at 400 °C. After that, a solution of N-[3-(trimethoxysilyl) propyl] ethylenediamine (TPED) was added to the g-C_3N_4- $SnFe_2O_4$ in toluene at 110 °C in the presence of N_2 atmosphere. The nano composite was then characterized using several techniques such as SEM, EDX, and FT-IR to confirm the structure. It is worth mentioning that this nano composite was prepared from low-cost and non-toxic chemicals. The sorbent was applied in the extraction procedure and the influence of different parameters on the extraction efficiency was investigated by experimental design. According to the results the lower quantity of the prepared adsorbent and less amount of the elution solvent were used in the enrichment process that made this technique more environmentally friendly.

Conclusions and remarks

Typically, the analysis of metal ions is done using analytical instruments such as FAAS, GFAAS, ETAAS, and ICP with different detectors (e.g. ICP-OES, ICP-AES, and ICP-MS). However, not all these instruments can detect the trace amounts of toxic metals directly in complex samples. Consequently, the development of efficient pretreatment techniques for the isolation of these inorganic pollutants from their matrices is important prior to instrumental analysis. The aim of this review is to give an overview of several carbonaceous sorbents and cover the recent applications of these materials in sorptive-based pretreatment methods (like SPE, SPME, DSPE, MSPE, and D-μSPE) for the environmental, food, and bio analysis of these target contaminants.

Carbonaceous sorbents and their composites have several outstanding features including chemical and thermal stability, large sorption capacity, the possibility of functionalization, wonderful optical and electronic properties, and large surface area. These outstanding characteristics make carbonaceous materials potential candidates in sorptive-based extraction methods for the enrichment of toxic metal ions. Among different carbon-based sorbents, graphene and carbon nanotubes have found more applications in sorptive-based pretreatment techniques due to the ease of preparation and functionalization. Therefore, since 2010 a great number of research articles have been published about the applications of these two class of sorbents in pretreatment of metal ions.

Although the number, of research papers that have used CNFs, fullerenes, CNHs, g-C_3N_4, and GCB in sorptive-based pretreatment methods is lower than graphene-based materials and CNTs, these sorbents offer some advantages in the extraction process. As an example, the large dimensions of CNFs can prevent the aggregation of this sorbent in SPE procedure and enhance the extraction efficiency without further modification. In addition, CNFs can be produced in large quantities via electrospinning. Moreover, the presence of several nitrogen-containing groups and the delocalized electron system in the structure of g-C_3N_4 make this sorbent be attractive in the enrichment of both organics and inorganics from sample solution.

Finally, carbon-based adsorbents have many superiorities over the conventional sorbents; however, the possible drawbacks of these adsorbents should not be ignored. For example, it is still important to develop carbonaceous sorbents with higher selectivity for the extraction of metal ions prior to analytical detection. Therefore, new modification methods are still required to diversify the surface of these materials and consequently enhance the sorption capacity and selectivity of the sorbenst. In addition, carbonaceous sorbents may cause some environmental contamination; therefore, recovery of these materials from sample solution is of great concern. Furthermore, it is important to develop novel synthesis procedures in which more environmentally friendly reagents are used for the preparation of different carbonaceous materials to reduce the hazardous impacts of toxic chemicals on both humans and the environment and consequently follow the rules of green chemistry.

Compliance with ethical standards The author(s) declare that they have no competing interests.

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