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Nanomaterial and their applications in Environmental sample preparation techniques: A Review

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Abstract: In this paper the use of both carbon based and metallic nano particles in separation and extraction of environmental samples, method of synthesis and modification is reviewed. Their use in preparation procedures for sample clean-up and preconcentration of analytes is a topic of growing interest in analytical chemistry. The properties of nanomaterials have been extensively exploited in different separation and enrichment techniques (e.g., SPE, microextraction and filtration). Nanomaterials can be used in different formats as single particles, aggregates, or powders or dispersed in a matrix. The aim of this paper is to present the recent application of nanomaterials in sample preparation procedure for sample clean-up and preconcentration of the analytes, which allow simplification of the method and the possibility of treating small amounts of sample.

Keywords: Nanomaterials, Separation, Carbon, Heavy Metals, Pollutants

1. INTRODUCTION

The definition of nanomaterial is based on the prefix “nano,” which is from the Greek word meaning “dwarf.” The word nanomaterials is generally used when referring to materials with the size of 0.1–100 nm; however, it is also inherent that these materials should display different properties from bulk (or micrometric and larger) materials as a result of their size¹. Nanomaterials, with physical features less than 100 nm in one or more dimensions, have attracted great attention from scientists in recent years, mainly

due to their unique, attractive, thermal, mechanical, electronic and biological properties². Their high surface-to-volume ratio, the possibility of surface functionalization and favorable thermal features provide the flexibility needed in a broad range of analytical applications³⁻⁶. The nanosized structures may be in the form of particles, pores, wires or tubes. The physicochemical properties of nanomaterials can be controlled through structural design, incorporation of suitable components or modification of their surfaces.

The aim of this paper is to present the recent application of nanomaterials in sample preparation procedure for sample clean-up and preconcentration of the analytes, which allow simplification of the method and the possibility of treating small amounts of sample.

2. SYNTHESIS METHODS OF NANOMATERIALS

There is a wide variety of techniques for producing nanomaterials. Nanotechnology offers not only the opportunities for changing manufacturing process using less raw materials for separation and pollution prevention, but also ways for promoting zero waste production and less energy consumption. For this purpose, various synthesis strategies have been continuously developed for the production of nanomaterials.

To improve the pore size range, chemical composition, or thermal/ hydrothermal stability of nanomaterials, a number of robust methods have been applied. The synthesis methods include sol-gel⁷⁻⁸, coprecipitation⁹, thermal spraying¹⁰, chemical vapor deposition (CVD)¹¹, arc discharge¹², laser ablation¹², catalytic growth¹², and electrodeposition¹³. Arc discharge may produce CNT with high quality, but their quantities are low¹². While CVD may generate CNT in large scales, there are defects in the final products. Out of the various methods reported, sol-gel process is the most widely applied techniques to synthesize nanoadsorbent for water treatment purpose.

Nanomaterials may also be constructed using bottom-up techniques by arranging atom by atom or molecule by molecule into a nanostructure that has new properties, which vary, such as self-assembly monolayer on mesoporous supports (SAMMS) or zero valent iron¹⁴, formed by the reduction of ferric/ferrous salts with sodium borohydride. Due to its ability to synthesize nanomaterials at the size of an atom, the bottom-up technique is considered to be the most advanced manufacturing technology. Despite their different natures, both synthesis techniques can improve the manufacturing of cost-effective products by increasing their efficiency, reducing the need for solvents, and minimizing waste generation.

3. FORMATS AND MODIFICATIONS OF NANOMATERIALS

The functionalization of nanoparticle surface is one method for tuning the overall properties of particles to fit targeted applications¹⁵. The surface modification of nanoparticles by functional molecules/particles/polymers has different tasks to fulfil:

- Stabilize the nanoparticles in solution to control the growth of the embryonic particles and determine their shape during the growth process
- Provide functional groups at the surface for further derivatization
- Enhancement of the nanoparticle solubilisation in various solvents to extend their application capabilities

- Capping layers can modify the electronic, optical, spectroscopic and chemical properties of the particles, providing a plethora of controllable nanotools
- Modify the capability to assemble the particles in specific arrays or the ability to target desired chemical, physical, or biological environments.
- Improve the mechanical and chemical performance of the nanoparticle surface, e.g. protection against oxidation
- In some instances a reduction of their toxicity is achieved (e.g. cadmium based quantum dots)

4. NANOMATERIALS IN SEPARATIONS AND EXTRACTION TECHNIQUES

Nanoparticles can be used for purposes such as sample treatment, instrumental separation of analytes, or even detection. In combination with the large variety of nanoparticles available, this provides a wide range of potential applications. The nanoparticles most widely used in analytical sciences at present include (a) silica nanoparticles, (b) carbon nanoparticles (mainly fullerenes, graphene and carbon nanotubes) and (c) metallic nanoparticles.

Nanoparticles have two key properties that make them particularly attractive sorbents. On a mass basis, they have much larger surface area than bulk particles. Nanoparticles can also be functionalized with various chemical groups to increase their affinity towards target compounds. It has been found that the unique properties of nanoparticles enable their development as high capacity and selective sorbents for metal ions and pollutants. Due to these reasons, now nanoparticles are designed and synthesized to act as either separation or reaction media for pollutants or scaffolds and delivery vehicles for bioactive compounds, thus providing unprecedented opportunities to develop more efficient and cost effective water purification processes and systems. Consequently, nanometre-sized material can selectively adsorb metal ions and have a very high adsorption capacity¹⁶⁻¹⁸.

Nanoparticles are used for the preconcentration and separation of pollutants from environmental sources. Investigation of the surface chemistry of highly dispersed metal oxides, e.g. TiO₂, Al₂O₃, ZrO₂, CeO₂ and MnO nanoparticles¹⁶⁻¹⁸, indicates that these materials have very high adsorption capacity and give promising results when they are used for trace metal analytes of different types of sample. Carbon nanotubes have been widely used as sorbents for solid-phase extraction. Ferric hydroxide is used to scavenge a variety of heavy metal contaminants. Nanoparticles have also been used in liquid chromatography e.g. by inserting them into a monolith column of vinylbenzyl chloride–ethylene dimethacrylate polymer.

4.1. Carbon Based Nanomaterials: Carbon-based nanomaterials, the important parts of these materials, have fascinated the scientific community since their discovery. In recent years, a large number of carbon-based nanoparticles have been investigated as sorbent material in sample preparation, including fullerenes, carbon nanotubes, graphene and carbon nanofibers as well as their functionalized forms. The characteristic structures of carbon-based nanomaterials allow them to interact with organic molecules via non-covalent forces, such as hydrogen bonding, π – π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions. These interactions and their hollow or layered, nanosized structures make them good candidates for use as adsorbents¹⁹.

Even though there are different formats of carbon based nanomaterials as described above, in this paper particular attention has been paid to carbon nanotubes and graphene because, recent applications mainly focus on the use of graphene and nanotubes (CNT)²⁰. In both cases, the basic structure is composed of a

layer of sp^2 -bonded carbon atoms, where each atom is connected to three other carbon atoms in the x - y plane and by a weakly delocalized π -electron cloud along the z -axis. This configuration, which resembles that of graphene, is responsible for the good electrical conductivity, the capability to form charge transfer complexes when in contact with electron donor groups²⁰ and the π -plasmon resonance observed in some of these particles²¹. Furthermore, this configuration is also responsible for the development of strong van der Waals' forces that significantly hamper the dispersion and solubility of carbon-based nanoparticles. To overcome these limitations different pretreatment methods have been proposed²²⁻²⁴, though the addition of polar groups (oxygen-, hydroxyl-, polyvinylpyrrolidone, and phenyl-)²⁵ and surface defects typically affect the stability²⁶ as well as the mechanical, magnetic, optical, and electrical properties²⁷.

4.1.1. Carbon Nanotubes: Carbon nanotubes (CNTs), discovered in 1991 by Iijima²⁸ have diameters from fractions to tens of nanometers and lengths up to several micrometers. CNTs can be considered as a graphene sheet in the shape of a cylinder capped by fullerene-like structures. Single-walled (SWCNTs) and multi-walled (MWCNTs) nanotubes are formed by seamless roll up of single and multi-layers of graphene lamella respectively. Their reported surface areas range from 150 to 1500 $m^2 g^{-1}$, which is a basis for serving as good sorbents²⁹. Furthermore, CNTs can be easily covalently or non-covalently functionalized with different organic molecules to provide a more selective interaction with analytes. Until now, CNTs have been the most used carbon-based nanomaterials in sample preparation, and hundreds of research articles and tens of critical review papers are available in this field^{30,31}.

The research group of Jiang first packed multi-walled carbon nanotubes into commercial SPE cartridge or disk for solid-phase extraction of organic pollutants from aqueous samples³². Since then, different types of CNTs, including non-functionalized or modified MWCNTs, and SWCNTs, were used as packing materials for preconcentration of phenolic compounds, pesticides, pharmaceuticals, inorganic ions and organometallic compounds in food, in environmental samples, or in biofluids, which were summarized in the review papers^{33, 34}. The excellent features of CNTs make them ideal sorbents in different micro-concentrators or micro-sorbent traps, which were reviewed by Hussain and Mitra²⁹.

The CNTs-SPME fibers were prepared through several procedures including sol-gel technology (the most widely used one), chemical bonding, and electrochemical polymerization. The fiber materials used in CNTs-SPME can be fused silica, hollow fiber, stainless steel, gold or platinum wire to acquire special properties^{29,33,34}. After oxidation under extreme conditions, CNTs possess hydroxyl, carboxyl and carbonyl groups on their surface and show exceptional adsorption efficiency for metal removal when the solution pH is higher than the isoelectric point of the oxidized CNTs.

Oxidized CNTs can be used as extraction materials for metallic compounds previous to their analytical determination. Oxidized CNTs can be grafted with functional groups (e.g., amines, esters, alkyl chains and polymers) via creation of amide bonds and radical addition with aryl-diazonium salts to efficiently or/and selectively pre-concentrate trace metal ions as described in the review paper of Sitko et al.³⁵. CNTs could also be used in a disk format, which possesses a larger surface area than the cartridge, resulting in good mass transfer and fast flow rate. To enhance the sorption capacity of the disks, double or even triple disks were used together³⁶.

Table 1: Recent applications of CNTs as SPME sorbents.

| Analyte | Matrix | CNTs type and characteristics | Substrate | Separation technique | Recovery (%) | LOD | Reference |
|--|-------------------------------------|---|----------------------|----------------------|--------------|-----------------------------------|-----------|
| 8 Volatile organic compounds (VOCs), 4 phenols, 5 PAHs | Deionized water | OH-MWCNTs, COOH-MWCNTs: o.d.: – | Stainless steel wire | GC-MS | - | - | 43 |
| 5 Polar aromatic compounds (PACs) | Pond water | Nafion/MWCNTs: o.d.: <5 nm | Stainless steel wire | GC-FID | 83–106 | 0.03–0.57 $\mu\text{g L}^{-1}$ | 44 |
| 7 Polybrominated diphenyl ethers (PBDEs) | Reservoir and waste water | OH-terminated silicone oil (TSO)-SWCNTs: o.d.: <2 nm | Fused silica fiber | GC-ECD | 74–109 | 0.08–0.8 ng L^{-1} | 45 |
| 3 Inorganic ions | rice | o-MWCNTs: o.d.: 10–40 nm | HF | DPASV | - | 0.0073–0.025 $\mu\text{g L}^{-1}$ | 46 |
| 6 Multi-class pesticides | Human hair and water | COOH-MWCNTs, NH ₂ -MWCNTs; o.d.: 10–15 nm | HF | HPLC-DAD | 79–94 | 0.003–0.095 $\mu\text{g L}^{-1}$ | 47 |
| 13 Multi-class pesticides | Green, oolong, white and flower tea | SWCNTs: o.d.: <2 μm | Fused silica fiber | GC-MS | 75–118 | 27–230 ng L^{-1} | 48 |
| 3 Triazines | River and wastewater and milk | MIP-MWCNTs | - | HPLC-UV | 59–110 | 0.08–0.38 $\mu\text{g L}^{-1}$ | 49 |
| 6 Phenols | Sea and tap water | COOH-SWCNTs: o.d.: – | Pt wire | HPLC-UV | 88–102 | 0.9–3.8 $\mu\text{g L}^{-1}$ | 50 |

A comparison study showed that the double-disk system (comprising two stacked disks with 60 mg of CNTs) exhibited extraction capability comparable to those of a commercial C18 disk with 500 mg sorbent for non-polar or moderately-polar compounds. Moreover, the two-disk system was more powerful than the commercial C18 disk for extracting polar analytes. The triple-layered CNT-disk system showed good extraction efficiency when the sample volume was up to 3mL.

Asensio-Ramos *et al.*³⁷ proposed the use of CNTs in the dSPE for trapping nine pesticides, which were later eluted using dichloromethane. This approach achieved a 100-fold enhancement of the sensitivity compared with direct determination. Similar methodology has been used for fast microextraction of phthalate-acid esters from beverages, environmental water and perfume samples³⁸.

Liu *et al.*³⁹ reported a chemical-bonding method for fabricating MWCNT/fused-silica fiber based on the surface modification of both materials. Briefly, MWCNTs were oxidized by mixed acids ($\text{H}_2\text{SO}_4 + \text{HNO}_3$) to create $-\text{COOH}$ groups. The silica fibers were firstly hydroxylated by NaOH solution in order to break the Si-O-Si bond to form Si-OH groups, which were then transformed to $-\text{NH}_2$ groups by reacting with 3-aminopropyl triethoxysilane. MWCNT/SPME fibers were formed in reaction between $-\text{COOH}$ and $-\text{NH}_2$ groups upon heat treatment. The covalent bonding gave high stability in acid, alkali, and organic solvents and at high temperature. The fiber was evaluated by extracting seven phenols from waters by direct immersion. By means of electrostatic absorption onto ionized silanol groups, a fused-silica rod was coated with polymeric NPs functionalized with quaternary ammonium groups and applied to anion analysis in real water samples⁴⁰. Desorption of the target analytes was performed by passing a 30 mM KOH eluent for 1 min over the loaded fiber.

Carbon nanotubes have also been utilized as sorbents for heavy metal ions. Early work by Li *et al.* demonstrated higher sorbent capacity of oxidized CNTs (compared to pristine CNTs) for various metal ions. The same researchers also reported that sorption capacities were 97.08 mg g^{-1} , 24.49 mg g^{-1} and 10.86 mg g^{-1} for Pb^{2+} , Cu^{2+} and Cd^{2+} respectively at room temperature, pH 5.0 and metal ion equilibrium concentration of 10 mg/l ⁴¹. More importantly, these MWNTs had larger sorption capacities than activated carbon and granular activated carbon by a factor of 3–4 times⁴¹. The sorption of heavy metal ions on CNTs appear to be due to a combination of electrostatic interactions, physical adsorption, precipitation and complexation reactions between the metal ions and the surface functional groups. Of all these interactions, complexation reactions appear to be dominant⁴².

4.1.2. Graphene: Since the first experimental evidence of the electronic properties of graphene in 2004, recent years have witnessed many breakthroughs in research on it^{51,52}. Graphene, which is considered the basic building block of all graphitic forms (including carbon nanotubes (CNTs), graphite and fullerene), possesses a single layer of carbon atoms in a closely packed honeycomb two-dimensional lattice. Graphene has a large specific surface area (theoretical value $2630 \text{ m}^2 \text{ g}^{-1}$)⁵³ and both sides of its planar sheets are available for molecule adsorption. Furthermore, the large delocalized π -electron system of graphene can form strong π stacking interaction with the benzene ring, which might make graphene a good choice for the extraction of benzenoid form compounds. Finally, graphene can be easily modified with functional groups, especially via graphene oxide.

Organic compounds can be adsorbed on nanoparticles (NPs) or nanostructured materials via non-covalent interaction including electrostatic interaction, hydrogen bonds, π - π stacking, dative bonds, and the hydrophobic effect⁵⁴. In the case of graphene, the very large delocalized π -electron system plays the

dominant role in formation of strong π - π stacking interaction with the aromatic rings of several organic compounds. Cation- π bonding can also be responsible for adsorption of metal ions^{55,56}.

4.1.3. Graphene in Magnetic Solid-Phase Extraction: Graphene can be modified with magnetic particles as magnetic solid-phase extraction (MSPE). In an MSPE process, short equilibrium time is required due to a fast mass transfer and the analyte-loaded sorbent can be easily separated via an external magnetic field⁵⁷.

The group of Wang synthesized magnetic graphene nanoparticles by in situ chemical co-precipitation of Fe^{2+} and Fe^{3+} in an alkaline solution in the presence of graphene and applied them in extracting a series of pollutants, such as phthalate esters⁵⁸, triazine herbicides⁵⁹, carbamate pesticides⁶⁰, triazole fungicides⁶¹, and neonicotinoid insecticides⁶² from liquid samples with enrichment factors from 247 to 5824. The Fe_3O_4 nanoparticles were well distributed on graphene sheets and this material, with specific surface area of $225 \text{ m}^2 \text{ g}^{-1}$, can be reused more than 10 times without a significant decrease in the extraction capability. The activated graphene, treated by HNO_3 , could easily combine with Fe_3O_4 spheres via a simple hydrothermal reaction with polyethylene glycol as the capping agent and trisodium citrate as a modification⁶³.

In order to protect Fe_3O_4 spheres from corrosion, oxidation and agglomeration, the particles were synthesized using a solvothermal method, followed by coating with silica through a sol-gel process to obtain $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ microspheres. Luo et al.⁶⁴ immobilized graphene sheets onto silica-coated magnetic microspheres by simple adsorption and used as an extraction media for the enrichment of trace amount of six sulfonamide antibiotics in environmental water samples. Liu et al.⁶⁵ further functionalized $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ microspheres with 3-aminopropyltriethoxysilane (APTES) to make the particles positively charged. Graphene oxide was assembled on the amino-functional silica-coated Fe_3O_4 spheres through electrostatic interactions. Finally, the graphene oxide sheets on the particle surface were reduced to graphene with hydrazine. The enrichment process was facile and quick, and there was no deterioration in analytical performance during the seven successive extractions for protein enrichment.

4.1.4. Graphene in Solid-Phase Extraction: Solid-phase extraction (SPE) is a popular sample preparation technique because of its simplicity, rapidity, minimal cost, low consumption of reagents, and ability to combine with different detection techniques whether in on-line or off-line mode^{66,67}. The sorbent material used, which is the core of SPE, determines the selectivity and efficiency of the method. Graphene was used as SPE sorbents by packing into a commercial cartridge to extract chlorophenols and heavy metals (Pb or Cr with different chelating reagents) in water samples^{68,69}, glutathione in human plasma and neurotransmitters from rat brain^{70,71}. Its performance was evaluated by comparing with several commonly used reversed-phase sorbent materials, including C18 silica, graphitic carbon, CNTs under same or optimum conditions. Graphene yielded the best recoveries of these sorbent materials and it surpassed CNTs by having both sides of its planar sheet and remaining hydrophilic groups. Furthermore, it can be reused for up to 50 adsorption-elution cycles with acceptable recoveries for the chlorophenols' and heavy metal preconcentration.

4.1.5. Graphene in Solid-Phase Microextraction: The solid-phase microextraction (SPME) technique is a solvent-free and miniaturized microextraction technique which integrates sampling, extraction, preconcentration and sample introduction in a single step⁷². It is based on the distribution equilibrium of analytes between the matrix and a fiber coated with a stationary phase, so the fiber coating material is critical in improving the SPME performance. Graphene was immobilized on the SPME fiber by different

non-covalent or covalent methods, most of which exhibited better extraction efficiency, higher mechanical and thermal stability, and longer life span than commercial materials in SPME. The group of Chen first prepared graphene coated SPME fiber by repeatedly immersing a clean stainless steel wire into graphene suspension and drying it in air to obtain 6–8 μm coating. Its extraction efficiency is approximately 1.5-fold higher than commercial 100 μm polydimethylsiloxane (PDMS) or 65 μm PDMS/divinylbenzene (PDMS/DVB) coating fibers. No obvious extraction efficiency change after 250 extractions, thermal or different solvent treatments were observed⁷³. The group of Wang used similar methods to prepare graphene-coated SPME fiber for determination of carbamate pesticides and triazine herbicides in water samples⁷⁴

Table 2: Some applications of graphene in sample preparation.

| Analyte | Matrix | Sorbent type | Sample preparation | Technique | Recovery (%) | LOD | Reference No |
|--------------------------------|--|----------------------|--------------------|-----------|--------------|---------------------------------|--------------|
| Chlorophenols | Tap and river water | graphene | SPE | HPLC-DAD | 77.2–116.6 | 0.1–0.4 ng mL ⁻¹ | 75 |
| Cr (III) | Water (tap, sea and river) | graphene | SPE | FAAS | 95.7–101.2 | 0.5 $\mu\text{g L}^{-1}$ | 76 |
| Pb | Water (tap, sea and river) and vegetable | graphene | SPE | FAAS | 95.3–100.4 | 0.61 $\mu\text{g L}^{-1}$ | 77 |
| Triazine herbicides | Water (reservoir, river and lake) | magnetic graphene | MSPE | HPLC-DAD | 89.0–96.2 | 0.025–0.040 ng mL ⁻¹ | 78 |
| Carbamate pesticides | Water (reservoir, river and pool) | magnetic graphene | MSPE | HPLC-DAD | 87.0–97.3 | 0.02–0.04 ng mL ⁻¹ | 79 |
| Triazole fungicides | Water (reservoir, river and sea) | magnetic graphene | MSPE | HPLC-UV | 86.0–102.0 | 0.005–0.01 ng mL ⁻¹ | 80 |
| Organochlorine pesticides | Water (river) | graphene oxide | HS-SPME | GC-ECD | 80.1–101.1 | 0.16–0.93 ng L ⁻¹ | 81 |
| Phenols | Pond water | polypyrrole/graphene | SPME | GC-MS | 4.1–103.9 | 0.34–3.4 $\mu\text{g L}^{-1}$ | 82 |
| Polybrominated diphenyl ethers | Canal water | graphene | SPME | GC-MS | 74.8–81.9 | 0.2–5.3 ng L ⁻¹ | 83 |

4.2. Metallic Nanomaterials: There are three key issues that often make sample treatment prior to analysis necessary⁸⁴:

- the physical state of the sample is incompatible with the features of the analytical method (e.g., the method requires a liquid sample but it is in a solid state);
- the sample presents interfering matrix components that may give either a false positive or negative reading in the measurement; and
- the analytes in sample are at too low a concentration to be detected by the analytical instrument and a preconcentration step is required. The use of MNPs in the sample treatment, in general, helps to simplify the two last cases.

Thus, MNPs, according to their participation and role in the sample treatment step, can be classified in the following groups:

- ❖ MNPs acting as sorbent agents. In this case there is a direct interaction between the analyte and the NPs.
- ❖ MNPs acting as an inert support. In this case the use of these NPs help to simplify the analytical procedure, and these NPs are functionalized with organic or inorganic groups used for the adsorption of target analytes.
- ❖ MNPs acting as enhancing agent of signal detection, as for example the use of gold NPs as active substrates for Surface Enhanced Raman Scattering (SERS).

Magnetic nanomaterials are particularly useful for extracting and enriching a large volume of target analytes because they provide high surface-to-volume ratio, easy surface modification, and strong magnetism. The extraction of environmental pollutants with magnetic nanomaterials is generally based on hydrophobic interaction, electrostatic attraction, and/or covalent bonding formation. Environmental pollutants adsorbed on the surface of nanomaterials are released by exchanging ligands, adjusting pH, or adding organic solvent. The liberated environmental pollutants are commonly detected by gas chromatography, high performance liquid chromatography, and inductively coupled plasma-optical emission spectrometry.

4.2.1. Heavy Metal Ions: Monitoring the level of heavy metal ions in an aquatic ecosystem has received significant attention over many years because they are severe environmental pollutants and have adverse effects on human health. For example, Pb^{2+} is a potential neurotoxin that can cause chronic inflammation of the kidney and heart, inhibit brain development, and decrease nerve conduction velocity. Moreover, highly toxic Hg^{2+} can damage the brain, heart, kidney, stomach, and intestines. The maximum levels of Hg, Cd, As, Pb, Cr, and Cu ions in drinking water permitted by the United States Environmental Protection Agency (U.S. EPA) are 2, 5, 10, 15, 100, and 1300 mg L^{-1} , respectively⁸⁵. The current methods for the analysis of heavy metal ions are based on the use of sensitive element-specific detectors, such as flame atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and ICP-optical emission spectrometry (ICP-OES).

Suleiman et al. modified silicacoated Fe_3O_4 NPs with bismuthiol for extracting Cr^{3+} , Cu^{2+} , and Pb^{2+} from environmental samples and determined the extracted metal ions by ICP-OES⁸⁶. Bismuthiol containing thiol and amine groups possesses strong affinity for Cr^{3+} , Cu^{2+} , and Pb^{2+} in the pH range of 3–8. The

extraction of 100 mL sample volume with bismuthiol-coated magnetic NPs resulted in approximately 100-fold improvement in sensitivity.

Huang and Hu synthesized silica-coated Fe_3O_4 NPs and modified them with 3-mercaptopropyltrimethoxysilane (MPTMS)⁸⁴. These kinds of NPs contain thiol groups so that selective extraction of Cd^{2+} , Cu^{2+} , Hg^{2+} , and Pb^{2+} is achieved through the formation of the metal ion–thiol complex. The adsorbed metal ions on the NP surface were liberated upon the addition of a solution containing 1M HCl and 2% thiourea. ICP-MS was used to analyze the extracted metal ions. Under the optimal extraction conditions (pH, sample volume, and eluent), the limits of detection (LODs) for Cd^{2+} , Cu^{2+} , Hg^{2+} , and Pb^{2+} were as low as 24, 92, 107, and 56 pg/L.

4.2.2. Pesticides and Phenolic Compounds: Modern agricultural production in many countries relies heavily on the use of pesticides, and thus they are present in soil, ground and surface water, and food. Some pesticides can cause adverse effects to human health. According to the European Union Directive on Water Quality, the maximum permissible concentration of each and total pesticides in drinking water are 0.1 and 0.5 mg L^{-1} , respectively⁸⁷.

Song et al. prepared superparamagnetic Fe_3O_4 NPs for extracting triazine pesticides from lake water⁸⁸. When Fe_3O_4 NPs were added to 400 mL sample, the capture of triazine pesticides was completed within 10 min through electrostatic attraction. After extraction and collection, 10 M HCl was added to dissolve Fe_3O_4 NPs. The obtained solution was neutralized with NaOH and then detected by HPLC-MS. The combination of Fe_3O_4 NPs and HPLC-MS provided low LOD (0.01–0.03 ng mL^{-1}) and large linear range (0.03–50 ng mL^{-1}). Shen et al. described the use of C18-functionalized Fe_3O_4 NPs for cleanup and enrichment of 14 kinds of organophosphorous pesticides⁸⁹. The extracted organophosphorous pesticides were determined by GC with a nitrogen/phosphorus detector.

Phenolic compounds are commonly used in several industrial processes to manufacture chemicals such as pesticides, explosives, drugs, and dyes. Because phenolic compounds are potentially carcinogenic, their maximum permitted level in drinking water by the U.S. EPA is 0.5 mg L^{-1} . HPLC combined with UV, fluorescence, electrochemical, or MS detection has been developed for the determination of phenolic compounds. A preconcentration step is prerequisite for the analysis of phenolic compounds because their concentration is quite low in environmental water samples.

Zhao et al. prepared cetyltrimethylammonium bromide (CTAB)-coated Fe_3O_4 NPs for the preconcentration of bisphenol A, 4-tert-octylphenol and 4-n-nonylphenol in the presence of CTAB⁹⁰⁻⁹¹. CTAB molecules were self-assembled on the surface of Fe_3O_4 NPs through electrostatic interaction between the head group of CTAB and the oppositely charged group on the Fe_3O_4 NPs. When more CTAB molecules were present in the solution, the hydrophobic interaction between the hydrophobic tails of CTAB led to the formation of admicelles. Under this condition, the mixed hemimicelles consisting of hydrophobic hemimicelles and ionic admicelles were formed on the surface of Fe_3O_4 NPs. Thus, the adsorption of analytes could be driven by both hydrophobic interaction and electrostatic attraction. In the mixed hemimicelle region, the extraction efficiency remarkably increased with an increase in CTAB concentration.

CONCLUSION

The use of nanomaterials in preparation procedures for sample clean-up and preconcentration of analytes is a topic of growing interest in analytical chemistry. The properties of nanomaterials have been extensively exploited in different separation and enrichment techniques (e.g., SPE, microextraction and filtration). Nanomaterials can be used as single particles, aggregates, or powders or dispersed in a matrix.

Owing to their special properties, carbon-based nanomaterials have found a wide range of applications in different sample preparation technologies: they can be used as sorbent agents, such as SPE or on-line SPE, by direct interaction between the analyte and the nanoparticles; they can be immobilized on fibers as SPME; they can have special magnetic properties, so the use of a magnetic field can help simplify the analytical procedure. Furthermore, sample preparation technologies based on these carbon nanomaterials have more advantages than conventional materials. For example, the SPME fibers, coating with graphene, CNTs, demonstrated superior extraction efficiencies, which were several times higher than a commercially available SPME fiber. These SPME fibers showed the improved thermal and chemical stability, and the coatings exhibited prolonged fiber lifetimes. There are different types of nanomaterials used for removal of environmental pollutants. CNTs present a higher adsorption capacity toward organic pollutants and metal ions than commonly used activated carbon, and the analytes retained on this solid phase can be easily desorbed. Wider practical applications of carbon nanotubes may be hampered by their relatively high unit cost. Moreover, metallic nanoparticles have given promising results for the removal of environmental pollutants. The studies mentioned in this review paper demonstrate that Fe₃O₄ NPs are an appealing alternative for the extraction and enrichment of environmental pollutants because of their high surface-to-volume ratio, ease of modification, and strong magnetism.

REFERENCES

1. C.N.R. Rao, A. Muller, A.K. Cheetham, the Chemistry of Nanomaterials (WILEY-VCH Verlag GmbH: Weinheim), 2004.
2. M. Liang, L.H. Guo, *J. Nanosci. Nanotechnol.*, 2009, **92**, 283.
3. M. Valca ´rcel, S. Ca ´rdenas, B.M. Simonet, Y. Molina-Martinez, R. Lucena, *Trends Anal. Chem.*, 2008, **79**, 34.
4. A.S. De Dios, M.E. Diaz-Garcia, *Anal. Chim. Acta*, 2010, **666**, 1.
5. K. Scida, P.W. Stege, G. Haby, G.A. Messina, C.D. Garcia, *Anal. Chim. Acta*, 2011, **69**, 16.
6. F.P. Zamborini, L. Bao, R. Dasari, *Anal. Chem.*, 2012, **84**, 541.
7. A. Kukovecz, Z. Balogi, Z. K ´onya, M. Toba, P. Lentz, S.I. Niwa, F. Mizukami, A. Moln ´ar, J.B. Nagy
8. I. Kiricsi, *Appl. Catal.*, 2002, 228, 83.
9. R. Kornak, D. Miznansky, K. Haimann, W. Tylus, K. Maruszewski, *Mater. Sci.*, 2005, **23**, 87.
10. X. Wei, R.C. Viadero, *Coll. Surf. A: Physicochem. Eng. Aspects*, 2007, 294, 280.

11. S. Giri, S. Samanta, S. Maji, S. Ganguli, A. Bhaumik, *J. Magnetism and Magnetic Mater.*, 2005, **285**, 296.
12. J.A. Brant, H. Lecoanet, M.R. Wiesner, *J. Nanopart. Res.*, 2005, **7**, 545.
13. Y.H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu, B. Wei, *Carbon*, 2003, **41**, 2787.
14. T.A. Kurniawan, Removal of Recalcitrant Contaminants from Stabilized Landfill Leachate by a Combination of Advanced Oxidation Processes and Granular Activated Carbon Adsorption, Doctoral Dissertation, The Hong Kong Polytechnic University, Hong Kong SAR, 2008.
15. W.X. Zhang, *J. Nanoparticle Res.*, 2003, **5**, 323.
16. A. Simón de Dios, M.E. Díaz-García, *Analytica Chimica Acta*, 2010, **666**, 1
17. R. Alexandrette, F. Dumitrache, I. Morjan, I. Sandu, M. Savoju, I. Voicu, C. Fleaca, R. Piticesu, *Nanotechnology*, 2004, **15**, 537.
18. R. P. Das, S. Anand, *Indian. J. Phys A*, 2004, **78**, 165.
19. K. Okuyama, I. W. Lenggoro, *Chem. Eng. Sci.*, 2003, **58**, 537.
20. K. Scida, P.W. Stege, G. Haby, G.A. Messina, C.D. García, *Anal. Chim. Acta*, 2011, **691**, 6.
21. M. Valcarcel, S. Cardenas, B.M Simonet, Y. Moliner-Martinez, R. Lucena, *TrAC, Trends Anal Chem.* 2008, **27**, 34.
22. T.M. Barnes, J. Lagemaat, D. Levi, G. Rumbles, T.J. Coutts, C.L. Weeks, D.A. Britz, I. Levitsky, J. Peltola, P. Glatkowski, *Phys Rev B.*, 2007 **75**, 23541001.
23. V.N. Khabashesku, J.L. Margrave, E.V. Barrera, *Diamond Relat Mater.*, 2005, **14**, 859.
24. V.N. Popov, *Mater Sci Eng, R*, 2004, **43**, 61.
25. J. Zhao, X. Chen, J.R.H. Xie, *Anal Chim Acta.*, 2006, **568**, 161.
26. E. Nakamura, H. Isobe, *Accounts Chem Res.*, 2003, **36**, 807.
27. R. Jackson, B. Domercq, R. Jain, B. Kippelen, S. Graham, *Adv Funct Mater.*, 2008, **18**, 2548.
28. A. Qureshi, W.P. Kang, J.L. Davidson, Y. D. Gurbuz, *Relat Mater.*, 2009, **18**, 1401.
29. S. Iijima, *Nature*, 1991, **354**, 56.
30. C.M. Hussain, S. Mitra, *Anal. Bioanal. Chem.*, 2011, **399**, 75.
31. B. Pérez-López, A. Merkoc, *Microchim. Acta*, 2012, **179**, 1.
32. C. Herrero Latorre, J. Álvarez Méndez, J. Barciela García, S. García Martín, R.M. Peña Crecente, *Anal. Chim. Acta*, 2012, **749**, 16.
33. H.Y. Niu, Y.Q. Cai, Y.L. Shi, F.S. Wei, J.M. Liu, G.B. Jiang, *Anal. Bioanal. Chem.*, 2008, **392**, 927.

34. A.V. Herrera-Herrera, M.A. González-Curbelo, J. Hernández-Borges, M.Á. Rodríguez-Delgado, *Anal. Chim. Acta*, 2012, **734**, 1.
35. K. Pyrzynska, *Chemosphere*, 2011, **83**, 1407.
36. R. Sitko, B. Zawisza, E. Malicka, *Trac-Trends Anal. Chem.*, 2012, **37**, 22.
37. H. Niu, Y. Shi, Y. Cai, F. Wei, G. Jiang, *Microchim. Acta*, 2009, **164**, 431.
38. P. Zhao, L. Wang, J. Luo, J. Li, C. Pan, *J. Sep. Sci.*, 2012, **35**, 153.
39. Y.B. Luo, Q.W. Yu, B.F. Yuon, Y.Q. Feng, *Talanta*, 2012, **90**, 123.
40. H. Liu, J. Li, X. Liu, S. Jiang, *Talanta*, 2009, **78**, 929.
41. M. Kaykhahi, G.W. Dicoski, R. Smedley, J. Pawliszyn, P.R. Haddad, *J. Chromatogr., A*, 2010, **1217**, 3452.
42. Y.-H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu and B. Wei, *Carbon*, 2003, **41**, 2787.
43. M.U_gurlu, I. Kula, M. H. Karao_glu, Y. Arslan, *Environ. Prog. Sustainable Energy*, 2009, **28**, 547.
44. R. Jiang, F. Zhu, T. Luan, Y. Tong, H. Liu, G. Ouyang, J. Pawliszyn, *J. Chromatogr. A*, 2009, **1216**, 4641.
45. W. Chen, J. Zeng, J. Chen, X. Huang, Y. Jiang, Y. Wang, X. Chen, *J. Chromatogr. A*, 2009, **1216**, 9143.
46. W. Zhang, Y. Sun, C. Wu, J. Xing, J. Li, *Anal. Chem.*, 2009, **81**, 2912.
47. Z. Es'haghi, M. Khalili, A. Khazaeifar, G.H. Rounaghi, *Electrochim. Acta*, 2011, **56**, 3139.
48. M. Ebrahimi, Z. Es'ihaghi, F. Samadi, M.S. Hosseini, *J. Chromatogr. A*, 2011, **1218**, 8313.
49. F. Wu, W. Lu, J. Chen, W. Liu, L. Zhang, *Talanta*, 2010, **82**, 1038.
50. F. Tan, M. Deng, X. Liu, X. Zhao, X. Li, X. Quan, J. Chen, *J. Sep. Sci.*, 2011, **34**, 707.
51. Q. Li, X. Wang, D. Yuan, *J. Chromatogr. A*, 2009, **1216**, 1305.
52. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science*, 2004, **306**, 666.
53. K.S. Novoselov, V.I. Fal'ko, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim, *Nature*, 2012, **490**, 192.
54. Q. Liu, J. Shi, L. Zeng, T. Wang, Y. Cai, G. Jiang, *J. Chromatogr. A*, 2011, **1218**, 197
55. M. Valcarcel, S. Cardenas, B.M. Simonet, Y. Moliner-Martinez, R. Lucena, *Trends Anal. Chem.*, 2008, **27**, 34.
56. Y. Gao, Y. Li, L. Zhang, H. Huang, J. Hu, S.M. Shah, X. Su, *J. Colloid Interf. Sci.*, 2012, **368**, 540.

57. J.C. Ma, D.A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303.
58. L. Chen, T. Wang, J. Tong, *Trac-Trends Anal. Chem.*, 2011, **30**, 1095.
59. Q. Wu, M. Liu, X. Ma, W. Wang, C. Wang, X. Zang, Z. Wang, *Microchim. Acta*, 2012, **177**, 23.
60. G. Zhao, S. Song, C. Wang, Q. Wu, Z. Wang, *Anal. Chim. Acta*, 2011, **708**, 155.
61. Q. Wu, G. Zhao, C. Feng, C. Wang, Z. Wang, *J. Chromatogr. A*, 2011, **1218**, 7936.
62. W. Wang, X. Ma, Q. Wu, C. Wang, X. Zang, Z. Wang, *J. Sep. Sci.* 2012, **35**, 2266.
63. W. Wang, Y. Li, Q. Wu, C. Wang, X. Zang, Z. Wang, *Anal. Methods*, 2012, **4**, 766.
64. C. Shi, J. Meng, C. Deng, *Chem. Commun.*, 2012, **48**, 2418.
65. Y.-B. Luo, Z.-G. Shi, Q. Gao, Y.-Q. Feng, *J. Chromatogr. A*, 2011, **1218**, 1353.
66. Q. Liu, J. Shi, M. Cheng, G. Li, D. Cao, G. Jiang, *Chem. Commun.*, 2012, **48**, 1874.
67. J. Qu, H. Chen, C. Lu, Z. Wang, J.-M. Lin, *Analyst*, 2012, **137**, 1824.
68. X. Lin, H.-F. Li, X. He, Y. Hashi, J.-M. Lin, Z. Wang, *J. Sep. Sci.*, 2012, **35**, 2553.
69. Q. Chang, S. Song, Y. Wang, J. Li, J. Ma, *Anal. Methods*, 2012, **4**, 1110.
70. Y. Wang, S. Gao, X. Zang, J. Li, J. Ma, *Anal. Chim. Acta*, 2012, **716**, 112.
71. K.-J. Huang, Q.-S. Jing, C.-Y. Wei, Y.-Y. Wu, *Spectrochim. Acta A*, 2011, **79**, 1860.
72. K.-J. Huang, S. Yu, J. Li, Z.-W. Wu, C.-Y. Wei, *Microchim. Acta*, 2012, **176**, 327.
73. G. Huang, H.-F. Li, B.-T. Zhang, Y. Ma, J.-M. Lin, *Talanta*, 2012, **100**, 64.
74. J. Chen, J. Zou, J. Zeng, X. Song, J. Ji, Y. Wang, J. Ha, X. Chen, *Anal. Chim. Acta*, 2010, **678**, 44.
75. Q. Wu, C. Feng, G. Zhao, C. Wang, Z. Wang, *J. Sep. Sci.* 2012, **35**, 193.
76. Q. Liu, J. Shi, L. Zeng, T. Wang, Y. Cai, G. Jiang, *J. Chromatogr. A*, 2011, **1218**, 197.
77. Q. Chang, S. Song, Y. Wang, J. Li, J. Ma, *Anal. Methods*, 2012, **4**, 1110.
78. Y. Wang, S. Gao, X. Zang, J. Li, J. Ma, *Anal. Chim. Acta*, 2012, **716**, 112.
79. G. Zhao, S. Song, C. Wang, Q. Wu, Z. Wang, *Anal. Chim. Acta*, 2011, **708**, 155.
80. Q. Wu, G. Zhao, C. Feng, C. Wang, Z. Wang, *J. Chromatogr. A*, 2011, **1218**, 7936.
81. W. Wang, X. Ma, Q. Wu, C. Wang, X. Zang, Z. Wang, *J. Sep. Sci.*, 2012, **35**, 2266.
82. V.K. Ponnusamy, J.-F. Jen, *J. Chromatogr. A*, 2011, **1218**, 6861.
83. J. Zou, X. Song, J. Ji, W. Xu, J. Chen, Y. Jiang, Y. Wang, X. Chen, *J. Sep. Sci.*, 2011, **34**, 2765.
84. H. Zhang, H.K. Lee, *J. Chromatogr. A*, 2011, **1218**, 4509.

85. A. R'ios, M. Zougagh, M. Bouri, *Anal. Methods*, 2013, **5**, 4558.
86. C. Huang, B. Hu, *Spectrochim. Acta, Part B*, 2008, **63**, 437.
87. J. S. Suleiman, B. Hu, H. Peng and C. Huang, *Talanta*, 2009, **77**, 1579.
88. J.-H. Lin, Z.-H. Wu, W.-L. Tseng, *Anal. Methods*, 2010, **2**, 1874.
89. Y. Song, S. Zhao, P. Tchounwou and Y. M. Liu, *J. Chromatogr., A*, 2007, **1166**, 79.
90. H.-Y. Shen, Y. Zhu, X.-E. Wen, Y.-M. Zhuang, *Anal. Bioanal. Chem.*, 2007, **387**, 2227.
91. X. Zhao, Y. Shi, Y. Cai, S. Mou, *Environ. Sci. Technol.*, 2008, **42**, 1201.

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