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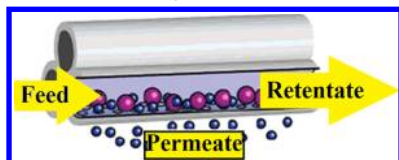
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Nanoadsorbents: Classification, Preparation, and Applications (with Emphasis on Aqueous Media)

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1. INTRODUCTION

In the past decade, nanoscale solid materials have become very important because of their special properties,[1,2] and the nanomaterials field has gained increasing attention from scientists and engineers.[3] A key reason for the change in the chemical and physical properties of small particles as their size decreases is the increased fraction of the "surface" atoms, which occurs under conditions (coordination number, symmetry of

the local environment, etc.) that are different from those of the bulk atoms. From the energy point of view, a decrease in the size of a particle results in an increase of the surface energy fraction.[4] Nanomaterials possess a series of unique physical and chemical properties. A very important one is that most of the atoms that have high chemical activity and adsorption capacity to many metal ions are on the surface of the nanomaterials.[2,5] The surface atoms are unsaturated and are thus subject to combination with other element ions by static electricity.[6] Therefore, nanomaterials can strongly adsorb many substances including trace metals[7] and polar organic compounds.[8]

Materials reduced to the nanoscale can suddenly show a variety of properties, compared to what they exhibit on a microscale, due to two effects:[9] (A) The first comprises the surface effects, which can be explained by (i) having more surface atoms compared to inner atoms, (ii) having more free energy surface available (this increased surface area and surface atoms results in the increase of surface energy associated with the particles), and (iii) the fact that increasing the surface area of a substance generally increases the rate of a chemical reaction. (B) The second comprises the volume effects, which are due to (i) a lower wavelength (higher frequency and higher energy), (ii) a blue shift of atoms for optical absorption spectra, (iii) superparamagnetism that occurs when the particle is smaller than the magnetic domain in a material, and (iv) the fact that, in a free electron model, average energy spacing increases as the number of atoms is reduced and this enhances the catalytic properties of nanoparticles.[10]

Auffan et al.[11] reviewed in detail the size-dependent properties of some inorganic nanoparticles (NPs) and concluded that there is a critical particle size of about 30 nm where particle properties change significantly.

Nanomaterials possess key physical characteristics which are dictated by the kind of nano-objects they contain. They are classified into compact materials and nanodispersions. The first type includes so-called "nanostructured" materials,[12] i.e., isotropic materials in their macroscopic composition, and consists of connecting nanometer-sized units that repeat structural elements.[13] Unlike nanostructured materials, nano-dispersions include a homogeneous medium (vacuum, gas, liquid, or solid) and nanosized inclusions dispersed in it and isolated from each other. The distance between the nano-objects in these dispersions can vary over broad limits from 10 nm to fractions of a nanometer. In the latter case, we are dealing with nanopowders where grains are separated by thin (often monatomic) layers of light atoms that prevent them from agglomeration.[4]

1.1. Classification of Nanomaterials as Nanoadsorbents

Nanomaterials are mainly divided into groups based on their role in adsorption applications which is dependent on their innate surface property and further external functionalization (Figure 1).

Nanoparticles include metallic nanoparticles (gold NPs), metallic oxide NPs (aluminum trioxide or titanium dioxide), nanostructured mixed oxides (nanostructured binary iron−titanium mixed oxide particles), and magnetic NPs (iron di- and trioxide). Carbonaceous nanomaterials (CNMs) are another important group based on sorbent properties that include carbon nanotubes (CNTs), carbon nanoparticles (CNPs), and carbon nanosheets (CNSs). In the same way, silicon nanomaterials (SiNMs) include silicon nanotubes (SiNTs), silicon nanoparticles (SiNPs), and silicon nanosheets
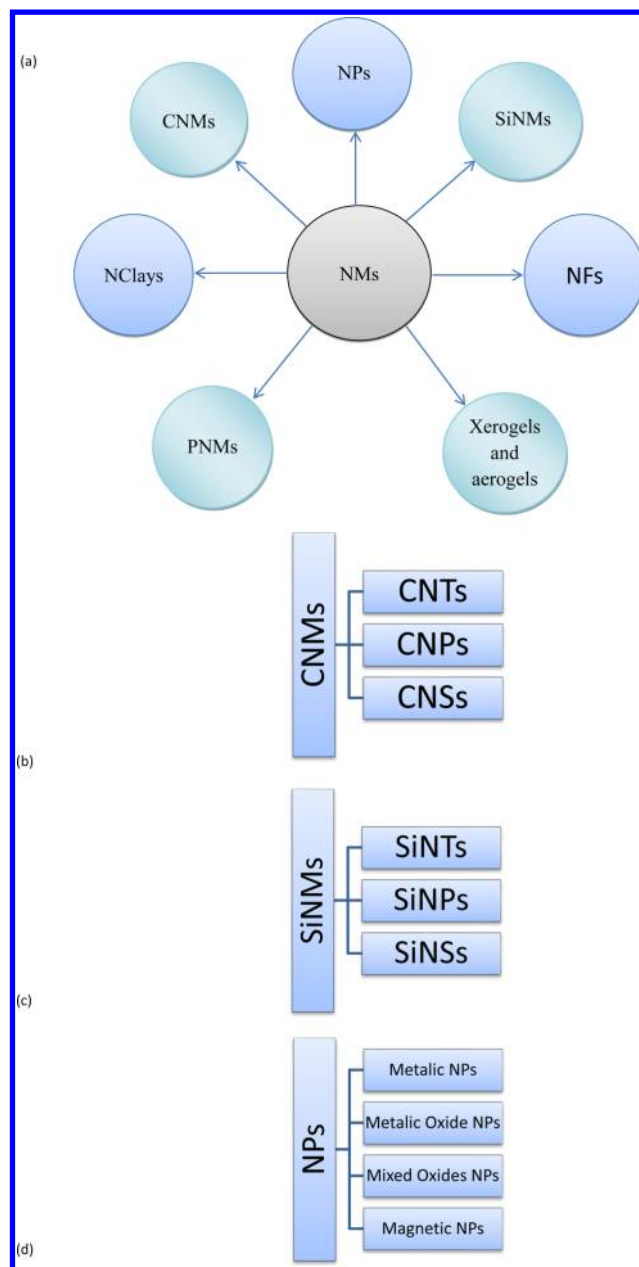
Figure 1. Classification of (a) nanomaterials, (b) carbon nanomaterials, (c) silicon nanomaterials, and (d) nanoparticles as adsorbents.

(SiNSs). Other nanomaterials for adsorption processes are nanofibers (NFs), nanoclays, polymer-based nanomaterials (PNMs), and xerogels and aerogels.

NPs with a size of approximately 1−100 nm have significant impact in many scientific fields, including chemistry, electronics, medicine, biology, and material sciences.[14−23] The physical, material, and chemical properties of NPs are directly related to their intrinsic compositions, apparent sizes, and extrinsic surface structures.[24−29] Thus, the design, synthesis, characterization, and applications of nanostructures are critical aspects for the emerging field of nanomaterials. The concept of nanoparticle-assisted sample separation and preconcentration plays important roles in many analytical methods.[30] The potential capability of NPs has been extensively studied in separation science for several years, and many advances have been achieved toward chromatographic and electrophoretic

systems for a couple of separation components or preconcentration media. NPs serve either as inner surface coating in permanent or dynamic mode, or as a pseudostationary phase added to the buffer and used in partial filling or continuous filling form.[31] A nanoparticle is a quasi-zero-dimensional (0 D) nano-object in which all characteristic linear dimensions are of the same order of magnitude (not more than 100 nm).[32] As a rule, NPs are shaped like spheroids. NPs with a clearly ordered arrangement of atoms (or ions) are called nanocrystallites. NPs with a clear-cut discontinuity of the system of electronic energy levels are often referred to as "quantum dots" or "artificial atoms" (most often, they have compositions of typical semiconductor materials).[33,34] The term "cluster", which had been widely used in the chemical literature in former years, is currently used to designate small nanoparticles with sizes less than 1 nm. Therefore, the term nanoclusters is wrong,[35] since all known clusters have nanometer dimensions.

Besides particle size, there are other parameters that control the properties of NPs.[36−38] The most important ones are (i) the surface chemistry (including surface functionalization and surface charge), (ii) the agglomeration state, shape, and fractal dimension, (iii) the chemical composition and crystal structure, and (iv) the solubility.

There are numerous review articles on the behavior of NPs in aqueous environments, e.g., by Baalousha et al.,[39] Lead and Wilkinson,[40,41] Nowack and Bucheli,[42] or Christian et al.[43] Concerning the environmental impact on the behavior of NPs, it is crucial to be aware that NPs might undergo significant alterations in the liquid phase.[44]

Recently, NPs have been used as sorbents due to their better intrinsic properties, such as chemical activity and fine grain size, as compared with the classic substances including normal scale titanium dioxide, alumina, etc.[2,45,46] NPs can be chemically modified by a reagent to obtain a new selective solid phase extractant for the preconcentration of metal ions.[47−49]

Although investigations of the surface chemistry of highly dispersed oxides, e.g., TiO_2, Al_2O_3, ZrO_2, SiO_2, and ZnO, indicated that these materials have very high adsorption capacity[50−54] and give promising results when used for trace-metal analysis of various types of water and solutions of high-purity alkali salts,[55−61] the separation of these particles from aqueous medium is difficult due to their very small dimension and high dispersion.[62] Often the retention efficiency depends on pH conditions, according to Vassileva et al.[63] The behavior is changed whether the pH is above or below the isoelectric point (IEP) of the oxide.[64] The versatility of these metal oxides for separating trace metals from a variety of water environments is illustrated in Table 1.[63,65−73]

1.2. Importance of Nanomaterials in the Preconcentration Process

Heavy metal ions are increasingly released into the environment, particularly as a result of industrialization, leading to serious pollution. Due to their important roles in our lives, the accurate determination of heavy metals at trace levels in environmental samples is one of the purposes of analytical chemists.[74−78] Some trace metals, such as cobalt, are essential to humans, but the daily requirement is only a few milligrams. However, if ingested at high levels, they can have harmful effects. Furthermore, the metal content in water, sediment, plants, and animals can also provide essential information on the levels of contamination in the environment.[79−81]

Table 1. Summary of Recent Applications of High-Surface Metal Oxides for the Separation of Trace Elements from Various Waters[a]

analyte	matrix	oxide	conc level	pH	flow rate	adsptn capacity	LOD	detection tech	ref
Cu, Hg, Au, Pd	lake water	mod Al_2O_3	6.6 4.03 0.62 0.29	3	1.5	10.4 16.3 15.3 17.4	6.6×10^{-5} 4.9×10^{-4} 4.6×10^{-4} 2.6×10^{-4}	ICP-MS	65
Cd, Cu, Pb, Zn, Fe	river water, wastewater	CeO_2	0.94–0.26 2.1–0.3 2.8–0.28 25.6–0.69 n.d.	≥7	3	13.27 13.31 13.33 n.d. n.d.	1×10^{-4} 2×10^{-4} 3×10^{-4} 1×10^{-4} 5.0×10^{-3}	ETAAS	66
Al, Bi, Cd, Co, Cr, Cu, Ga, In, Mn, Mo, Ni, Pb, Tl, V, Sb, Sn, Zn, Fe	river water, sea water	ZrO_2	1.06–60.8 for all (Fe ~56.1), ~14 for all sea water (Fe ~13.7)	8	3	4.97–7.89 range for all	3×10^{-5} to 9×10^{-3} (Fe 7.0×10^{-3}) for all	FI-ICP-AES	67
Bi, Cd, Co, Cr, Cu, Ge, In, Mn, Ni, Pb, Sb, Sn, Te, Tl, V, Zn, Fe	natural waters	TiO_2	1.3–7.3 range for all (Fe 9.57)	8	3	4.6–9.01 range for all (Fe n.d.)	1×10^{-2} to 3×10^{-2} range for all (Fe 4.0×10^{-2})	ETAAS	63
Cr, C, Mn, Ni	lake water	TiO_2	170–33 600 range for all	8	1	2–7.7 range for all	0.34–1.78 range for all	ICP-AES	68
Cr^{3+}, Cr^{6+}	rain water	TiO_2	0.03–0.42 range for all	8, 2	3	7.50	0.03, 0.024	ETAAS	69
Se(IV), Se(VI)	natural water	TiO_2	0.18–11.97	8	0.1	n.d.	0.06, 0.03	HPLC-ICP-MS	73

[a]conc level in $\mu g\ L^{-1}$; flow rate in mL min^{-1}; adsptn capacity in g kg^{-1}; LOD in $\mu g\ L^{-1}$; n.d. = not determined.

Sample pretreatment methods, such as separation and/or preconcentration prior to the instrumental detection, have developed rapidly due to the increasing need for accurate and precise measurements at extremely low levels of analytes in diverse matrices. Sample preparation processes, including separation and preconcentration, have a direct impact on accuracy, precision, and detection limits for many analytical methods. This process is also the determining step of the analytical method.[45] It is evident from the literature[82−85] that, besides separation of interfering matrix components and preconcentration of ultratrace levels of analytes, applied sample pretreatment schemes should offer a number of benefits such as high efficiency in terms of sample throughput or sampling frequency, reduced sample and reagent consumption and waste production, improved precision, low limits of quantification (LOQs), minimal risk of sample contamination, potential improvement of selectivity through kinetic discrimination under chemically nonequilibrated conditions, and automation.

Different techniques are used for the separation and preconcentration of metals in the solution. These include liquid−liquid extraction, precipitation, cation-exchange resins, cloud point extraction, and solid phase extraction.[86−92] However, disadvantages such as significant chemical additives, solvent losses, complex equipment, large secondary waste, prefiltration problems, and time-consuming procedures, limit the application of most of these techniques. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes.

Solid phase extraction (SPE) is a good tool to solve these problems. This technique has some advantages over other preconcentration procedures in view of (1) simple preparation of solid phase, (2) lower cost and less time-consuming, (3) easy use, (4) low consumption of reagents, (5) safety with respect to hazardous samples, (6) higher selectivity, (7) easy automation, (8) high preconcentration factor, (9) eco-friendly methods, (10) reusability of the adsorbent, and (11) more flexible to combine with other modern detection techniques in an online or off-line mode. However, the basic disadvantage of these solid sorbents is the lack of metal selectivity, which leads to other species interfering with the target metal ion(s). To overcome this problem, one can use intrinsic compositions, apparent sizes, and extrinsic surface structures that could be elicited by the use of particular materials. These lead to a number of factors that enhance the selectivity and sensitivity of the method, namely high surface area, active sorption sites, and chemical activity. However, modification of the adsorbents' outer surface is often necessary. Chemical or physical modification of the sorbent surface with some organic compounds, especially chelating ones, is normally used to load the surface with some donor atoms such as oxygen, nitrogen, sulfur, and phosphorus.[93,94] These donor atoms are capable of selective binding with certain metal ions.[95] Wang and Hansen[85] stated that, in order to prepare SPE packed columns, as one of the most frequently used sample pretreatment techniques, a number of factors influencing the performance of the column separation or preconcentration system should be taken into account. Some of the most important comprise the sorption (break-through) capacity of the sorbent material for both the analyte and the other constituents that might act as interferents, the extent of the interferent effect and the level of interferents, and the particle size of the adsorbent.

Hence, the role of solid phase adsorbents in sample pretreatment methods to attain sensitivity and precision is of great significance. To date, many adsorbents, including modified ZrO_2 and fullerene,[96] activated carbon,[97] XAD resins,[98,99] Chromosorb 101,[100] modified silica gel,[101,102] cellulose,[103] eggshell membrane,[104] and ion exchange resins,[105] have been employed in SPE. The research for new adsorbents is of importance in order to improve analytical parameters such as selectivity, affinity, and capacity in SPE techniques.[106] Compared with micrometer-sized particles used for SPE, nanometer-sized materials have been found to offer not only a significantly higher surface area-to-volume ratio that promises much greater extraction capacity and efficiency,[107,108] but also an easily modified surface functionality to improve the selectivity of SPE.[109] On this basis, the application of nanomaterials as the new category of adsorbents for trace metal and organic compounds analysis, like solid phase extraction, should be interpreted on the basis of their innate surface properties and further functionalization to deliver faster, easier, and safer procedures and to provide more accurate and precise data with reasonable quantification limits compared with conventional adsorbents like organic polymers, inorganic substrates, and chelating and ion-exchange resins.

Indeed, if sorption would be the key mechanism, the substantial increase in surface area of the nanoform would significantly increase its capacity in this respect. In order to improve the selectivity of the sorbent, the modification of the adsorbent is usually needed. The most often used procedure is to load a kind of specific chelate reagent by physical or chemical methods on the surface of this material. The former procedure is simple, but the loaded reagent is prone to leaking out from the sorbent, while the chemical-bonded material is more stable and can be used repeatedly.[110]

Researchers in science and engineering show an increased interest in the use of nanoparticles due to their unique physical and chemical properties. One area of particular interest focuses on environmental cleanup,[111−115] especially regarding public health and drinking water quality. Electronic waste (e-waste, i.e., waste generated from cell phones, computers, toys, and other electronics) has become the most rapidly growing waste stream in the industrialized world, growing 4% annually.[116] Considerable attention has been raised over the amount of e-waste that is improperly disposed of each year since it contains several metals which eventually may find their way into potential sources of drinking water. While naturally distributed levels of metals found in rocks and soils are usually not cause for concern, anthropogenic activities (e.g., industrial, agricultural, and military sources, and incorrect disposal of e-waste) often disperse metal pollution throughout the environment, which may pose human health risks at high levels.[117] Currently, the U.S. Environmental Protection Agency regulates at least 10 metals, such as Pb, Cd, and Cu, which are found in e-waste and other sources, as primary contaminants in drinking water. More unregulated metals like Ni and Zn, which are also e-waste contaminants, might be monitored in the future because of their comparable detrimental health effects.[118]

In order to be most effective, a sorbent material must be able to retain the contaminants it adsorbs without becoming exhausted. As metal ions are removed from water by adsorption, the concentration adsorbed on the sorbent becomes greater than the concentration in the water itself. If the sorbent releases these contaminants back into the solution, the process is called exhaustion, which must be avoided.
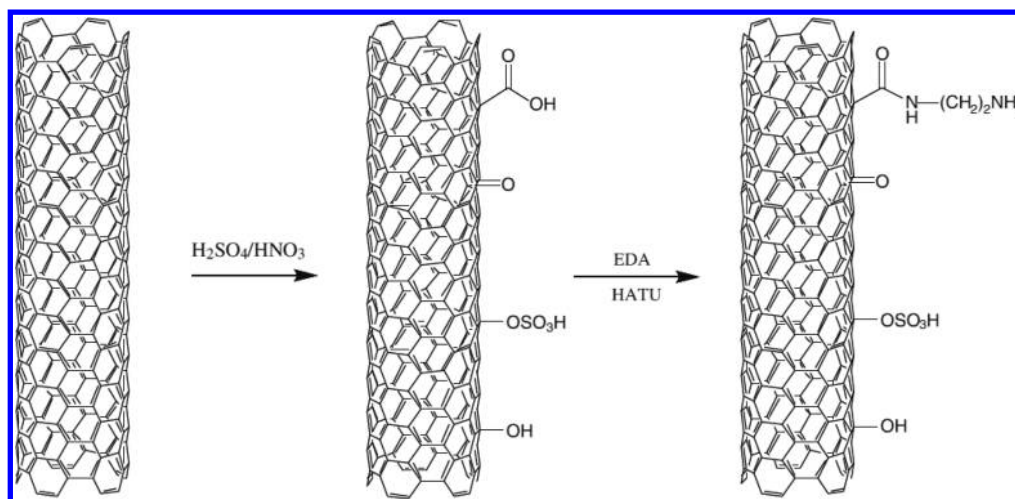
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Figure 2. Functionalization of CNT with ethylenediamine.[124] Reprinted from ref 124, with Permission from Elsevier. Copyright 2010.

Eventually, all sorbents will exhaust their adsorption capacity for the contaminants, so it is important to establish these limits when considering a sorbent for metal removal. However, few studies have been conducted on spent or exhausted nanoparticle sorbents in regards to their maximum limits for metal contaminant removal.[119]

The main objective of this paper is to review not only the charactristics, mechanisms, and behavior of nanomaterials in aqueous systems and sample solutions, but also the major preparation methods, either simple processes done in laboratories or complicated instrumental techniques, illustrated in different original papers or review articles. We will focus as well on the different applications of these nanomaterials, which have been used as adsorbents for environment, water, food, and other different samples in the past two decades.

2. MECHANISMS AND PROPERTIES OF NANOMATERIALS AS ADSORBENTS

The applications of the nanoadsorbents discussed in this review are extremely dependent upon on their innate surface properties, which result from being near the threshold of the nanometric scale, as well as on their external functionalization, which is construed sometimes as an inseparable route for the selectivity and sensitivity of the used preconcentration and separation method. Hence, a clear description of these two issues is of great importance.

2.1. Innate Surface Properties

The physical, material, and chemical properties of NPs are directly related to their intrinsic compositions, apparent sizes, and extrinsic surface structures.[120] As mentioned earlier, it is widely recognized that as particle size decreases to the nanometer scale, there are a variety of reasons, including quantum confinement effects, that cause their physical and chemical properties to differ from those associated with their bulk form. Equally important and widely acknowledged, but seemingly less understood, is recognition that a large portion of the atoms in nanoparticles are at or near the surface of the particles.[121]

Determining the nature and distribution of active sites on nanostructured surfaces is an important challenge. The following are the basic innate factors which influence the function as adsorbent of nanoparticles in solution or substrate: location of the most atoms in the surface, high surface area,

high chemical activity, high adsorptive capacity, lack of internal diffusional resistance, and high surface binding energy.

Each of the above properties successively leads to the significant fraction of atoms or molecules associated with surfaces and interfaces and increases the potential impact of surface accessibility and affinity, surface enrichment, number of active sorption sites, and, accordingly, surface energy toward specific analytes. Because of capillary and sorption effects, the high surface area present in nanoparticles may retain solvents in circumstances that can surprise researchers. Even using surface tools, it can sometimes be difficult to characterize the nature of the actual nanoparticle surfaces.[121] While metal and metal oxide nanoparticles have became excellent candidates as adsorbents in sample preparation processes and can advantageously replace conventional sorbents for separation and preconcentration routes, like solid phase extraction and solid phase microextraction, other morphologies of nanomaterials introduce new adsorption properties and characteristics. This is particularly so with carbon nanoparticles thanks to their especial π-electron configuration.[122] A great number of articles in the literature have noted that the importance of nanoparticle surface chemistry, especially as applied to separation science, has been surprisingly underemphasized.

2.2. External Functionalization

Using the various functional groups, a number of changes emerge in the surface properties of nanomaterials. Coupling the wide variety of nanomaterials with different external functionalization methods will result in excellent adsorption properties. Further functionalization of the surface prevents NPs from aggregating and provides their selectivity. Intended coatings may have a significant impact on a variety of nanoparticle properties. Functionalized groups induce important characteristics to the adsorbents such as high absorption capacity (often measured as the breakthrough volume for a flowing system) and rapid desorption.[123]

The quest for functionalized groups is an important factor to improve analytical parameters such as selectivity, affinity, and adsorption capacity. This is done by introducing various organic donor atoms to the nanomaterials' surface and improving the interactions with the analytes of interest, such as hydrophilicity or polarity. Amino and oxygen groups are known to be able to coordinate to transition metals via electrostatic interactions.[124] Vukovic et al.[124] functionalized

MWCNT with ethylenediamine by amide bond formation via the carboxyl groups on the oxidized CNT surface (Figure 2) and quantified Cd(II) uptake from water samples. They declared that sorption was strongly dependent on the solution's pH, because it affects the surface charge of the functionalized MWCNT, the degree of ionization, the metal speciation in aqueous solution, and the surface properties of the MWCNT.

Zeta potential (ζ-potential) is usually concluded as a basic parameter to measure the surface charge of colloidal and nanosized materials dispersed in a liquid, i.e., electrophoretic mobility, as velocity, when subjected to an electric field. The point at which the ζ-potential equals to zero is called the isoelectric point (IEP), and it is used to assess the adsorbent surface charge quantitatively. Meanwhile, surface functionalization has a critical influence on the retention efficiency of adsorbents and may shift the IEP of nanomaterials with respect to the pH of the solution. For instance, when the pH of the solution is higher than the IEP of nanoadsorbents, the negative charge on the surface provides electrostatic attractions that are favorable for adsorbing cations. However, the regime could be changed whether the pH is above or below the IEP.

Oxidation is another way to induce functionalization to the nanomaterials surface. Musameh et al.[125] described this concept for carbon nanotubes. They mentioned that oxidation of CNT introduces hydroxyl, carboxyl, and carbonyl groups at defect sites within the CNT. These groups have the ability to retain a variety of metals when the pH is above the isoelectric point of the oxidized CNT. Typical oxidation methods include nitric acid reflux[126,127] or use of other oxidizing agents, for example, hydrogen peroxide[128] or permanganate.[129] Such oxidation processes can increase the surface area by removing impurities and introducing surface defects that enable the introduction of oxygen-containing functional groups.[127] Studies have shown that the ends are more reactive than the surface and that they tend to be opened upon oxidation resulting in the creation of defects, including pentagons and carboxyl and hydroxyl groups, which are responsible for the enhanced adsorption capacities.[130]

Often the modification of the surface charge is preceded as a function of pH and ionic strength of the media. The pH at which the positive and negative charges are balanced, and no net charge is available on nanomaterials surfaces making a colloid or nanoparticle mobile in an electric field, is called point of zero charge (PZC). In fact, the PZC determines if a nanomaterial is hydrophilic in an aqueous suspension and further determines its mobility. Related to the fact that nanomaterial stabilization and aggregation are influenced by the surface charge, being in the vicinity of PZC nanomaterials dispersion is the least stable and has the highest propensity to aggregate due to the lack of surface charge repulsion.

Different types of nanomaterials are discussed here according to their properties and behavior as a sorbent. Although the variety of nanomaterials used by researchers for analytical purposes and adsorptive processes is widespread and several of nanoadsorbents have been introduced in recent years, we will focus on the most well-known nanomaterials based on their importance and long-term applications.

2.3. Nanoparticles

Potentiometric titrations of NPs and bulk particles could be conducted to determine the surface charge, σ, calculated as a function of pH based on eq 1 below

$$\sigma(C_m^{-2}) = F(C_A - C_B + [OH^-] - [H^+])r_{sw}^{-1}SSA^{-1} \qquad (1)$$

where F is the Faraday constant (96 485 C mol^{-1}), C_A and C_B are the total concentrations of acid and base added, respectively (mol L^{-1}), [OH$^-$] is the OH$^-$ concentration (mol L^{-1}) given by $10^{-(14-pH)/\gamma OH-}$, [H$^+$] is the proton concentration (mol L^{-1}) given by $10^{-pH/\gamma H+}$, r_{sw} is the TiO$_2$ concentration (g L^{-1}), and SSA is the specific surface area (m^2 g^{-1}). The titration curve must be normalized to the surface area unit. The point of zero charge (pH$_{PZC}$) would be the pH value where $\sigma = 0$.

2.3.1. Metallic Oxide Nanoparticles. *2.3.1.1. Aluminum Trioxide Nanoparticles (Al₂O₃ NPs).* Nanosized alumina is characterized by a strong adsorption capacity and porosity attributed to its high surface area, mechanical strength, degree of surface reactivity, low temperature modification,[80,131] and absence of internal diffusion resistance and high surface binding energy.[132,133] Nanometer-sized alumina is resistant to pH changes and has a strong resistance to swelling when placed in organic solvents. Given nanometer-sized alumina's high surface area, high chemical activity, and high adsorption capacity, it has been successfully applied for the separation and determination of trace metal ions in environmental samples.[134]

Generally, pH$_{PZC}$ is the point at which the net electrical charge density on a surface is zero. This is generally determined in relation to the pH of the medium, and therefore, it is also called the pH at which the surface of a particle shows no net charge.[135,136] Ghosh et al.[137] investigated the colloidal behavior of aluminum oxide NPs as a function of pH. With the aid of ζ-potential data, they clearly showed that the surface charge of the NPs decreases with increasing pH and reaches the point of zero charge (PZC) at pH 7.9. Moreover, another study also demonstrated a pH$_{PZC}$ of 9.5 for Al₂O₃ NPs.[138] Surface charge of the Al₂O₃ NPs also was found to decrease with the addition of natural organic matter like humic acids. The Al₂O₃ NPs tended to aggregate as the pH of the suspension approached PZC, where van der Waals attraction forces dominate over electrostatic repulsion. Nevertheless, the NP colloidal suspension could be stable in pH values far from PZC.[137]

However, nonmodified alumina nanoparticles are hydrophilic and do not show ideal adsorption capacity for organic compounds.[139] Retention in nonmodified alumina NPs is not quantitative owing to the weak interaction between this organic compound and the hydrophilic surface of alumina; therefore, chemical or physical modification of the surface of γ-Al₂O₃ NPs with certain functional groups containing some donor atoms is necessary.[140,141]

2.3.1.2. Zinc Oxide Nanoparticles (ZnO NPs). Nanoscale ZnO shows different physical and chemical properties from those of microscale ZnO. ZnO nanostructures offer a great advantage applied to a catalytic reaction process because of their large surface area and high catalytic activity. It has been confirmed that not only the morphologies of ZnO but also their particle sizes and surface areas are variable according to the content of precursors used in their preparation. Their morphologies and their physical and chemical properties have been investigated in terms of the content of zinc precursor doped in the matrix.[142] Rupasinghe[143] obtained the PZC for ZnO nanoparticles of sizes 4, 7, and 15 nm from ζ-potential experiments. For this purpose, a series of suspensions of ZnO were prepared at different pH values and the ζ-potentials were measured. pH$_{PZC}$ was obtained by linear extrapolation between pH 8 and 10, and the value (8.75) was in agreement with the literature value which is in the range 8.5−9.0 for 4 nm ZnO

nanoparticles. When pH of the medium is below this pH (8.75), the ZnO surface is positively charged. Below the pH_{PZC}, acidic water donates more H^+ ions than OH^-, so that the surface of the adsorbent gets positively charged. Conversely, above this pH the surface is negatively charged as a result of dominant OH^- ions. The pH_{PZC} values for 7 and 15 nm samples were also obtained by plotting ζ-potential versus pH followed by linear extrapolation. Observed values were close to that of 4 nm samples.

Zinc oxide has been widely used as a catalyst in the photodegradation of many organic pollutants and also proved to be an inexpensive and highly efficient catalyst in various organic reactions, due to its high zinc content (80%) and highly predictable reaction kinetics and adsorption capacity. ZnO is a commodity sorbent and good candidate for the removal of dangerous, toxic, and corrosive gases. ZnO nanoparticles have a very high porosity, which results in their high surface area and pore volume; therefore, they can scavenge gaseous pollutants much faster than bulk ZnO. These important key characteristics provide a wide range of potential applications in various industries, and spent ZnO sorbent is usually considered nonhazardous for solid waste disposal.[144]

2.3.1.3. Titanium Dioxide Nanoparticles (TiO₂ NPs). In general, TiO_2 is preferred in anatase form due to its high photocatalytic activity, since it has a more negative conduction band edge potential (higher potential energy of photogenerated electrons), is nontoxic, is photochemically stable with high specific area, and is relatively inexpensive. The performance of TiO_2 for certain technical applications is dominantly affected by its crystallite size, phase structure, surface area, impurity (dopant) type, and concentration.[145]

TiO_2 exhibits very favorable ligand sorption properties through inner sphere complex formation,[146−148] or, as suggested also, because of electrostatic interaction and hydrogen bonding between TiO_2 and organic polar side groups.[149] It has also been reported that TiO_2 anatase nanoparticles exhibit a different chemical behavior, catalytic reactivity, and surface acidity based on the type of surface.[150]

One particular study of Pb adsorption onto TiO_2 nanoparticles showed bulk materials exhibiting more adsorption and higher adsorption capacity when normalized for surface area,[151] but further investigations of these parameters are required with a more expansive list of metals to determine if trends exist.

Solution pH has an effect on the surface's active site distribution on metal oxides, such as titanium dioxide, and the surface hydroxyl group provides the ability to bind metal cations.[152] If the solution pH is less than the point of zero charge (PZC) on the surface of the TiO_2 particle, the surface becomes positively charged ($Ti-OH^{1/2+}$); in the opposite case, it becomes negatively charged ($Ti-OH^{1/2-}$).[146] Furthermore, the extent of adsorption for a particular metal may be influenced by other metals competing for the same surface sites, thereby affecting the removal rates and efficiency of the sorbent. By focusing on surface area and its attributes to sorption surface reactions, NPs may increase the overall environmental efficiency of water treatment strategies to remove metals by developing proper affinity, capacity, and selectivity for contaminants.[153] Studies have shown that the pH_{PZC} of TiO_2 nanoparticles ranges from 4.8 to 6.2,[154] with an average reported bulk TiO_2 pH_{PZC} of 5.9.[155]

The Langmuir isotherm (eq 2) is the most suitable model to characterize metal adsorption onto TiO_2 anatase nanoparticles and bulk particles:[119]

$$q = \frac{bq_m C}{1 + bC} \tag{2}$$

Here, b is the adsorption energy constant (L μmol^{-1}), C is the metal concentration in solution (μmol L^{-1}), and q_m is the solid maximum adsorption capacity (μmol g^{-1}). Adsorbed species interact with independent adsorbate surface adsorption sites wherein active sites can be occupied by only one molecule at a time to form a monolayer on the adsorbent.[156]

Sorbents are frequently evaluated by determining the distribution coefficient, K_d (mL g^{-1}, eq 3), which is simply a partition coefficient of the liquid phase to the solid phase:

$$K_d = \frac{(C_{in} - C_f)}{C_f} r_{ws} \tag{3}$$

Here, C_{in} is the initial concentration of metal (μg L^{-1}), C_f is the final concentration of metal (μg L^{-1}), and r_{ws} is the water-to-solid ratio (mL g^{-1}). The higher the K_d value, the greater the ability of the sorbent to retain the species of interest. In general, a K_d value of 1×10^3 is a good sorbent, and higher than this is exceptional.[157]

The nature of the sites on anatase TiO_2 potentially available for adsorption is discussed in detail in previous work.[158] Depending on the conditions of pretreatment of this material (T of activation), approximately 5% of these sites are hydroxyl groups.[159] The other sites arise from coordinatively unsaturated surface (cus) ions that have a tendency for additional coordination. The breaking of the crystal lattice at the surface leads to the appearance of these ions, with a lower coordination number than that in the bulk. Cations (essentially Ti^{4+}) possess an uncompensated positive charge and coordinate molecules with a free electron pair, i.e., they are Lewis acids; while the cus oxygen anions (O^{2-}) are Lewis bases and adsorb acidic molecules and cations.[159] The isoelectric point (IEP) of TiO_2 is 6.2.[160] When the pH of the solution is higher than this value, the titanium dioxide surface is covered essentially with OH^- groups and is negatively charged, and the adsorption of cations is favored.[158] However, not all cus. $Ti^{4+}-O^{2-}$ couples may be available for this adsorption, as shown in the case of Cu^{2+}, Co^{2+}, and Ni^{2+} cations. In contrast, when pH < 6.2, the titanium dioxide surface is positively charged, because it is covered essentially with hydroxonium groups, and adsorption of anions is favored. It is more difficult to explain the mechanism of cation adsorption under acidic conditions.[161]

There have been reports in the literature on the preconcentration and separation of trace elements in biological samples by means of nanometer TiO_2 material. But some heavy metal cations are poorly adsorbed on nanometer TiO_2 when the pH value is less than 6. Although some metals cations can be adsorbed on nanometer TiO_2 when the pH value is equal to 8, they are more likely to be precipitated under a higher pH value. Therefore, in order to improve the selectivity and adsorption capacity, modification by attaching to its surface organic and inorganic compounds, which comprise heteroatoms such as oxygen, nitrogen, sulfur, and phosphorus, is quite necessary.[162]

According to Qian et al.,[163] compared with nanometer-size TiO_2 powder, the colloid has the following advantages as a new adsorbent: (1) It has a stronger adsorption ability, a higher adsorption rate, a smaller grain size, and a more specific surface. (2) It is more stable and more dispersive without agglomeration, giving it a higher adsorptive repeatability. (3)

With slurry sampling, the elution step could be omitted so that high sample contamination and loss of analyte are avoided.

2.3.2. Metallic Nanoparticles. *2.3.2.1. Gold Nanoparticles (Au NPs).* Au NPs are gradually attracting a great deal of attention for their use in future technologies, including catalysis, biosensors, drug carriers, optical materials, electronic devices, and high contrast cell imaging.[164−169] Au NPs have been widely used in analytical methods due to their size dependent electrical properties, high electrocatalytic activity, and functional compatibility with molecules and polymers.[170] Besides, biomolecules containing thiol (SH) or amino (NH$_2$) groups can be adsorbed spontaneously onto gold surfaces to generate well-organized, self-assembled monolayers.[164] Even though Au NPs provide a large surface area to interact with column surface and analyte, very little research has been devoted to understanding their impact on separation science. Although the application of Au NPs is still in its infancy, previous studies have demonstrated their potential as multifunctional components to improve chemical stability, analytical selectivity, and separation efficiency.[171]

2.3.3. Nanostructured Mixed Oxides. *2.3.3.1. Fe−Ti Mixed Oxide Nanoparticles.* Very recently, the synthesis of nanometer scale mixed oxide particles, such as spinel ferrite,[172−174] Fe$_3$O$_4$ as pigment,[175] titanium-based various binary and ternary mixed oxides,[176] and indium(III)−tin(IV) binary mixed oxide,[177] have been reported for their remarkable electrical, magnetic, and conducting properties.

The point of zero charge (pH$_{PZC}$) is an important property for the materials to be used as sorbent. The lower the pH$_{ZPC}$ value is, the longer the pH range should be for scavenging cations; also, the higher the pH$_{ZPC}$ value is, the longer the pH range should be for scavenging anions from their aqueous solutions.[178] The plot of pH$_f$ against pH$_i$ for the point of zero charge (pH$_{PZC}$) of nanostructured mixed oxides could be drawn, and would show the change of the pH of the equilibrium solution (pH$_f$) against the initial pH (pH$_i$). It has been found that, for some solutions with an initial pH below a special value, the pH increased after the equilibrium time was reached; accordingly, it decreased for those solutions whose initial pH was above that value. Therefore, the pH corresponding to the (pH$_{PZC}$) of nanostructured mixed oxide particles is *V* (±SD), where *V* stands for the special value of pH$_{PZC}$. Hence, the surface of nanostructured mixed oxides should be positively and negatively charged at pH below and above pH$_{PZC}$, respectively, because of the following surface reactions:

$$S-OH + H_3O^+ \rightleftarrows S-OH_2^+ + H_2O \quad (pH < V) \quad (4)$$

$$S-OH + OH^- \rightleftarrows S-O^- + H_2O \quad (pH > V) \quad (5)$$
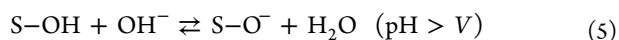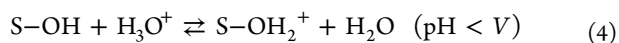
Here, S stands for the metal of the solid mixed oxide surface. Therefore, the reactions (eqs 4 and 5) indicate that the oxide surface is sensitive to (i) the anion sorption at pH < *V* (±SD) that should take place with electrostatic force of attraction or anion exchange, and (ii) the cation sorption at pH > *V* (±SD) that should take place with electrostatic attraction force or cation exchange. On the other hand, the polar molecule sorption should take place with electrostatic attraction force. The pH$_{pzc}$ value of Fe−Ti mixed oxide nanoparticles has been calculated to be 6.0 (±0.05).[179]

2.3.4. Magnetic Nanoparticles (MNPs). Currently, the unique physical properties of nanoparticles are under intensive research. A special place belongs to the magnetic properties where the difference between a massive (bulk) material and a nanomaterial is especially pronounced. The magnetic properties of NPs are determined by many factors; the key of these include the chemical composition, the type and the degree of defectiveness of the crystal lattice, the particle size and shape, the morphology (for structurally inhomogeneous particles), the interaction of the particle with the surrounding matrix, and the neighboring particles. By changing the nanoparticle size, shape, composition, and structure, one can control to an extent the magnetic characteristics of the material based on them. However, these factors cannot always be controlled during the synthesis of NPs that are nearly equal in size and chemical composition; thus, the properties of nanomaterials of the same type can be markedly different.[4]

Recently, the use of iron oxide MNPs has found extensive applications in a variety of fields.[180−204] Both forms of magnetic iron oxide nanoparticles, Fe$_3$O$_4$ (magnetite) and Fe$_2$O$_3$ (maghemite), have superparamagnetic properties.[185] Literature by, e.g., Lee et al.[205] stated that the point of zero charge (PZC) value of MNP, magnetite (Fe$_3$O$_4$), was pH 7 which was measured by the titration method. Superparamagnetic NPs have large magnetic moments that make them behave as a giant paramagnetic atom with a fast response to the external magnetic field and with negligible remanence and coercivity.[184] These NPs can be easily attracted to a magnetic field, but after their removal no magnetic property remains. This characteristic, and the resulting negligible risk of agglomeration, makes them attractive in separation and biomedical applications.[187,188] Also, in environmental applications, collecting the nanoparticles from large volumes of aqueous samples is rather easy and suitable.[189,206,207] MNPs are suitable sorbents in SPE due to their good dispersion in solution, their very high specific surface area, and their ability to be controlled and separated with an external magnetic field. Recently MNPs of iron oxide were used as a new sorbent in SPE of different analytes.[186,190−193] For inorganic analytes both forms of naked and functionalized MNPs have been used,[194] but for organic pollutants mostly coated particles have been used.[185] Compared to other conventional extraction methods, which often use large volumes of solution, magnetic solid phase extraction (MSPE) has several advantages: high efficiency and recovery as result of high specific surface area, ease of handling, and rapid speed and low cost.[190,195]

Magnetic separation provides a suitable route for online separation, where particles with affinity to target species are mixed with the heterogeneous solution. Upon mixing with the solution, the particles tag the target species. External magnetic fields are then applied to separate the tagged particles from the solution. However, it should be pointed out that pure inorganic nanoparticles (such as Fe$_3$O$_4$ and Fe$_2$O$_3$) can easily form large aggregates, which may alter their magnetic properties.[196−198] Moreover, these nanometer-sized metal oxides are not target-selective and are unsuitable for samples with complicated matrices. Thus, a convenient coating is essential to overcome such limitations. Physical or chemical modification of the sorbent surface with some organic compounds, especially chelating ones, is normally used.[199] Moreover, these nanometer-sized metal oxides are not target-selective and are unsuitable for samples with complicated matrices. Therefore, the modification of these magnetic nanoparticles with a suitable coating has been proven to be one of the most efficient ways.[208]

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2.4. Carbonaceous Nanomaterials (CNMs)

Carbonaceous materials have valence and conduction bands which are separated by an energy gap or band gap. Some carbonaceous nanomaterials for adsorption processes are well-known.

CNMs have a set of unique properties making them very attractive for application in micro- and nanoelectronics and molecular electronics, hydrogen power engineering, catalysis, medicine, etc. There is evidence[209−211] on the possibility of effectively using CNMs as sorbents for analytical purposes, including solid phase extraction. The physicochemical properties of CNMs and their sorption capability are mainly determined by the ways in which they are manufactured and their further treatment. In connection with this, it is crucial to characterize CNMs with respect to their morphology, purity, specific area, and sorption activity depending on their treatment after synthesis. It is also very important to study the potential of CNMs, as sorbents in solid phase extraction, to concentrate a series of metal cations in the static and dynamic regimes and, thus, to decrease their detection level by sensitive instruments such as ETAAS[212] and ICP-MS[213] and even more simple instruments like FAAS.[214]

2.4.1. Carbon Nanotubes (CNTs). Carbon nanotubes can be considered to be hollow graphitic nanomaterials comprising one (single walled carbon nanotubes, SWNTs) or multiple (multiwalled carbon nanotubes, MWNTs) layers of graphene sheets. The lengths of the nanotubes can range from several hundred nanometers to several micrometers, and the diameters from 0.2 to 2 nm for a SWNT and from 2 to 100 nm for a coaxial MWNT.[215] Nanotubes are characterized by their high surface areas and good electrical, mechanical, chemical, and conducting properties (among other features). These characteristics have made nanotubes the subject of intensive investigation since their discovery. In fact, carbon nanotubes may display metallic and semiconducting electron transport properties, and they possess hollow cores that can store guest molecules. One of their more remarkable characteristics is their large elastic modulus.[216−221]

Both SWNTs and MWNTs are new classes of carbonaceous materials that show excellent promise for both gas and liquid phase preconcentration. They have high aspect ratios,[222] and molecules can adsorb on the outside surfaces and in the interstitial spaces. The surface area and structure of CNTs' mass transfer has led to fast desorption, as it has been reported to be in the range 150−3000 m^2 g^{-1}.[223] This makes them attractive adsorbents for different applications such as SPE,[224−229] solid phase microextraction (SPME),[230] gas phase microconcentration, and chromatography.[222,231−233]

High adsorption capacity and efficient desorption[234] have been reported for these sorbents where the large specific capacity came from strong solute−sorbent interactions. An important consideration for CNTs is that, by introducing different functional groups on their surface, properties including polarity and hydrogen bonding potential can be altered, which in turn can affect sorption selectivity and capacity.[235−239]

Carbon nanotubes also make interesting analytical tools, for two reasons. First, they exhibit interesting chemical properties, when used as sorbent and electrical properties, that make them suitable for use in electrodes. Second, nanotubes open up new approaches to full integration, providing exceptional possibilities for further miniaturization.[240]

The chemical inertness and strong van der Waals interactions between nanotubes complicate their fabrication. Thus, it is important to separate individual nanotubes from the bundles to maximize the influences of the intrinsic mechanical properties of carbon nanotubes; so, nanotube solubilization is a key issue. From an analytical point of view, many applications of nanotubes, when used as either an analytical target or an analytical tool, are limited because of their low solubility, which is an area that is currently being investigated extensively. Haddon and co-workers[241] compared analytical techniques for evaluating the purity of single walled carbon nanotubes, including electron microscopy (both scanning and transmission), spectroscopic techniques such as Raman and near-infrared (NIR), and thermogravimetric analysis. The authors showed that the most accurate purity evaluation was achieved by the appropriate dispersion of nanotubes in solution followed by NIR and Raman analysis, with the sample preparation and homogenization being a critical step.

Different carbon-based sorbents have been utilized for preconcentration of analytes, including activated carbon, carbon molecular sieves, graphitized carbon black, and porous carbon.[242,243] These differ in their physicochemical characteristics, for example, pore size/shape, surface area, pore volume, and surface functionality. Kinetic and thermodynamic properties of carbon-based sorbents such as breakthrough volumes, adsorption isotherms, and intermolecular interaction mechanisms at the adsorbate/carbon sorbent interface strongly affect reconcentration.[244,245] The sorbent can affect the adsorption by providing a large number of available sorption sites, and by facilitating specific interactions such as hydrogen bonding. As already mentioned, at a functional level the important characteristics are high absorption capacity (often measured as the breakthrough volume for a flowing system) and rapid desorption.[246−249] In CNTs, the sorption occurs mainly on the outer surface and in the hollow spaces of the open tubes. Thus, their release by both thermal processes and solvents is relatively simpler and not limited by diffusion. Therefore, a wide range of compounds from small molecules to large semivolatile compounds can be easily concentrated on, and desorbed from, CNTs.[250,251] Other factors are also important. The exceptionally high aspect ratio (in millions) of CNTs provides a special confinement effect,[252] which leads to a completely different physical behavior compared with more conventional sorbents. Moreover, outer tube surfaces create a large number of intertubular spaces, which provide specific adsorption sites. As a result, the sorption capacity is higher than would be expected on the basis of BET surface area measurement.[253,254] Various approaches have been used to describe adsorption on CNTs. The high sorption capacity of CNTs has been explained on the basis of the presence of high-energy adsorption sites, for example CNT defect and interstitial and groove regions between CNT bundles, and the phenomenon of multilayer adsorption during microsorption on CNTs.[255,256] Capillary forces in nanotubes can also be strong, which may draw molecules from vapor or liquid phases by van der Waals attractive forces and dipole−induced-dipole interactions.[257,258] Hydrophobicity and capillarity can provide ordering and orientation of sorbents on the sorbate.[259] Adsorption studies have revealed rapid rates of equilibration, high adsorption capacity, low sensitivity to pH range, and minimal hysteresis in dispersed CNT, as well as consistency with traditional Langmuir, BET, or Freundlich isotherms.[260] Moreover, high dispersion energy and the overlapping force of adjacent carbon walls increase sorbent−sorbate and sorbent−sorbent interactions, resulting in condensation within nanotubes.[261,262]

The filling of nanotubes may explain why some models describe adsorption capacity above the physical surface area of a CNT.[263,264] Studies have shown that polarizability[265] and the strong adsorptive interaction between the polarizable graphene structure of CNT and sorbate, due to the $\pi-\pi$ electron-donor–acceptor interactions, are also important factors.

The point of zero charge is a useful measurement to assess the surface acidity of multiwalled carbon nanotubes and to characterize functional groups on the multiwalled carbon nanotube surface. The PZC is an important characterization parameter in order both to optimize loading and to anchor the metal complex precursor to maximize dispersion (high dispersion and anchoring of the precursor leads to high dispersion of the metal on reduction). At extremely low or high pH, adsorption is inhibited over all surfaces by high ionic strength. This results in an optimum pH for maximum loading. McPhail et al.[266] reported that the carbon nanotube surfaces may have a wide range of PZC values resulting from different functionalization methods, e.g., refluxing in H_2SO_4/HNO_3 or nitrosylation. Lee et al.[267] prepared and characterized multi-walled carbon nanotubes with points of zero charge that range from 2.2 to 11.8. They investigated the systematic variation of the PZC of the surface of nitric acid oxidized MWCNT where the density and functionality of the oxygen containing groups have been varied by reduction using $LiAlH_4$ and high temperature treatment in an inert atmosphere and the acidity correlated with functionality of oxygen and nitrogen surface groups.

2.5. Silicon Nanomaterials (SiNMs)

2.5.1. Silica Dioxide Nanoparticles (SiO_2 NPs). Grafted materials are the simplest and most accessible form of nanomaterials, obtained by simple attachment of a nano-object to an organic polymer matrix or an oxide matrix (most frequently SiO_2, for reasons of cost, accessibility, uses, and above all for the numerous usable grafts). This attachment is generally made using one or several covalent bonds to link the matrix to a precursor. The choice of support depends on the intended objectives. Silica is an inorganic polymer that does not have good interaction with nonpolar organic compounds. Thus, the use of nanosilica for extraction of organic pollutants is rather inconsiderable. To overcome this problem, nanosilica particles must be grafted with an organic modifier.[268] The PZC of SiO_2 is about 2–3, as reported in the literature;[269] therefore, silica nanoparticles are negatively charged at higher and nutrient pH, and consequently, their dispersions in various water and biological media would be stable.

Silica nanoporous materials have been widely used because of their unique properties, among them its high surface area. Modified silica nanoparticles have been used for preconcentration of organic pollutants and many metal ions, and promising results have been achieved when used for trace analysis of different samples.[270−273]

2.5.2. Silica Nanotubes (SiNTs). Silica nanotubes are ideal vehicles for proof-of-concept experiments because they are easy to make, have cross-linked structure, and are highly convenient for the formation of a delicate recognition site.[274] Silicon is more polarizable than carbon due to the presence of more electrons in its outer shells. Therefore, it is anticipated that SiNTs can be tailored to achieve a stronger van der Waals attraction to adsorbed molecules than CNTs. Lan et al.[275] evaluated the hydrogen adsorption on the SiNT arrays. They

found that the capacity of hydrogen adsorption on SiNT arrays is considerably higher than that on CNTs.

Silicon nanotubes offer some interesting advantages for chemical applications. However, at present the application of these nanotubes is not common compared to nanoadsorbents of interest of the same material, e.g., SiNPs.

2.6. Nanofibers (NFs)

Nanoparticles and nanofibers have been in the center of focus, and many reports about NP applications, including as adsorbents for SPE, have been published. However, the NP-packed SPE column also has high backpressure, which makes it difficult to adapt high flow rates in the column's dynamic extraction mode and very high filtration rates in the static batch mode.[276]

Many polymers with sufficiently high molecular weight can be electrospun according to the characteristics of the object samples. Nylon6 is an interesting example because the primary chemical structure of nylon consists of amide groups separated by methylenic sequences. The amide group is essentially planar due to the partial double-bond character of the C−N bond. The chains are oriented in such a way as to maximize hydrogen bonding between the amino and carbonyl groups.[277] The aqueous phase used to carry the hydrophobic analyte through the nylon nanofibers is one of the main factors in determining the successful extraction. For hydrophobic analytes, nonpolar interactions are expected between these compounds and the methylenic chains of nylon. On the other hand, the hydrophilic amide groups are expected to enhance the water movement into the sorbent, improving mass transfer and making it more effective.[278] Over recent years, some researchers have investigated different parameters influencing nylon6 nano-fibers,[279−281] and it becomes very interesting to explore the use of nylon6 nanofibers as sorbents for SPE. Nylon6 nanofibers as absorbent possess high surface-to-volume ratio and length-to-diameter ratio that could achieve larger specific surface, and more active sites for adsorption. Accordingly, the attachment of the target molecules would be easy and sufficient, and satisfactory recoveries could be obtained. Also, for this reason, a small amount of nanofibers is sufficient for the extraction, which greatly reduces the volume of desorption solvent. Xu et al.[282] found that a larger section area of nanofibers, compared with SPE cartridges, made the pressure drop allowing sample processing at higher flow rates. Thus, it is much easier to deal with large volume samples to obtain a better enrichment coefficient and meet lower LOD.

2.7. Nanoclays

Clay, a natural source, has primary particles with at least one dimension in the nanometer scale, so that clay and clay minerals may be regarded as nanomaterial of geological and pedological origins.[283] The main structure in clays includes tetrahedral silicate and octahedral aluminum layers, and the diversity in clays is based on the arrangement of these layers. This arrangement includes three types of clays: type of 1:1 in which tetra- and octahedral layers alternate, type of 2:1 in which two tetrahedral layers sandwich an octahedral layer, and type 2:1:1 in which octahedral layers are in a 2:1 type clay layer. Clay minerals are characterized by certain properties; such as a layer structure with one dimension in the nanometer range, where the thickness of the 1:1 layer is about 0.7 nm, and that of the 2:1 layer is about 1 nm.[284] The contour space between clay layers is called the gallery. Exposure of the clay minerals in the sample solution makes them swell, which enhances the galleries

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and results in a larger surface area. Clay minerals can react with different types of organic compounds in several ways. The penetration of organic molecules into the interlayer space of clay minerals is called intercalation. The interlayer cations can be exchanged by different types of organic cations. Normally, organic surfactants are used to make the surface of clay platelets organophilic and swell clay galleries. An organophilic surface and interlayer environment can be produced by replacing naturally occurring inorganic exchangeable cations with a variety of organic cations, such as ionic long alkylammonium chains.[285] The adsorption of organic molecules to these minerals is affected by various parameters, such as the exchangeable cations, the distance between the clay mineral layers, and the existence of water molecules between the layers.[287] Hydration of exchangeable cations and the presence of Si−OH clay mineral groups contribute to the hydrophilic nature of clay mineral surfaces, suppressing the adsorption of hydrophobic molecules: nonpolar organic chemicals cannot effectively compete with the water molecules for adsorption sites on the clay mineral surface. In the absence of water, clay minerals have a higher affinity for hydrophobic compounds.[286],[288] For instance, the adsorption of benzene, toluene, and xylene to "wet" organo-clay minerals is significantly reduced relative to that of organic vapors on dry organo-clay minerals of the same type.[289]

Clay, in particular montmorillonite (MMT), a 2:1 phyllosilicate, naturally occurs as stacks of platelets as in talc and mica but possesses various layer charges. This leads to isomorphic substitution within layers (e.g., Al^{3+} is replaced by Fe^{2+}or Mg^{2+}) and generates a negative charge exchange capacity. In order to improve organophilicity, natural montmorillonite is usually modified with organic quaternary ammonium ($R_4N^+X^-$). The selection of different R groups for clay modification leads to the required interaction between clay and the analytes. The replacement of inorganic exchange cations with organic onium ions on the gallery surfaces of clays not only serves to match the clay surface polarity with the polarity of an organic matter like polymer, but also expands the clay galleries. Each platelet is less than 10 Å thick, but over 200 times more in width. The gallery spacing separates each platelet. These spaces in MMT can be enhanced to 2−3 nm using quaternary ammonium salts. This facilitates the penetration of the gallery space by intercalation or exfoliation of either the polymer precursor or preformed polymer. If the extended chains are inserted in the self-assembled, well-ordered gallery spaces, it is called an intercalated structure. If the individual silicate layers are no longer close enough to interact with adjacent layers, it is called a delaminated or exfoliated structure. Both of these hybrid structures can coexist.[290]

2.8. Polymer-Based Nanoadsorbents

Polymer-based nanoadsorbents are gaining more and more attention in sample pretreatment processes. Organic polymers, either as a system into which inorganic nanosized materials can be inserted for improving their chemical, mechanical, thermal, and sorption properties or as a bed or template to synthesize and grow nanoparticles, are being considered among the adsorbents of interest. Nanopolymer spheres also could be counted as desirable adsorbents for separation purposes. Polymer-based nanoadsorbents have been widely used in SPE to preconcentrate various metal and organic contaminants. One of the most important factors for harnessing the nanoscale inorganic particles within polymeric beads is that these tiny

particles cannot easily be used in fixed-bed columns or any plug-flow-type configuration due to excessive pressure drops and poor durability. Also, regeneration and reuse of the polymer−inorganic nanoscale hybrid adsorbents is more amenable than that of solo nanoparticle sorbents. One of the most apparent advantages for polymer−inorganic nanoscale hybrids is good adsorption capacity and good chemical stability in a wide pH range due to ease of functionalization through different polymeric units, such as epoxide, epoxy, and so on. Moreover, the remarkable resistance of the polymeric groups and their linkage to acid and to base hydrolysis are an additional advantage to use them as ligand carrying polymers.[291] Hu et al.[292] reported a kind of magnetite (γ-Fe_2O_3) that was used for the removal of Cr(VI) ions from wastewater. Although this adsorbent could be separated rapidly from the post-treatment wastewater system, its maximum adsorption capacity was only 17.0 mg g^{-1}. In order to achieve high maximum adsorption capacity, conventional adsorbents have been modified by inserting them into a polymeric shell with various functional groups, including carboxylate, hydroxyl, sulfate, phosphate, amide, and amino groups. The surface functionalization of magnetic nanoparticles can be tailored if a chemical modification of polymeric shells is elaborately designed. Thus, selective adsorption on different metal ions can be achieved.[293]

Nanoporous polymers are drawing significant attention because of a variety of emerging applications in electrodes,[294] chromatography,[295] and in hydrogen storage,[296] where these materials may play a pivotal role. Nanoporous polymers fall into three broad categories: (i) cross-linked polymers prepared via polymerization in the presence of a porogen, which have surface areas of up to about 1000 m^2 g^{-1} and have been used extensively as separation media for several decades; (ii) hypercrosslinked polymers, with achievable surface areas of more than 2000 m^2 g^{-1}; and (iii) polymers with intrinsic microporosity with surface areas reaching 1000 m^2 g^{-1}.[297]

Reports in the literature have stated that the sorption of some metals on polymer-based nanoadsorbents strongly depends on the chemistry of the adsorbent's surface on which the type and number of functional groups present change the PZC of the sorbent surface. Kaya et al.[291] surveyed the pH_{PZC} for glycidyl methacrylate-based polymer (GMD) and nanosized ferric oxide loaded glycidyl methacrylate-based polymer (GMDFe). The PZC for the GMD adsorbent is at pH 6.3, whereas it is shifted to pH 6.86 for the GMDFe adsorbent. The adsorbents' surfaces are positively charged at pH values below the PZC because the oxygen containing groups are undissociated and the GMD and GMDFe samples will remove anions from solution under these conditions. Upon loading of Fe nanoparticles onto the surface there is a net increase in the positive potential of the particle's surface.

2.9. Xerogels and Aerogels

Xerogels and aerogels typically have a relatively large surface area, high porosity, and internal pore volume, and are ideal candidates as sorbent and catalyst support materials for many applications. Silica xerogel is probably the most studied and documented porous material in the sol−gel system.[298] Although silica has several crystalline forms, only amorphous silica gel is used as a desiccant (sorbent). Another important material in this category is γ-alumina xerogel. One of the outstanding characteristics of sol−gel-derived γ-alumina xerogel is its excellent mechanical properties. The preparation of

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porous γ-alumina granules with good mechanical properties and desirable pore structure is of great importance in the development of novel catalysts and sorbents for various applications. These superior mechanical properties can be derived from the unique microstructure of the granule, which results from compacting small γ-alumina crystallite particles bound together by the bridges of the same material formed through coarsening or sintering. These well-adsorptive characterized particles also demonstrate high thermal and chemical stability, high sorption capacity, and high reactivity toward many substances such as metal ions and pollutant gases. Aucoin et al.[299] enumerated several advantages for xerogels, including the opportunity to produce them in defined shapes or thin films and the ability to manipulate their physical characteristics including porosity, hydrophobicity, and optical properties.

As compared with xerogels, aerogels have a larger surface area, larger pore volume, and higher porosity. Alumina aerogels with a specific surface area as high as 1000 m^2 g^{-1} and a pore volume as high as 17.3 cm^3 g^{-1} have been represented as good adsorbent material, but very limited information on their adsorption properties was found.[300] A super water adsorbent consisting of 17−30% of CaCl$_2$ doped on SiO$_2$ aerogel showed an effective reversible adsorption capacity of 100 wt %, and the adsorption capacity of hydrophilic silica aerogels can be fully recovered after regeneration.[301]

The PZCs for different xerogels and aerogels have been measured and reported in the literature. Regalbuto and co-workers[302] extended the PZC characterization to carbon xerogel supported catalysts. Four carbon xerogels of varying pore sizes (18, 32, 68, and 90 nm) all have a PZC of 9.4 as-prepared, and after nitric acid oxidation, the PZC is 2.4.

2.10. Destructive Adsorbents

Nanoparticle metal oxides exhibit high intrinsic surface reactivities and high surface areas, and strongly chemisorb acidic gases and polar organics. Since dissociative chemisorptions are usually observed, these new materials have been dubbed destructive adsorbents, and are finding use in antichemical/biological warfare, in air purification, and as an alternative to incineration of toxic substances.[3] Enhanced surface reactivities of destructive adsorbents are strongly predicted by their surface area alone. A monodentate type adsorption mode is observed by these nanoscale crystals while, comparably, the larger ones favor a bidentate mode. In the case of acidic gases like CO$_2$, HCl, HBr, and SO$_3$ with high pressure, multilayer adsorption occurs for destructive adsorbents in which the more ordered surfaces on the crystallites become more important. This multilayer adsorption is encouraged by higher gas pressure, although weak physisorption rather than chemisorption is involved. It is possible that both polarization (electronic) effects and morphological effects are involved in these adsorption processes. Among the most promising destructive adsorbents are MgO and Al$_2$O$_3$ nanocrystals, which are reported to have enhanced surface reactivity toward acid gases. Adsorption mechanisms are mostly considered on the basis of their innate surface properties. Also, strong reactions with polar organic molecules, usually by chemisorption processes, are examples of destructive adsorbents. This behavior has been observed with aldehydes, ketones, and alcohols on MgO and Al$_2$O$_3$ nanocrystals in which strongly exothermic interaction takes places. In the case of acetaldehyde

on MgO, almost one mole of the aldehyde was destructively adsorbed for every mole of MgO employed.[303]

Another important point in destructive adsorption is that, at ambient and elevated temperatures, adsorptions take place in such large amounts that the metal oxides can be considered as almost stoichiometric reagents.[3] Destructive adsorption does not occur on high surface area carbonaceous adsorbents. Therefore, nanocrystalline metal oxides, with their polar nature and high surface reactivities, bring a new useful dimension, and this has proven valuable in the quest to find protective measures against chemical and biological warfare.[304]

3. PREPARATION METHODS

Nanostructured materials find their applications in information technology, magnetocaloric refrigeration, medical diagnostics, semiconductors, ferrofluids, optoelectronics, and many other purposes. Therefore, the synthesis of such materials has gained increasing importance in the field of material science. The existing techniques rely on high pressure, sol−gel, salt−solvent-mediated high temperature, thermal vaporization, coprecipitation using surfactants, surface capping agent, or organometallic precursor mediated growth process, and the types of oxides that can be synthesized are rather limited.[305−308]

The physical characteristics of NPs are known to be substantially dependent on their dimensions. Unfortunately, most of the currently known procedures of synthesis provide NPs with rather broad size distributions (dispersion $s > 10\%$). The thorough control of reaction parameters (temperature, stirring velocity, time and concentrations of reactants and stabilizing additives) does not always allow one to narrow down this distribution to the needed range. Thus, together with the development of procedures for synthesis of NPs with a narrow size distribution, the techniques of separation of NPs into rather monodisperse fractions are being perfected. This is done using controlled precipitation of particles from surfactant-stabilized solutions followed by centrifugation (the coarsest fraction is the first to be precipitated). After decantation, the precipitate can again be dissolved and subjected to precipitation/centrifugation. The process is repeated until NP fractions with specified sizes and dispersion degrees are obtained.[309]

The procedures of NP preparation cannot be detached from stabilization methods. For 1−10 nm particles with a high surface energy, it is difficult to select a really inert medium because the surface of each NP bears the products of its chemical modification, which appreciably affect the NP properties.[309] Nevertheless, the general procedures for NP synthesis not directly related to stabilization and the procedures where NP formation is accompanied by stabilization (in matrices, by encapsulation, etc.) will be considered separately.

If the procedures used to prepare NPs are classified in terms of the type of precursor and the features of their processing, the following key approaches to the formation of NPs can be distinguished: (i) preparation from macroscopic materials by dispersion, (ii) chemical synthesis, i.e., targeted change in the substance composition with termination (in some way) of the nascent phase growth at the nanosize stage, and (iii) transformations of NPs with changes in composition.[4]

3.1. Preparation of Nanoparticles

3.1.1. Metallic Oxide Nanoparticles. *3.1.1.1. Aluminum Trioxide Nanoparticles (Al$_2$O$_3$ NPs).* The preparation of alumina nanoparticles is very simple and inexpensive compared

to that of other commercially available solid phase materials. The main method for the preparation of fine Al_2O_3 nanoparticles, including aerogels and xerogels, is controlled hydrolysis of aluminum alkoxides. Simple aluminum salts could be useful for the preparation of alumina nanoparticles or aerogels like $(TiO_2)_x(Al_2O_3)_{1-x}$ via pyrolysis of an ethanolic solution of appropriate metal alkoxides. Other widely used processes are hydrothermal synthesis and vaporization of volatile precursors, followed by thermal decomposition in a reactor; the latter is called the aerosol method.[310]

3.1.1.2. Zinc Oxide Nanoparticles (ZnO NPs). The sizes and shapes of ZnO nanoparticles depend on the method of preparation, such as chemical vapor deposition (CVD), electrodeposition, vapor phase transport, thermal evaporation using ZnO powders, etc.[311−315] Zinc oxide nanostructures with large surface area have been synthesized also by a matrix-assisted method in which the precursors of metal oxide are uniformly doped on the surface of the matrix with a large surface area and then the matrix is removed by calcination at high temperature.[142] ZnO nanostructures were prepared with various content of the doped precursor on the surface of activated carbon by a matrix assisted method, according to Park et al.[142]

3.1.1.3. Titanium Dioxide Nanoparticles (TiO$_2$ NPs). Many methods have been reported for the production of TiO$_2$ NPs, such as chemical solution decomposition (CSD),[316] chemical vapor decomposition,[317,318] two-step wet chemical method,[319] sol−gel,[320,321] ultrasonic irradiation,[322,323,325] and thermal or hydrothermal processes.[326,327]

Recent studies revealed that sol−gel is the most commonly used procedure for the preparation of photocatalysts, like TiO$_2$ or doped TiO$_2$. The advantage of the wet chemical methods (which include sol−gel) is that they facilitate the synthesis of nanometer-sized crystallized TiO$_2$ powder of high purity at a relatively low temperature.[324] Modified sol−gel procedures have also been used,[328,329] such as ultrasonic assisted sol−gel method,[330] aerogel method,[331] method similar to sol−gel,[332] sol−gel and photoreductive decomposition,[333] precipitation,[334,335] two-step wet chemical method,[319] and extremely low temperature precipitation.[336] One commonly encountered problem is that these methods may generate amorphous or low crystallinity products, which necessitate a subsequent annealing for crystallization or further crystallization. However, such a thermal annealing may cause hard aggregation and even interparticle sintering.[337] Plasma-assisted processes exhibit good crystallinity.[338] Recently, there has been a surge in interest to study plasma-assisted nanocrystalline titania synthesis processes by optical emission spectroscopy (OES), in order to better understand the detailed chemistry involved. Oxidation of titanium was extensively studied in laser-ablated plasmas,[339,340] in magnetron sputtering,[341] transferred arcs,[342] and microwave discharge plasma systems.[343] Distinct advantages of plasma processing, in terms of powder synthesis, reside in the resultant particles being of high purity and largely dispersed.[337] Flame aerosol processing and plasma processing using liquid precursors have also been used.[337] The main disadvantage of the solution precursor plasma route is that it consumes considerable amounts of energy for vaporization of the solvent.[344]

3.1.2. Metallic Nanoparticles. *3.1.2.1. Gold Nanoparticles (Au NPs).* In the past decades, though many synthetic strategies have been developed to prepare gold nanoparticles in organic or aqueous solvents,[345−347] the citrate reduction

procedure has remained the best candidate to fit the growing demand for Au NPs because of its advantages, such as inexpensive reductant, nontoxic water solvent, and low pollution in the reaction.[348,349] In the pioneering work on the citrate reduction procedure, Turkevich et al. reported, in 1951, the basic experimental approach and the influence of temperature and reagent concentration upon nanoparticle size and size distribution,[350] and in 1973, Frens published the control of size variation of Au NPs by changing the concentration of sodium citrate.[351] Then, in 1994, Chow and Zukoski published a sol formation mechanism and a particle growth model.[352] The citrate reduction method for the synthesis of gold NPs has known advantages but usually provides the products with low nanoparticle concentration and limits their application.[353] Although gold nanoparticles are among the most intensely studied nanoscale materials, the actual mechanisms of their formation often remain unclear due to limited accessibility to *in-situ*-derived time-resolved information about precursor conversion and particle size distribution.[354] Although various strategies for modification of the gold NP surface have been established, including additional coating, ligand modification, and ligand exchange, after 10 years of extensive studies the synthesis of functionalized gold NPs still presents a major challenge, especially in cases when the desire is to conjugate a defined number of types of biomolecules onto the surface of individual gold NPs.[354,355] Plenty of methods have been published in the past decades, including the classical citrate synthesis procedure via *in situ* SAXS and XANES using synchrotron radiation (Figure 3),[354] two-step UV irradiation−
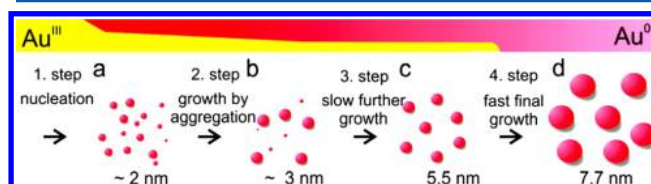
Figure 3. Schematic illustration for the deduced process of gold nanoparticle formation.[354] Reprinted with permission from ref 354. Copyright 2010 American Chemical Society.

reduction,[356] thermal UV irradiation reduction by citrate and ascorbic acid,[357] deposition−precipitation (DP),[358] direct anionic exchange (DAE),[359] photocatalytic deposition (PD),[360] sonication−reduction of HAuCl$_4$,[361,362] peptide-induced deposition (Figure 4),[361] surfactant-free,[363] surface-bound interdigitated bilayers,[364] pulsed laser-induced ablation from solid targets,[354,365] and sol−gel.[366−368]

Self-assembly is the fundamental principle which generates structural organization on all scales from molecules to galaxies. Self-assembly is defined as reversible processes in which pre-existing parts or disordered components of a pre-existing system form structures of patterns. Surface self-assembly of molecules onto Au NPs can be classified as either a static or dynamic process. During the utilization of Au NPs for separation or preconcentration, molecular assemblies are formed spontaneously by the immersion of an appropriate size of NPs in a solution. Self-assembly techniques for the NP applications utilize physisorption (e.g., electrostatic adsorption of charged molecules from a NPs colloidal suspension) or chemisorption (e.g., covalent bond formation between an organic molecule and NPs) interaction.[171]

Figure 4. Schematic diagram of the protein immobilization process: (a) polymer pattern produced by soft lithography; (b) immobilized protein on the patterned substrate; (c) protein pattern after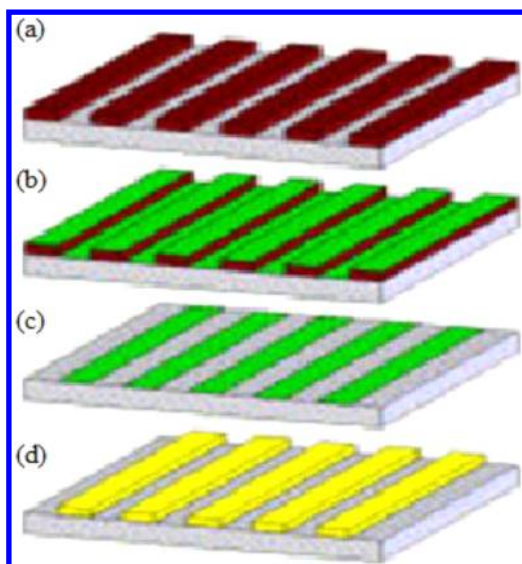 lifting off of the polymeric sacrificial layer; and (d) gold nanoparticles reduced on the protein pattern.[361] Reprinted from ref 361, with Permission from Elsevier. Copyright 2011.

Surface modification with functional groups of molecules is a key procedure to prevent the prepared NPs from aggregating and to control particle size. It also provides extra selectivity when the NPs are used as separation media. The fabrication of structures by means of the self-assembly strategy has attracted much attention due to the simplicity and flexibility of this approach.[369] A couple of procedures have been proposed for the self-assembly of Au NPs onto surfaces functionalized with SH and NH_2 groups.[370] These functionalized Au NPs have served as stationary phase materials for different separation and preconcentration systems, and the most commonly employed techniques are SPE, GC, HPLC, OTCEC, microchip, and CE, which have been summarized elsewhere.[171]

3.1.3. Nanostructured Mixed Oxides. *3.1.3.1. Fe–Ti Mixed Oxide Nanoparticles.* The main method for the preparation of fine Fe–Ti mixed oxide nanoparticles is the coprecipitation technique proposed by Gupta et al.,[179] which is considered as a simple and low cost method. The procedure includes several steps: slowly adding the source solutions of iron ($FeCl_3$) and titanium ($TiCl_4$) with constant mixing, optimizing the pH of the supernatant solution, aging of the gel-like hydroxide precipitate formed within the mother liquor, filtering and washing to obtain a chloride-free precipitate, drying, and finally breaking into the desirable fine particles by treating with ice cold water.

3.1.4. Magnetic Nanoparticles (MNPs). The coprecipitation process is an easy and suitable way to synthesize magnetic iron oxide NPs. Size, shape, and composition of the MNPs are very dependent on iron salt, Fe^{2+}/Fe^{3+} ratio, reaction temperature, pH value, and ionic strength of the media.[199]

A number of general procedures for the synthesis of these nanoparticles have now been developed.[371] An essential feature of their synthesis is the preparation of particles of specified size and shape (at least, the scatter of sizes must be small and controllable). The shape control and the possibility of synthesis of anisotropic magnetic structures are especially important. In order to eliminate (or substantially decrease) the interparticle

interactions, MNPs often require being isolated from others with a coating around the particle. The synthetic procedure must be relatively simple, inexpensive, and reproducible. The methods for generation of MNPs in the gas or solid phase using high-energy treatment of the material are usually called physical, while the nanoparticle syntheses often performed in solutions at moderate temperatures are chemical methods. Chemical methods for the preparation of MNPs have been developed most intensively in recent years; however, the physical methods must not yet be considered as outworn.[4]

3.1.4.1. Physical Methods for the Preparation of MNPs. 3.1.4.1.1. Condensation Methods. Nanoparticles (clusters) are prepared using different ways of metal evaporation: laser vaporization,[372,373] thermal vaporization,[374,375] arc discharge, plasma vaporization,[376] and solar energy-induced evaporation.[377] For each procedure, special installations with different engineering solutions are employed.[378] All the procedures for metal evaporation listed above allow the study of both the physicochemical characteristics of NPs in the gas phase (before the metal vapor deposition on the substrate) and the properties of films and powders obtained upon deposition. The use of the metal vapor method (MVM) gives unique opportunities to prepare at room temperature supported catalysts and precursors with "atomically dispersed" metal particles on the surface. Furthermore, the high activity of MVM prepared metal supported catalysts and precursors could be due to the atomically dispersed states of metal on the support surface and to the optimal balance between metal and acidic sites.[379] Metals in MVM method are evaporated in a vapor synthesis device with a rotating reactor using resistive heating and electron gun-type furnaces under high vacuum.[380]

The MVM improves the preparation of many transition metal solutions directly from metal atoms and organic solvents as ligands. These metal solutions are thermally very unstable and may easily excrete organic ligands weakly bonding to the metal. With an increase in the surface temperature, obviously, the initially highly dispersed metal particles may aggregate to form less active bulky metal species. In order to prevent the aggregation of the highly dispersed metal particles on the support surface, catalyst precursors must be reduced at low temperatures as much as possible.[381]

Also, another instance of metal atom chemistry is presented with the use of the solvated metal atom dispersion (SMAD) technique. This method allows the production of very small, zerovalent bimetallic particles. It involves the simultaneous evaporation of the metals and their co-condensation with the vapor of a chosen solvent at 77 K. The technique involves a reactor in which an activated precursor like SiO_2 or Al_2O_3 is placed. The technique allows metal particles and solvents evaporating simultaneously at 77 K. The metallic particles are produced "*in situ*" and reacted with the activated precursor previously introduced in the reactor bottom.[382] A competition occurs between the solvation and the clusterization of metal–metal to form a small amorphous particle[383] and to incorporate fragments and/or solvent molecules on the particle's surface. These fragments dramatically modify the properties of metallic particles,[384] but can be removed by heating the solids over 100 °C. The amount of solvent incorporated depends on the metal and solvent.[385]

Recently, the cryogenic procedure has been used to prepare NPs. In this case, the condensation of metal atoms and metal compounds occurs at low temperatures in a cryogenic matrix, most often, in a liquid inert gas. This procedure allows the

preparation of chemically highly pure NPs uniform in composition and structure and having no pores or other morphological inhomogeneities. The preparation of nanoparticles by metal vapor spraying is a rather well-developed procedure in both practical and theoretical aspects. Thermal or laser vaporization allows the synthesis of gram amounts of nanoparticle powders. These methods can be used for dispersing metals, alloys, or oxides; however, the cost of nanomaterials obtained in this way remains rather high.[4]

3.1.4.1.2. Methods of Nanodispersion of a Compact Material. Electrolytic erosion can also be used to disperse metals and alloys. In this case, spraying takes place inside a dielectric liquid, and the liquid transformation products coat the surface of the NPs formed.[386] Presumably, small particles are formed on quenching the metal vapor, while large ones are produced from molten drops. Using electrolytic erosion, NPs with a complex composition for permanent magnets have been obtained.[387]

Electrochemical generation is used as a procedure for the synthesis of substantial amounts of rather small (1–2 nm) NPs with a narrow dispersion. A standard electrochemical cell containing an alcohol solution of tetraalkylammonium halide was used to obtain cobalt particles. On passing the current, the cobalt anode dissolved to give Co NPs near the cathode (glass carbon).[388] The electrochemical process was used also to obtain γ-Fe$_2$O$_3$ NPs (3–8 nm), stable in organic solvents due to the adsorption of cationic surfactants.[389]

3.1.4.2. Chemical Synthesis of Magnetic Nanoparticles. Diverse metal-containing compounds (MCCs), including metal carbonyls, organometallic compounds, metal carboxylates, etc., are used as the precursors in the synthesis of MNPs. Most often, precursors are decomposed on heating or UV irradiation. Other types of treatment of MCCs, resulting in nanoparticles, have also been developed.[4] Besides coprecipitation, as the most promising method for chemical synthesis of MNPs, other techniques used are described below.

3.1.4.2.1. Thermolysis of Metal-Containing Compounds. Thermal decomposition of metal-containing compounds has been studied in detail in relation to the development of the scientific grounds of the metal organic chemical vapor deposition (MOCVD) technique, which is used successfully to obtain nanoparticles. In a one-step CVD synthesis of nanodispersed Fe oxides, [Fe(OBu^t)$_3$]$_2$ has been proposed as the MCC.[390] When the reaction is performed in a liquid medium in the presence of surfactants or polymers, it is possible to stabilize the resulting amorphous nanoparticles with diameters of up to 10 nm. An interesting example of two-stage thermolysis of Fe(CO)$_5$ has been reported.[391] First, an iron oleate complex is formed from Fe(CO)$_5$ and oleic acid at 100 °C, and then at 300 °C the complex decomposes to give primary "loose" nanoparticles (4–11 nm). After maintaining them at 500 °C, they are converted, as shown by X-ray diffraction, into crystalline α-Fe nanoparticles. Laser photolysis of volatile MCC (most often, metal carbonyls) is also suitable for this purpose.[392]

3.1.4.2.2. Decomposition of Metal-Containing Compounds by Ultrasonic Treatment. In this procedure, metal carbonyls and their derivatives are used as metal-containing compounds, although cases of the successful use of other organometallic compounds are also known. For example, Co nanoparticles were synthesized by ultrasound-induced decomposition of a solution of Co$_2$(CO)$_8$ in toluene.[393] In order to retain the monodispersity and prevent aggregation of the

particles formed, sodium bis(2-ethylhexyl)sulfosuccinate was added to the solution. Amorphous Co-containing nanoparticles were also obtained by ultrasonic treatment of a solution of Co(CO)$_3$(NO) in decane in the presence of oleic acid. For the synthesis of Fe-containing magnetic nanoparticles, Fe(CO)$_5$ is most often used.[394] Ultrasonic decomposition of iron pentacarbonyl in polyvinylpyrrolidine resulted in amorphous γ-Fe$_2$O$_3$ NPs. Their dimensions were determined by the nature and concentration of the surfactants present in the solution.[395] It was experimentally shown that ultrasonic treatment of labile MCC is a suitable way of producing NPs under mild conditions, which is important for the preparation of metastable aggregates. However, there are no procedures for controlling their dimensions.

3.1.4.2.3. Reduction of Metal-Containing Compounds. Magnetic metallic nanoparticles can be prepared from metal salts using strong reducing agents, namely, alkali metal dispersions in ethers or hydrocarbons, alkali metal complexes with organic electron acceptors (e.g., naphthalene), NaBH$_4$, and other complex hydrides. By using NaBH$_4$ in aqueous solutions at room temperature, both homo- (Fe, Co, Ni) and heterometallic (Fe−Co, Fe−Cu, Co−Cu) NPs were obtained as amorphous powders containing substantial amounts of boron (20 mass % or more). The reduction of CoCl$_2$ with LiBEt$_3$H in the presence of trialkylphosphines yields nanoparticles of pure cobalt ε-phase with sizes between 2 and 11 nm (depending on the alkyl chain length in trialkylphosphine).[396] The general procedure for the preparation of metallic nanoparticles by reducing metal salts in aprotic solvents has been documented.[397] High-boiling alcohols are often used as reducing agents. The reduction of cobalt acetate with dodecane-1,2-diol at 250 °C in oleic acid in the presence of trioctylphosphine gives 3–8 nm metal particles.[398] Nickel-containing nanoparticles have been prepared in a similar way.[399] Yet another procedure of synthesis is represented by radiation chemical reduction of metal ions in aqueous solutions. In particular, γ-irradiation of deaerated solutions of Co^{2+} and Ni^{2+} perchloratesin the presence of sodium formate and a stabilizer (surfactant) affords spherical nanoparticles (2−4 nm) of these metals with a narrow pore size distribution.[400]

3.1.4.2.4. Synthesis in Reverse Micelles. Recent years have seen an intensive development of the synthesis NPs in nanosized reactors, as the size of nanoreactors can be controlled within certain limits. A micelle is an example of these nanoreactors. Reverse micelles are tiny drops of water stabilized in a hydrophobic liquid phase because of the formation of a surfactant monolayer on their surface. Owing to the exactly measured amount of MCC in each micelle (as the nanoparticle formation occurs without substance supply from the outside), it is possible not only to control the composition and the average size of the particles, but also to obtain monodisperse samples with a narrow particle size distribution. Thus, Co NPs have been synthesized by mixing two colloid solutions of reverse micelles with the same diameter (3 nm), one containing CoCl$_2$ and the other containing sodium tetrahydroborate at the same concentration.[401] Magnetic NPs with an average diameter of 5.8 nm and a polydispersity of 11% have been obtained in hexane as a colloid dispersion stable against aggregation and oxidation during a week. Syntheses of cobalt NPs in reverse micelles are described in detail in the literature.[402]

3.1.4.2.5. Sol−Gel Method. The sol−gel method is widely used in a number of technologies.[403] In nanotechnology, it is used most often to obtain metal oxides but is also applicable to

the synthesis of nanosized metals and fused bimetallic and heteroelement particles. For example, reduction of Ni^{2+} and Fe^{2+} ions inserted in silica gel in a 3:1 ratio with hydrogen at 460−650 °C resulted in Ni_3Fe nanoparticles (4−19 nm) within the SiO_2 matrix.[404]

3.1.4.2.6. Synthesis of Magnetic Nanoparticles at a Gas− Liquid Interface. NPs can also be synthesized in the absence of solid substrates or matrices by redox reactions at an interface between two phases, one containing a metal compound (precursor) and the other the reducing agent. A new approach to the synthesis and self-assembly of nanosized structures including magnetic ones in a fully anisotropic two-dimensional reaction system has been reported.[405,406] NPs were synthesized in a Langmuir monolayer of amphiphilic molecules, incorporating the precursor molecules at a gas−liquid interface. Decomposition of metal compounds in such a monolayer initiates the appearance and nucleation of active intermediates and the two-dimensional growth of nanoparticles on the liquid surface. The surfactant molecules of the monolayer can react with the nanoparticles formed and affect the growth processes. The growth and self-organization of nanoparticles can also be affected by changing the chemical composition of the liquid or gas phase, i.e., by adding compounds that react with NPs on the liquid surface, by varying the temperature, or by exposing the monolayer to electric or magnetic fields or different types of radiation (including light).[4] The decomposition of the precursor molecule at the interface can be induced by electromagnetic radiation (in particular, light). This photochemical decomposition of iron pentacarbonyl in the Langmuir monolayer under contact with air produces nanoparticles and nanostructures of iron oxides, mainly γ-Fe_2O_3.[405]

An unavoidable problem associated with particles in this size range is their intrinsic instability over longer periods of time. Such small particles tend to form agglomerates to reduce the energy associated with the high surface area-to-volume ratio of the nanosized particles. This directly lowers their adsorption properties in separation applications. Moreover, naked metallic nanoparticles are chemically highly active, and are easily oxidized in air, generally resulting in loss of magnetism and dispersibility. Thus, it is crucial to develop coating strategies to chemically stabilize and functionalize the naked magnetic nanoparticles during or after the synthesis.[407]

One method for the functionalization of magnetic nanoparticles is ligand exchange, by which the as-synthesized magnetic nanoparticles in an organic phase can be converted into water-soluble ones. Frankamp and co-workers[408] reported that iron oxide nanoparticles dispersed in a toluene solution can be completely transferred into aqueous solution under stirring with octa(tetramethylammonium)−polyhedral oligomeric silsesquioxane (TMA−POSS). Interestingly, this TMA−POSS exchange strategy can be applied to different monolayer-protected magnetic nanoparticles, such as oleic acid stabilized iron oxide nanoparticles, and oleic acid, oleylamine, or hexadecanediol-stabilized FePt nanoparticles. The water-soluble nanoparticles obtained have excellent stability in biologically relevant pH ranges and salt concentrations.

Among the functional groups available are amine, carboxylic acid, aldehyde, thiol, epoxy, hydroxyl, streptavidin, protein A and G, albumin, biotin, and different antibodies.[409] These functional groups anchored to the surface of the magnetic particles are responsible for the separation process, which may occur according to biocompatibility, shape recognition, fluorescent signaling, antigen detection, or physisorption

(Figure 5).[409] However, the immobilization protocols developed should minimize nonspecific adsorption; that is, the
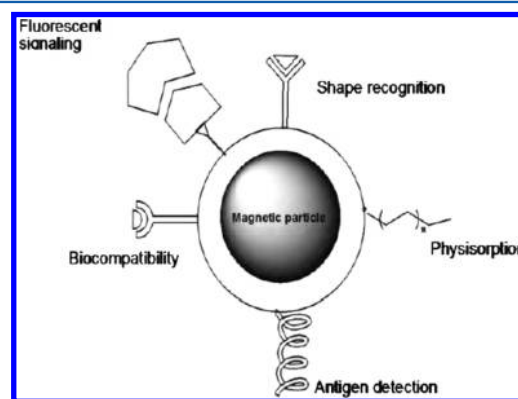

Figure 5. Processes for the analyte adsorption on the surface magnetic particles.[409] Reprinted from ref 409, with Permission from Elsevier. Copyright 2010.

interaction between the functional group and particle surface should be controlled. It has been observed that covalent binding improves particle stability and helps to control the binding sites. Although this has been noted in protein immobilization, it might also be extended to the binding of other active functional groups on magnetic particles. Glutaraldehyde, epoxy compounds, and cyanogen bromide are commonly used cross-linkers for protein immobilization.[410]

3.2. Preparation of Carbonaceous Nanomaterials (CNMs)

3.2.1. Carbon Nanotubes (CNTs). Carbon nanotube synthesis techniques may be classified under three major categories: laser ablation, catalytic arc discharge, and CVD.[411] For analytical purposes, the latter is probably the most interesting, because it permits synthesis on a surface of vertically aligned carbon nanotubes. Various versions of preparation have been used for scale up in which synthesis is performed at relatively low temperatures, with high yields and purity.[412−414] The synthesis of CNTs generally involves catalytic dissociation of organic precursors or graphite, during which nontubular carbons (NTCs) are also formed. Often, the NTCs are formed when the catalyst is exhausted, so most CNT preparations are coated with NTCs on the surface. Unlike the CNT, the NTC tends to have porous structures, leading to a different retention/trapping mechanism that can be diffusion controlled. These NTCs do not have the excellent sorbent characteristics of the CNTs, so purity of the CNTs is an important factor that affects its overall effectiveness as a sorbent.[415,416] The purified CNTs provide more sorption sites on the wall and interstitial spaces between the tubes making it easily accessible for adsorption and desorption, thereby enhancing preconcentration. The NTC cover on the CNTs reduces their availability, because the sorbate has to diffuse through the NTC to reach the CNTs. Moreover, the porous structure of NTC introduces mass transfer limitations, slowing both adsorption and desorption. Understanding these characteristics is important for their applications as separation media.[240]

Acid treatment and gas phase oxidation are the most commonly employed methods for removal of the NTCs and residual catalysts.[417−419] However, these procedures generate oxygen-containing functional groups, for example OH, C=O, and COOH, which increase the polarity, hydrophilicity, and

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ion-exchange capability of the CNTs. Gas phase oxidation of activated carbon mainly increases the concentration of hydroxyl and carbonyl surface groups, and oxidation in the liquid phase particularly increases the content of carboxylic acids.[420] The amount of carboxyl and lactone groups on CNT treated with nitric acid was reported to be higher than when this process was conducted using H_2O_2 and $KMnO_4$.[421] However, one of the main drawbacks of acid-oxidation procedures is CNT fragmentation (shortening) and defect generation in the graphitic network.[422] Besides acid concentration and exposure time, the high ultrasonic power typically employed to disperse CNT agglomerates during oxidation has been identified as an additional source of fragmentation.[423] Gentler methods, for example microwave treatment with dilute acids and chelating agent, can be used as alternatives.[424−426] Thus, a compromise between purification conditions and CNT damage is necessary.

Carbon nanotubes usually contain amorphous carbon and metal catalyst residues as a consequence of the production procedure. In addition, the method produces carbon nanotubes of different sizes, so a purification step is essential before they can be used in many applications. Thus, analytical methodologies are needed so that the nanotubes can be characterized and purified. The raw material can be treated in different ways, such as by adding solvent together with ultrafiltration,[427] via flocculation using surfactants[428] and oxidation,[429] and by acid washing followed by centrifugation, resuspension in surfactant or polymeric media, or cross-flow filtration. Once purified, the carbon nanotube sample obtained is still a broad mixture of SWNT or MWNT with a wide range of lengths and diameters. These geometrical characteristics can dramatically affect the electrical properties of the nanotubes, and they influence their ability to be dispersed in organic or aqueous media and even their interactions with other compounds such as surfactants, polymers, or aromatic compounds. More specifically, gel electrophoresis has been proposed as a preparative procedure for the purification of fluorescent SWNT fragments. As a result, three main fractions are obtained. The method is tedious, and further fractioning of previously separated bands is also required.[430] For this second step, liquid chromatography and (more frequently) capillary electrophoresis have been proposed. Taking into account the poor solubilization of carbon nanotubes in aqueous media, capillary electrophoresis has demonstrated its potential for separating and purifying SWNTs from particulate impurities and for fractioning them by size/length.[240] As indicated in Figure 6,[240] nanotube solubilization is a critical step toward determining purity via capillary electrophoresis. For SWNTs, this shortcoming has been circumvented by suspending the nanotube in either polyvinylpyrrolidone[431] or SDS.[432] Better results were obtained with the latter, as the electrophoretic peaks obtained were narrower. Raman detection was employed in both cases. The purities of the different fractions were confirmed by atomic force microscopy. The main limitation of this methodology is the low reproducibility between runs with regard to the numbers and positions of the peaks that can be ascribed to the heterogeneous nature of the nanotube suspension.[240]

However, CNTs produced by all the methods usually contain NTC and residual catalysts such as Fe, Co, and Ni. Metallic impurities can be as high as 30−40% by weight. An important consideration is the defects that are generated during the purification process and the fact that CNTs may even be oxidized, leading to an alteration of their sorbent characteristics.
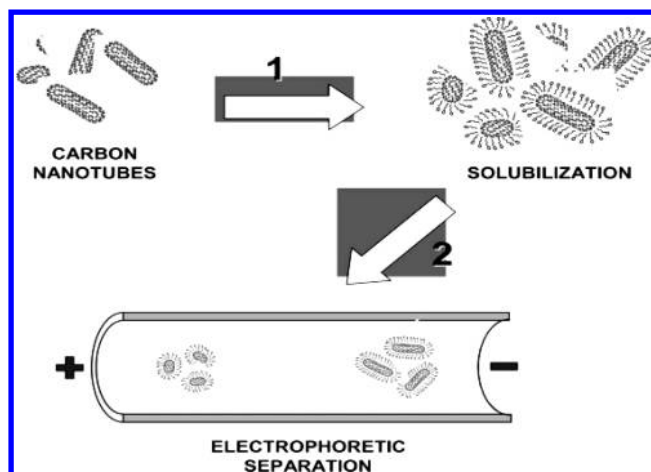

Figure 6. Scheme of the characterization or analysis of carbon nanotubes by capillary electrophoresis.[240]Reprinted from ref 240 with kind permission from Springer Science and Business Media. Copyright 2005.

In general, methodologies for carbon nanotube dispersion/solubilization can be classified into three groups, namely (i) dispersion upon oxidative acid treatments, (ii) noncovalent stabilization, and (iii) covalent stabilization. One of the most commonly used solubilization procedures involves oxidative acid treatment steps such as refluxing in diluted nitric acid or refluxing/sonication in a concentrated H_2SO_4/HNO_3 mixture.[433]A dark supernatant solution containing carboxylated carbon nanotubes is obtained after oxidative acid treatment and several washing/centrifugation cycles. However, this solubilization method can generate surface defects, and it sometimes results in tube shortening. For this reason, many researchers have recommended the noncovalent stabilization of carbon nanotubes in solution, since the structures and properties of the nanotubes are usually preserved after dispersion. This approach means that the carbon nanotubes are solubilized/dispersed in an aqueous environment through derivatization or complexation with micelles, polymers, or other aggregate systems. These aggregates have a hydrophobic core, which contains the nanotube, and a hydrophilic surface, resulting in solubility in water.[434] Sodium dodecyl sulfate (SDS), Triton X-100, and sodium dodecylbenzene sulfonate (SDBS) are typical surfactants used for nanotube dispersion. Nanotube solubilization involves the organic functionalization of the nanotube surface that leads to the product being highly soluble. Although many reactions in this area have been described, the developments of controllable procedures for modifying carbon nanotubes with biologic or bioactive species are probably the most popular, as these represent another important step toward the use of carbon nanotubes in biological and biomedical fields.[435] These modifications, which are particularly important for the development of sensors in analytical science, have been reported in detail elsewhere.[240] Functionalization of CNTs offers a unique opportunity of altering the physical and chemical characteristics of the CNTs.[436,437] The presence of a covalently attached functional group can alter the retention/affinity of the CNT surface and important properties including polarity, hydrophilicity, and other specific interactions. The functional groups may also alter diffusional resistance, reducing the accessibility and affinity of CNT surfaces for certain analytes. Functionalization also enhances interaction with polymers and other

materials, therefore, facilitating the formation of composites which can be used as microtrapping substrates.[438,439] These include polymers and sol−gel type immobilization.[440] Details of CNT functionalization have been presented in several reviews.[441,442]

A variety of covalent or noncovalent approaches have been developed for functionalization of CNTs[443−448] and the synthesis of hybrid structures with interesting properties.[449,450] For example, covalent functionalization can be used to generate functional groups such as COOH or NH$_2$ which can dramatically alter the chemical properties of CNTs and enhance their performance in SPE. This may be particularly relevant to the analysis of polar pharmaceutical compounds with a wide range of pK_a, where pH adjustments are normally warranted to accomplish high extraction efficiency. From a practical standpoint, this poses a major problem in the analysis of mixtures because multiple extractions at different pH values become essential.[451]

3.3. Preparation of Silica Nanomaterials (SiNMs)

3.3.1. Silica Dioxide Nanoparticles (SiO$_2$ NPs). SiO$_2$ NPs received recent attention due to their superior properties over the microsize particles. Different procedures of preparation have been reported for SiO$_2$ nanoparticles including the Stober process,[452] hydrolysis of elemental silicon,[453] sol−gel processing,[454−456] sol-precipitation method,[457,458] ultrasonic irradiation method,[459] microemulsion method,[460] and spark discharge method.[461]

Microporous and mesoporous materials also have become very attractive in sample pretreatment and separation procedures.[462,463] A family of mesoporous materials, the so-called MCM materials (Mobil composition of matter), was developed in 1992 by Beck et al.[464] with Mobil Oil Corporation. These materials have a very high surface area (>1000 m^2 g^{-1}), ordered pore structure (mostly hexagonal packed cylindrical pore channels), and extremely narrow pore size distribution. The pore diameter can be adjusted from 2 to 15 nm. For these reasons, MCM materials have application in sorption and catalysis. The preparation methods involve mixing ceramic precursors, such as silica, in a surfactant solution and reacting the agents at temperatures below 150 °C. An organic surfactant in an aqueous medium forms rod-like micelles that are used as templates to form two or three monolayer silica nanoparticles encapsulating the micelles' external surface. By removing the organic species from well-ordered organic−inorganic condensed phase (by calcination at high temperature, e.g. 450 °C), a porous silicate material with nanosized particles and uniformly porous structure remains.

3.3.2. Silicon Nanotubes (SiNTs). SiNTs have been synthesized by several procedures including the CVD[465] and the hydrothermal methods.[466,467] Martin et al. pioneered a technology, called template synthesis, for preparing mono-disperse nanotubes of nearly any size and composed of nearly any materials.[468,469] These nanotubes offer some interesting advantages for chemical application. However, at present the application of these nanotubes is not common.[470] Zhuqing et al.[471] report a simple method for applying an ion imprinting technique to imprint functional groups into the walls of the template-synthesized sol−gel nanotubes for separation of copper ions.

3.4. Preparation of Nanofibers (NFs)

Nanofibers could be easily fabricated by a process commonly known as electrospinning (e-spinning). Nanofibers possess a high surface-to-volume ratio that leads to a larger specific surface. Furthermore, electrospinning has the ability to control the diameter, morphology, secondary structure, and spatial alignment of electrospun nanofibers.[472] In fact, electrospun nanofibers usually were obtained as a form of membrane or so-called "mat". The major advantages of membrane or mat are a larger media cross sectional area and a decrease in pressure, which allows sample processing at higher flow rates, so it is much easier to deal with large volume samples to obtain a better enrichment coefficient. Therefore, the electrospun nanofibers mat may be a good candidate for use as sorbents for SPE.[282]

3.5. Preparation of Nanoclays

While it is more common to use commercial clays like montmorillonite (in sodium or calcium form, i.e., NaMMT or CaMMT), there are also natural clay minerals like kaolinite (KC), halloysite (HC), and bentonite (BC), or even road dust.[473,474] Several methodologies exist for clay preparation including the sol−gel method,[475] the microemulsion method,[476] the solution-based layer-by-layer (LBL) deposition technique,[477] and the sonication technique.[478] Pascua et al.[479] report the synthesis of a homogeneous monolayer-thick Zn-smectite that will benefit specific applications requiring ultrathin and monodispersed layered nanomaterials. However, most natural and synthetic clay nanoparticles require often tedious preparation methods to remove crystalline impurities and to obtain completely exfoliated forms. Furthermore, the wide range of particle sizes characteristic of commonly available synthetic and natural clays can lead to variable properties and unexpected reactions. Thus, characterization and modification processes are the necessary steps after preparation.

3.6. Polymer-Based Nanoadsorbents

Several methodologies for nanopolymer sphere fabrication have been described, including precipitation, spraying, phase separation, and/or emulsion techniques. Niwa et al.[480] reported a spontaneous emulsification solvent diffusion (SESD) method in which nanosized particles of PLGA or PLA (polylactide) can be obtained by the use of a binary mixture of a water-miscible organic solvent, such as acetone, and a water-immiscible solvent. The particles are formed in the water phase via an emulsification process and a subsequent solvent-evaporation with moderate mechanical stirring. They described four steps for particle formation: (1) the formation of emulsion droplets in the aqueous phase when the polymeric solution is added, (2) quick diffusion of acetone out from each emulsion droplet, drastically reducing its size to nano-order, and (3) the consequent "solvent-evaporation" process, in which the remaining dichloromethane is removed from the system, solidifying the droplets to final polymeric nanoparticles. Murakami et al.[481] pointed out that this method sometimes causes a severe aggregation in the particle formation process due to a considerable amount of residual dichloromethane. Since the water solubility of dichloromethane is slight, the residue can act as liquid bridge and increase particle collisions. They suggested a modified method in which a mixture of two water-miscible organic solvents is used for the polymer solvent, instead of the mixture of water-miscible and water-immiscible organic solvents, and a low hydrolyzation and polymerization grade of poly(vinylalcohol) (PVA) is used as the quasiemulsifier. Their results indicated that the selection of the combination of binary organic solvents is very important for the preparation of nanoparticles. In their preparation of 50/50

(copolymer ratio) poly-D,L-lactide-*co*-glycolide (PLGA) nano-particles, the combination of binary organic solvents, acetonitrile, and alcohol enabled the production of nano-particles without aggregation.

The most common technique for preparation of polymeric templates used in polymer-based nanoadsorbents is the suspension polymerization method. Kaya et al.[291] used this method to produce ethylene glycol dimethacrylate (EGDMA) copolymer beads and the coprecipitation method to prepare nanosized ferric oxide in order to synthesize polymer-based hybrid nanoadsorbents. The obtained EGDMA copolymer beads were further modified with diethylamine and then cross-linked amine-containing beads quarternized with chloroacetone by soaking in a solution of chloroacetone/dimethylformamide. The quaternization yield was followed by analysis of the chloride ions in the final product, which was performed by the mercuric thiocyanate method. The magnetic hybrid sorbent was prepared by coprecipitating Fe^{2+} and Fe^{3+} ions in a NaOH solution and treating under hydrothermal conditions. The chemical reaction may be written as follows:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \qquad (6)$$
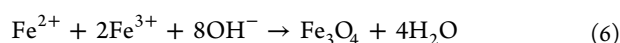
According to this reaction an initial molar ratio of Fe^{3+}/Fe^{2+} (2:1) is needed for the production of Fe_3O_4. Finally, nanosized ferric-oxide-loaded glycidyl-methacrylate-based polymer (GMDFe) was obtained by adding glycidyl methacrylate-based polymer GMD beads into an aqueous solution containing $FeCl_3$ and $FeCl_2$ under vigorous stirring.

3.7. Xerogels and Aerogels

Sol−gel processing refers to the fabrication process of ceramic materials by preparation of a sol, gelation of the sol, and removal of the solvent. Sols are dispersions of colloidal particles in a liquid solvent, and a gel is a solid matrix encapsulating a solvent. In a sol−gel process, the sol can be formed from a solution of colloidal powders or hydrolysis and condensation of alkoxides or salt precursors. In the latter approach, which is much more popular, primary particles of uniform size are formed and grown in a sol, and connect to each other to form aggregates during gelation. These aggregates forming the network of the gel are broken apart into the primary particles in the drying step. Upon calcination and sintering, these primary particles are strongly bound together to form a very rigid and solid network, and a large interparticle space with uniform nanoscale pores is formed. Xerogels are obtained by drying the gels through evaporation at normal conditions under which capillary pressure causes shrinkage of the gel network, while aerogels are produced by drying the wet gels at supercritical conditions where the liquid−vapor interface is eliminated, and relatively little shrinkage of the gel network occurs. The sol−gel process offers a very high flexibility to tailor xerogels and aerogels for specific applications by manipulating the synthesis conditions.[482,483] A microporous silica that was synthesized with tetraethyl-ortho-silicate (TEOS) as precursor had an average pore size of 6.4 Å, pore volume of 0.24 cm^3 g^{-1}, and Brunauer−Emmett−Teller (BET) surface area of 588 m^2 g^{-1}. However, this material lost about 90% of its microporosity when it was heated at 600 °C for 30 h. By doping with 1.5% of alumina, the thermal stability of this microporous silica was significantly improved.[484]

3.8. Decreasing the Size Distribution of Nanoadsorbents

The most significant issues in the preparation of well-defined nanomaterials for further studies and applications ares

purification and selection of size distribution. Many methods have been reported for the size-based separation and/or concentration of NPs, such as centrifugation,[485] size exclusion chromatography,[486] gel electrophoresis,[487] diafiltration,[488] size-dependent solubility,[489] and fractional crystallization.[490] These approaches may lead to issues with aggregation, instability, cost, undesired coatings, and less effective protocols for NPs of smaller size. As a result, these methods are time intensive, expensive, toxic, or inefficient. In particular, nanoparticles, which are smaller than 100 nm, are important in a natural system because of their high surface area and surface reactivity and their associated properties of adsorbing or binding to organic and trace metal contaminants. This is most likely due, at least in part, to differences in surface and near-surface atomic structure, as well as crystal shape and surface topography as a function of size in this smallest of size regimes.[491] Therefore, these variations may make a difference in the kinetics and mechanisms in nanoparticle reactions. Mayo et al.[492] reported that 12-nm particles of magnetite are roughly 200 times more effective at removing As(III) and As(V) from water than 20- and 300-nm particles, indicating significant size-dependent effects.

High degrees of purity and monodispersity are often crucial, and those preparation methods in which high purity, free of excess ligand, salt, and starting material would be maximized and low polydispersity and down-sizing the distribution could be accessible are superior. Also, removal of nanoparticle monomers and aggregates from well-defined self-assembled nanoparticle superstructures is considered a great challenge.

Compared to conventional methods such as centrifugal, vacuum/pressure, and syringe-driven filtration separation, ultracentrifugation is considered as one of the most qualifying methods to separate fine particles, including nanoparticles, from solutions. However, nanoparticles are more difficult to separate than coarse particles because they need more time and higher centrifugal force for sedimentation.[493] Microfiltration and ultrafiltration have been widely used for separating fine particles, colloids, and nanosized materials for basic chemicals and synthetic fertilizers, wastewater treatment, environmental protection, drinking water treatment, the food industry, and biotechnology, as well as others.[494] The efficiency of membrane filtration is dependent on the feed suspension properties (particle size), membrane properties (i.e., pore size, membrane charge, morphology, and hydrophobicity), and hydrodynamics (pressure, flow velocity).[495]

Diafiltration is an alternative way that shows considerable potential for the efficient and convenient purification and size separation of water-soluble nanoparticles, allowing for the removal of small-molecule impurities and for the isolation of small nanoparticles from larger nanostructures in a single process.[488]

Diafiltration is a membrane-based method wherein pore size dictates the retention and elution of material from a sample, as depicted in Figure 7.[488] This approach offers the opportunity to consolidate purification and size separation into a single step, making diafiltration more efficient than any combination of previously reported techniques. Due to simple equipment requirements and the scalability of the technique, diafiltration is affordable, convenient, and versatile. Furthermore, the membranes can be reused, and organic solvent dependence is reduced, contributing to greener nanoparticle syntheses.[496] According to Sweeney et al.,[488] when the volume of material eluted is equal to the hold-up volume in the reservoir, this is
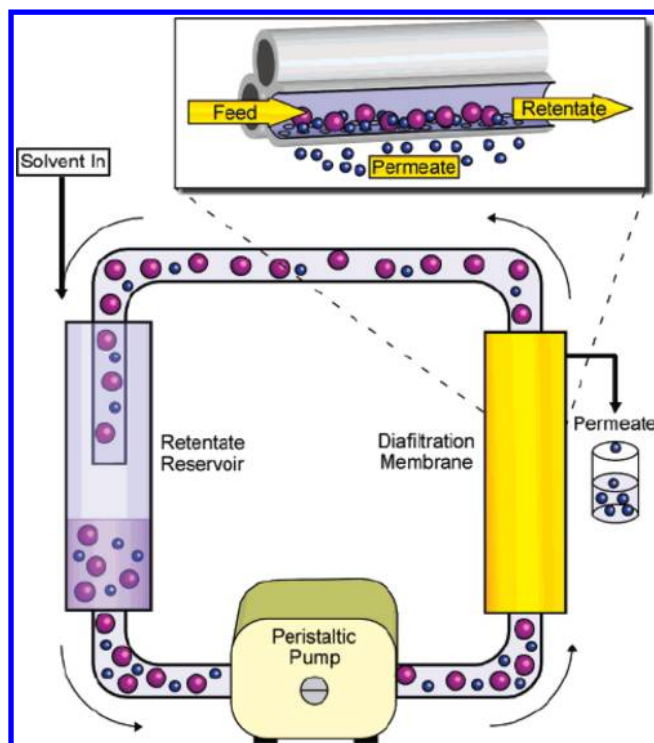
Figure 7. Schematic of the continuous diafiltration setup used in this study. Sample and makeup solution are introduced to the retentate reservoir. The solution is pumped by the peristaltic pump through the diafiltration membrane. Small molecule impurities or small nano-particles (blue) are eluted in the permeate, while the large nanoparticles (purple) are retained. The expanded view is of a hollow-fiber-type diafiltration membrane and depicts the elution of small impurities and nanoparticles and the retention of larger particles.[488] Reprinted with permission from ref 488. Copyright 2006 American Chemical Society.

considered one diafiltration volume. The diafiltration is continued through a number of volumes until the purification or size separation is complete. The relationship between the percent purity (% P) and the number of diafiltration volumes (V_D) is given by

$$P\% = \left(1 - e^{V_D(1-\sigma)}\right) \times 100 \tag{7}$$

where V_D is diafiltration volumes and σ is the rejection coefficient, which is determined experimentally for different solutes and is affected by pore morphology, nanoparticle properties (such as core diameter and surface functionality), and solution properties (such as ionic strength). In the case of purification, σ is 0; meaning that five diafiltration volumes are necessary to see complete purification. In the case of size separation, 15 volumes ($\sigma = 0.33$) are often necessary. Moreover, diafiltration membranes are rated by their nominal molecular weight cutoff (MWCO). In the case of nanoparticles, the MWCO can be correlated to such nanoparticle properties as core size, ligand shell thickness, and hydrodynamic radius, and to solution properties such as pH and ionic strength.

Unlike other membrane filtration techniques, such as dialysis or stirred-cell ultrafiltration, diafiltration is considered a continuous flow process, wherein the sample to be purified or separated is continually passed over the membrane surface. While traditional ultrafiltration can be hindered by the buildup of material on the membrane surface, the continuous flow and constant volume of diafiltration contribute to a lower incidence of membrane fouling. As compared to dialysis, wherein filtration occurs via passive means, hydrostatic pressure as a result of continuous flow is the driving force behind diafiltration. Additionally, each diafilter contains a number of membrane surfaces, greatly enhancing the surface area available for filtration. Due to the continuous flow and high surface area of this technique, diafiltration allows for very efficient and rapid purification and size separation.[497]

4. APPLICATIONS IN AQUEOUS MEDIA

As mentioned before, although nanomaterials have a wide range of applications in different scientific and technological fields, the aim of this paper is to review the nanomaterials which have been used for analytical purposes and investigate their role in the past two decades as adsorbents in preconcentration and clean up processes. According to the variety of inorganic and organic analytes of interest in the environment, and, on the other hand, since the interactions between nanoadsorbents and metal ion/organic compounds are totally different, the applications of investigated nanomaterials in this section are divided into different categories, evaluating their role as adsorbents and in separation processes of metal ions, organic compounds, and gaseous species.

4.1. Nanoparticles

4.1.1. Metallic Oxide Nanoparticles. *4.1.1.1. Aluminum Trioxide Nanoparticles (Al₂O₃ NPs). 4.1.1.1.1. Metal Ions.* The preparation of this nanoalumina is very simple and inexpensive compared to other commercially available solid phase materials. Fine Al_2O_3 nanopowders, with a large specific surface, have been widely used as sorbents in recent years. Solid phase extraction of trace quantities of copper ions on modified alumina nanoparticles was investigated by Manzoori et al.[134] They assessed modification of the surface via SDS and examined various parameters such as pH, amount of ligand, flow rate, type of eluting agent, and volume of eluent. The volume of the sample was also investigated. The method was successfully applied to the determination of Cu in water and food samples by flame atomic absorption spectrometry (FAAS). Afkhami et al.[498] investigated adsorption conditions for Pb(II) and Cr(III) ions on alumina nanoparticles prior to their determination by flame atomic absorption spectrometry (FAAS). The sorbent was prepared by immobilization of 2,4-dinitrophenylhydrazine on nanoalumina coated with sodium dodecyl sulfate. For utilization of the sorbent, the procedure was examined according to several factors including sample pH, flow rates of samples and eluent, type of eluent, breakthrough volume, and potentially interfering ions. Lastly, the method was successfully applied to the evaluation of these trace and toxic metals in various water, food, industrial effluent, and urine samples. Kalfa et al.[499] used nanoscale alumina on single walled carbon nanotubes for determination of cadmium ions and its adsorption capacity. The mentioned adsorbent was synthesized through a sol–gel method, and it was shown that attaching nanoparticles to the surface of materials alters some of the most important properties of the matrix and offers the possibility of creating composite materials with unique physical properties and reactivity. It was notably mentioned that the adsorption capacity of the synthesized material to cadmium ion was higher than that of SWCNT and the physical condition of the material is more appropriate to use in a column technique than SWCNT alone. A more homogeneous column could be obtained with

alumina on SWCNT. Finally, cadmium(II) ions were determined by FAAS.

4.1.1.1.2. Organic Compounds. Afkhami and Bagheri[140] presented a sensitive method for the determination of formaldehyde (FA) based on the use of modified alumina nanoparticles for its preconcentration and followed by UV−vis spectrophotometry. Alumina nanoparticles were chemically modified by immobilization of 2,4-dinitrophenylhydrazine (DNPH) via sodium dodecyl sulfate as a surfactant. The formaldehyde retained on the modified adsorbent was then desorbed and determined via its catalytic effect on the oxidation of thionine by bromated ion. Factors affecting the preconcentration and determination of formaldehyde, like pH, amount of sorbent, shaking time, flow rate, nature of the eluent, eluent volume, and sample volume, were investigated. Preconcentration by this method significantly improves the limit of quantification over other methods. Also, preconcentration using DNPH-γ-Al$_2$O$_3$ is one of the most sensitive approaches for formaldehyde detection without requiring derivatization methods, while being considerably more rapid. An important feature of this study is that the authors grafted functional groups on the surface of inorganic substrate γ-Al$_2$O$_3$ nanoparticles. These functionalized nanoparticles exhibited high sorption ability for FA from real samples. This novel design strategy provided superior advantages for the nanosorbent in practical applications. Considering that amine groups can adsorb FA from samples, the amine grafted γ-Al$_2$O$_3$ nanoparticles were employed to extract FA. For both column and batch experiments, the results indicated that the modified adsorbent provides better sorption ability in comparison to naked alumina. The method was successfully applied to the quantitation of formaldehyde in water, food, and certain biological samples.

The characterization of nanosized mesoporous γ-alumina obtained by the template method using dodecylamine and aluminum isopropoxide as the aluminum source, and its potential application as Congo red adsorbent from aqueous solution, was assessed by Renuka et al.[500] Congo red is a secondary diazo dye, which is known to metabolize to benzidine, a human carcinogen. Allergic reaction and anaphylactic shock also have been reported on exposure to Congo red. The dye removal after filtration and optimization of the adsorption studies were carried out using UV−vis spectrophotometry. Meso alumina was identified as the most efficient solid for the adsorptive removal of Congo red. The high surface area that is achieved due to the nanosize and mesoporous texture of the particles is decisive in attaining this high activity. Apart from this, abundant surface hydroxyl groups also contribute to higher adsorption efficiency of the system, as metal cationic centers generated by the release of OH$^-$ from the surface are believed to be the active centers for Congo red adsorption in meso alumina nanoparticles.

4.1.1.2. Zinc Oxide Nanoparticles (ZnO NPs). 4.1.1.2.1. Gaseous Species. Zinc oxide (ZnO) is considered as an excellent candidate for gas cleaning applications. A nanosize ZnO was synthesized by a matrix-assisted method, and a study on the synthesized ZnO was carried out to determine a new possible application to the hot gas desulfurization (HGD) process in the integrated gasification combined cycle (IGCC) power plants.[501] Sorbents for an ultragas cleaning in HGD are needed in order to have not only a fast reaction rate in a gas−solid phase reaction, but also a high sulfur capacity to reduce the concentration of sulfur compounds contained in a gasified

fuel gas from 50 ppmv to 60 ppbv. Sorbents have to present a high surface area to meet this requirement. Park et al.[142] formulated nanosize zinc oxide sorbents for the effective removal of sulfur compounds (H$_2$S) at a very low concentration (under 50 ppmv) in a gasified fuel gas. In this study, the sorbents were prepared by a matrix-assisted method. An active carbon was used as a matrix, and zinc acetate (Zn-(C$_2$H$_3$O$_2$)$_2$·2H$_2$O) was selected as a precursor. About 10−40 wt % of zinc was doped over the activated carbon in the preparation of the sorbents. The content of zinc doped over the activated carbon had an influence on the morphology of the zinc oxide nanostructure. The reactivity tests for desulfurization of the ZnO nanostructures, with various morphologies, were performed in a fixed bed reactor. Their reactivity increased as their sizes became smaller and their surface areas became larger. The outlet gases from the reactor were automatically analyzed by gas chromatography (GC). Most prepared nanosize zinc oxides showed an excellent performance for the removal of H$_2$S at a very low concentration.

4.1.1.3. Titanium Dioxide Nanoparticles (TiO$_2$ NPs). Anatase-TiO$_2$ due to its strong photoinduced redox power was found to be a superior photocatalytic material for purification and disinfection of water and air, as well as remediation of hazardous waste.[502] TiO$_2$ NPs have been widely used for preconcentration and separation of trace and ultratrace metal ions and organic pollutants.

4.1.1.3.1. Metal Ions. Recently, the determination of ultratrace metals, including cadmium, in environmental and food samples has become more serious because of increasingly lower limits imposed on the trace metal contents of such samples. The direct determination of extremely low concentrations of metals by modern spectroscopic methods is still difficult due to insufficient sensitivity of the techniques and matrix interferences. In order to overcome this problem, preliminary separation and/or preconcentration techniques for the separation of trace metals from complex matrices into a known matrix are widely used. Among the preconcentration techniques, SPE has been increasingly used compared with other classical methods. Numerous substances have been synthesized and used as solid phase extractor.[2]

Advantages are the following: There is no need for loading of any chelating and/or complexing agent or microorganism onto the sorbent before the preconcentration procedure to obtain quantitative recovery of metal ions. This minimizes possible contamination and interferences due to the reagents. This feature also allows repeated use of the sorbent. The method permits the study in acidic medium that minimizes precipitation of metal hydroxides. The main disadvantage of the proposed procedure is the duration time of the preconcentration.[2,9]

Quétel et al.[161] assessed the Fe-solid phase extraction from coastal seawater using anatase-TiO$_2$ nanoparticles. Adsorption processes were compared in batch and on-(mini)column extraction approaches combined to external calibration and detection by inductively coupled plasma mass spectrometry (ICP-MS). TiO$_2$ (anatase) was optimally used at pH 7 for the extraction of iron from seawater, and the results also showed that it is more efficient with seawater than with ultrapure water. At pH 2 there also was retention, but it was 6.9 and 4.8 times lower for the ultrapure water and the seawater, respectively. They also investigated the TiO$_2$ surface sites interacting with Fe by Fourier transformed infrared (FTIR) spectroscopy under varying conditions of salinity and pH. The use of TiO$_2$ for the

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extraction of Fe from seawater samples at μg L^{-1} levels was novel.

4.1.1.3.2. Organic Compounds. Mesoporous TiO$_2$ NPs have been observed to be the most efficient for the degradation of 4-chlorophenol. The TiO$_2$ has smaller particle sizes and higher surface area than the catalysts, and less pore volume, attributed to less reactivity for the degradation of 4-chlorophenol. Each of the operating variables applied in this study,[503] such as ultrasonic irradiation time, power density, reactor sizes, temperature of the reaction mixture, stirring effect, and the H$_2$O/TTIP (titanium tetraisopropoxide as the precursor) ratio, was found to have a specific and major role in controlling the physicochemical properties of the TiO$_2$ particles investigated, but no greater influence was observed with liquid phase reaction. Gaseous pollutants may show high influence on slight changes of the parameters of TiO$_2$.

Shahrezaei et al.[504] explored the potential application of TiO$_2$ nanoparticles for removal of phenol and phenolic derivatives from petroleum refinery wastewater. The removal of phenol was investigated in terms of various parameters, namely pH, temperature, and catalyst concentration. The determination of phenol and phenolic derivative compounds was carried out by GC. The results showed that, at optimum conditions, remarkable removal of 90% of phenol after 2 h can be achieved. The main feature was the use of inexpensive and recoverable nanosized titania, which may be considered for preliminary application in the refinery wastewater treatments after physicochemical treatments to avoid solids and colloids.

4.1.2. Metallic Nanoparticles. *4.1.2.1. Gold Nanoparticles (Au NPs). 4.1.2.1.1. Metal Ions.* Layer-by-layer self-assembly has become a popular and promising alternative for immobilization of enzyme molecules mostly owing to its simplicity, versatility, and the establishment of a high level of order on a molecular scale. Gold nanoparticles can be strongly bound to the surface through covalent bonds with the polymer functional groups, such as CN, NH$_2$, or SH, and a gold nanoparticles monolayer can be prepared by self-assembly on the polymer-coated substrate. Gold nanoparticles can immobilize enzymes on the basis of chemical adsorption. What is more, biological macromolecules retain their activity when adsorbed on gold nanoparticles. Yang et al.[505] developed a renewable potentiometric urease inhibition biosensor based on self-assembled gold nanoparticles for the determination of mercury ions. Gold nanoparticles were first assembled on the surface of a PVC-NH$_2$ membrane containing *N,N*-didecylaminomethylbenzene (DAMAB) as a neutral carrier. Then, urease was immobilized on the gold nanoparticles through chemical adsorption. The response characteristics of the DAMAB/PVC-NH$_2$ pH-sensitive membrane and the effects of the nanoparticles' size were investigated. An advantage of the self-assembled immobilization is that the assembled gold nanoparticles and inactive enzyme layers denatured by Hg^{2+} can be rinsed out via a saline solution with acid and alkali successively. This sensor is generally of great significance for inhibitor determination, especially in comparison with expensive base transducers.

SPE is one of the most widely used tools for the preconcentration and cleanup of analytical samples, for the purification of various chemicals, and for the removal of toxic or valuable substances from aqueous solutions.[506] SPE has gained wide acceptance because of its ease of operation, high recoveries, reproducibility, and commercial availability of appropriate sorbents. Gunduz et al.[507] used gold nanoparticles

(Au NPs) as a new chemical modifier for the determination of arsenic and antimony in salt solutions by electrothermal atomic absorption spectrometry (ETAAS). The Au NPs were prepared by reducing chloroauric acid with sodium citrate. The effects of pyrolysis and atomization temperatures, as well as the amounts of interferents and modifier on the sensitivities of arsenic and antimony, were investigated. The authors successfully utilized Au NPs for the determination of the two metals in certified reference materials and spiked seawater samples. Leopold et al.[508] applied gold-coated silica as a preconcentration phase for the determination of total dissolved mercury in natural waters using atomic fluorescence spectrometry (AFS). The adsorbent was prepared by chemical reduction of a Au(III) solution with hydroxylamine in the presence of suspended silica particles. The resulting Au nanoparticles on the silica surface were highly efficient for adsorbing different mercury species from acidified waters without additional reagents. The acidified aqueous samples were passed over the microcolumn in which gold-coated silica adsorbent is packed, either incorporated in a fully automated flow injection (FI) system directly coupled to the AFS or as part of a portable FI system for *in situ* preconcentration. After rinsing and drying of the column, Hg^0 was released by heating and directed to the AFS cell for quantification. The method offers significant advantages because no reagents are needed for species conversion, preconcentration, sample storage, or desorption, and therefore the risk of contamination is minimized and blank values are lowered.

4.1.2.1.2. Organic Compounds. Self-assembly arrays of Au NPs have several applications in separation processes. The selective determination of cysteine by the resonance light scattering technique based on self-assembly of gold nanoparticles was examined by Li et al.[509] They studied the interaction between cysteine and gold nanoparticles and concluded that through the covalent combination with the SH group and the electrostatic binding with the NH$_3^+$ group of cysteine, gold nanoparticles can self-assemble to form a network structure, which results in greatly enhanced resonance light scattering (RLS) measuring with fluorescence spectrometry. The experimental results demonstrate that the RLS technique offers a sensitive tool for investigations of self-assembly of nanoparticles. On the other hand, the RLS method can be applied to selectively determine cysteine with high sensitivity and simple operation, and none of the amino acids found in proteins interferes with the determination. Parameters influencing the determination of cysteine, such as pH of solution, buffer concentration, concentration of gold nanoparticles, and the influence of incubation time on RLS intensity, were respectively routed and optimized. Moreover, the principle of the proposed method offers high selectivity for the determination of cysteine because only cysteine contains both the NH$_3^+$ and the SH groups among all kinds of amino acids found in proteins. Therefore, this method can be applied directly to determine cysteine in the mixture of amino acids found in proteins without separation.

The applications of Au NPs in solid phase extraction for HPLC,[510−512] GC,[513] and CE[514] analysis of different organic samples have been reported. A novel alternative approach using the so-called solid phase nanoextraction (SPNE) for the preconcentration of polycyclic aromatic hydrocarbons (PAHs) from drinking water by using Au NPs as adsorbent was proposed by Wang et al.[510,511] The optimization of experimental parameters led to a novel procedure with excellent

analytical figures of merit, high recovery, and short analysis time. Moreover, as the entire extraction procedure consumes less than 100 μL of organic solvents per sample, the method can be considered an environmentally friendly approach for routine analysis of numerous samples. The small volume of extracting solution makes SPNE a relatively inexpensive extraction approach in comparison with other micro and conventional SPE procedures. In particular, preconcentration of aromatic analytes on Au NPs was successfully used to improve the analytical recovery during the analysis of monohydroxy-PAHs (OH-PAHs) in urine samples.[511] In this case, a typical SPE-HPLC procedure is profitably combined with SPNE. The reported data from human urine samples provide a general prospective for the excellent potential of the new approach for the analysis of OH-PAHs. Liu[514] studied preconcentration and separation of neutral steroid analytes by the use of gold nanoparticles. This work describes the preconcentration of three neutral steroids (testosterone, progesterone, and testosterone propionate) through a combination of off-line preconcentration using a Au NP-coated silica gel SPE sorbent prior to online preconcentration using sweeping micellar electrokinetic chromatography (MEKC). In the initial phase of this study, the sweeping-MEKC parameters for the capillary electrophoresis (CE) separation of the steroid analytes were optimized. Next, under the optimized sweeping-MEKC operating conditions, a commercial C_{18}-bonded silica gel, and a Au NP-coated silica gel were tested for their use as SPE sorbents for the SPE–sweeping-MEKC preconcentration of steroid-spiked urine samples. Of these two sorbents, the Au NP-coated SPE sorbent displayed superior cleanup efficiency toward the sample matrix. Size exclusion chromatography (SEC) was used to characterize the interactions between urinary proteins and the Au NPs. The results indicated that the removal of the interfering signals from the urinary proteins was probably due to their interactions with residual Au metal surfaces of the Au NP-coated SPE sorbent. When combining the optimized sweeping-MEKC operating conditions with an SPE strategy for the analysis of steroid-spiked urine samples, the authors found that the use of Au NP LBL-coated SPE materials not only concentrated the neutral steroids effectively through hydrophobic interactions with the Au NP-capped silica gel, but also removed the interfering signals from urinary proteins through their interactions with residual Au metal surfaces. The results suggest that this Au NP-coated silica gel is a suitable SPE sorbent for the preconcentration of neutral analytes for clinical sample analysis.

The first application of Au NPs in capillary GC was described by Gross et al. in 2003.[515] They prepared monolayer-protected Au NPs by covalent immobilization of dodecanethiol onto the Au surface. A Au NP film was deposited in a 2-m-long and 530-μm-i.d. deactivated silica capillary by using gravity to flow the solution containing the Au NP material through the capillary. By SEM analysis, the average film thickness was estimated to be 60.7 nm and uniformly distributed over the majority of the inner capillary surface.

In addition, more impressive GC separations were afforded by using a dodecanethiol Au NP stationary phase within a microchannel environment with a 1.3-m-long, square (100 μm × 100 μm) capillary column as a model for high speed microfabricated GC.[516,517] The thickness of the Au NP phase along the capillary walls was determined to be 15 nm by SEM analysis. When the film depth was very uniform, the chromatographic performance was very high, and even mixtures

of seven analytes were well-separated within 2 s.[518] Furthermore, application of the square capillary Au NPs column as the second column of a comprehensive 2D GC system was also explored carefully.

It has been reported that the number of layers of Au NPs coated on the silica gel affect the preconcentration performance for steroids.[171] The efficacy of preconcentration prior to GC analysis by using a sorbent constructed from silica gel capped with self-assembled noctadecanethiol and Au NPs has been described.[518] Qu and co-workers[518] also synthesized the organic–inorganic hybrid of n-octadecanethiol (C_{18}–Au NPs) and packed the material into a 100-μm-i.d. capillary column to conduct capillary HPLC (μHPLC) experiments. They considered that Au microspheres have great potential to become promising substitutes for silica-based stationary phases for μHPLC because of their stability at high pH, enough rigidity, and easily chemical modification. Their results showed that the new packing material behaves basically as a reversed phase.

An alternative mode of capillary electrochromatography (CEC) is OTCEC, in which the stationary phase is coated on the inner wall of the open capillary column. When compared to packed-column CEC, the main advantages of OTCEC are its high efficiency, its simple instrumental handling, and the short conditioning times. The first covalent immobilization of Au NPs on the prederivatized fused silica capillaries, and their application in OTCEC was published by O'Mahony and co-workers in 2003.[519] Liu et al.[520] investigated the self-assembly strategy of Au NPs onto OTCEC columns to enhance the phase ratio. To increase the loading density of Au NPs on the surface of the capillary, LBL assembly is a simple preparation technique for the structural organization of a large variety of Au NPs into multilayer films.[520,521] The covalently immobilized Au NPs are either modified with several alkanethiols of variable lengths (1-hexanethiol, 1-octanethiol, 1-dodecanethiol, and 1-octadecanethiol) to create a hydrophobic monolayer film, or LBL technology based on the (several times) repeated modification of the Au NPs surface with 1,9-nonanedithiol and Au NPs is employed to provide a multilayered film on the inner capillary wall (Figure 8, left).[171] The effect of Au NP layers was studied, and retention of the hydrophobic analytes significantly increased with the number of layers created in the capillary; the four-layer film was considered to be the optimal arrangement (Figure 8, right). Through the self-assembly onto Au NP-coated capillaries, three neutral steroid drugs, testosterone, progesterone, and testosteronepropionate, were successfully separated on OTCEC columns prepared by the LBL process.[521] In addition, this system provides reproducible retention times and characteristic reversed phase behavior.[31]

The use of alternating NPs was studied in CE systems[522,523] at least 10 years ago. However, the first article describing the real application of Au NPs for CE separation was reported in 2001.[524] Grushka and co-workers used capillaries[524] and microchannels[525] coated with organically modified Au NPs to improve selectivity and control the electroosmotic flow (EOF). Recently, Au NPs with either covalently functionalized carboxylic acid or amine surface groups were applied to CE separation of neutrotransmitters (DA, EP, and pyrocatechol).[526] Grushka and co-workers describe three Au NP-specific mechanisms to explain the impact of the presence of Au NPs and their surface chemistry in separation. CE is now a powerful analytical tool for biomolecule analysis.
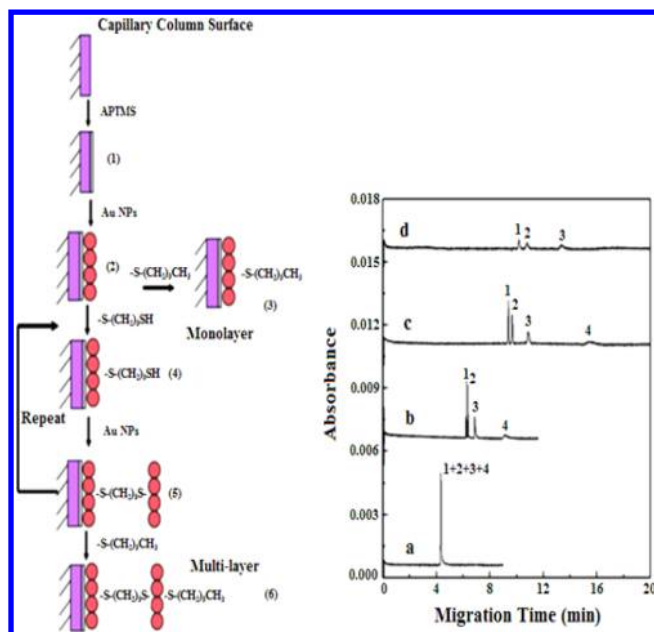
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Figure 8. (Left) Schematic representation of the process used to coat capillary columns with films of self-assembled alkanethiols on monolayers and multilayers of Au NPs. (Right) Electrochromatograms obtained from the CEC separations of a test mixture of steroid drugs: (a) one, (b) two, (c) four, and (d) seven layers. Samples: (1) EOF, (2) testosterone, (3) progesterone, and (4) testosterone propionate.[171] Reprinted from ref 171 with kind permission from Springer Science and Business Media. Copyright 2011.

4.1.3. Nanostructured Mixed Oxides. 4.1.3.1. Fe–Ti Mixed Oxide Nanoparticles. 4.1.3.1.1. Metal Ions.

Gupta et al.[179] reported the use of iron–titanium binary mixed oxide for arsenic removal from the groundwater environment of West Bengal (India) and Bangladesh. Iron(III) oxide, available in various mineralogical forms, had been used for the removal of arsenic from water and reported to have higher sorption affinity for arsenic(V) than for arsenic(III).[527] Moreover, the groundwater environment of West Bengal (India) and Bangladesh is anoxic, and the concentration of arsenic(III) had been reported to be much higher than arsenic(V) in the groundwater in those areas. Harvey et al.[528] reported the ratio of As(III) to As(total) to range between 0.6 and 0.9 in groundwater at Bengal basin. Therefore, when the separate hydrous iron(III) oxide and hydrous titanium(IV) oxide packed beds were used for the filtration of groundwater with high arsenic contents, the former showed lower efficiency than the latter,[529] because titanium-(IV) oxide, a well-known photocatalyst, can oxidize arsenic(III) to arsenic(V)[530,531] and As(V) can be sorbed in the packed bed. Moreover, recent trends showed the use of nanostructured materials for the arsenic sorption.[532,533] Thus, considering this scenario on the use of nanomaterials, it is thought that titanium(IV) incorporated nanostructured hydrous iron(III) oxide might be a material that could be capable of scavenging arsenic from the contaminated groundwater with better efficiency than the pure hydrous iron(III) oxide.

4.1.4. Magnetic Nanoparticles (MNPs).

Functional magnetic nanoparticles have been chosen for new sorbents considering these main advantages: Magnetic nanoparticles can be produced in large quantities with simple methods. It can be expected that their adsorption capacity is higher because of their larger surface area. As these particles are super-

paramagnetic, the metal-loaded sorbent can be easily separated from the treated aqueous media via an external magnetic field.

MNPs have been successfully applied to separate some proteins, organic compounds, and metal ions.[62,534]

4.1.4.1. Metal Ions.

Hu et al.[535] employed magnetic Fe_2O_3 nanoparticles as sorbent for the removal and recovery of Cr(VI) from wastewater. The adsorption capacity was found to be very high. Fe_3O_4 NPs modified by mercaptopropyltrimethoxysilane or gum Arabic were explored for preconcentration of some heavy metal ions and tellurium.[536] Cyanex 272 was used to prepare magnetic alginate doped microcapsules for nickel adsorption.[537] Khajeh et al.[199−204] used magnetic nanoparticles for copper, lead, manganese, and zinc uptake from water and biological samples. Poly(1-vinylimidazole)-grafted magnetic nanosorbent was also synthesized and used to separate copper ions.[538]

Suleiman et al.[539] investigated separation/preconcentration of trace amounts of Cr, Cu, and Pb in environmental samples by magnetic solid phase extraction with Bismuthiol-II-immobilized magnetic nanoparticles and their determination by inductively coupled plasma optical emission spectrometry (ICP-OES). The separation of the target analytes from the aqueous solution containing the target analytes and Bismuthiol-II-immobilized magnetic nanoparticles was simply achieved by applying an external magnetic field. Optimal experimental conditions including pH, sample volume, eluent concentration and volume, and coexisting ions were studied and established. Finally, the method was successfully applied to the determination of target analytes in river and lake water samples. In comparison with well-known methods, the method proposed by the authors is characterized with high enrichment factor, fast separation, and low detection limits.

4.1.4.2. Organic Compounds.

Bai et al.[540] used a magnetic solid phase extraction utilizing a new sorbent of carbon-ferromagnetic nanocomposite proposed for the extraction of PAHs in environmental samples. The sorbent was specially designed with a hydrophobic sublayer and a hydrophilic surface, which endows the sorbent with some unique features: the former shows high extraction capability for the PAHs, and the latter provides benign compatibility with the sample matrix. The sorbent can be easily dispersed in aqueous solutions for extraction, and no additional stirring or shaking was necessary to facilitate the dispersion, which may bring operational convenience especially for on-site sampling and extraction. Parameters affecting the extraction efficiency were nanoparticle amount, shaking speed, extraction time, desorption solvent, desorption time, and salt addition. Finally, the new sorbent was successfully used for the extraction of PAHs in lake water samples prior to determination by gas chromatography–mass spectrometry (GC–MS).

Cetyltrimethylammonium bromide-coated magnetic nanoparticles were used by Zhao et al.[541] for the preconcentration of phenolic compounds from environmental water samples. Their research investigated the adsorption of cation surfactants, cetyltrimethylammonium bromide (CTAB) and cetylpyridiniumchloride (CPC), onto magnetic nanoparticles and the application of this mixed hemimicelles solid phase extraction method for the preconcentration of several typical phenolic compounds from environmental water samples. In this novel SPE method, the charged surfactants CTAB and CPC form mixed hemimicelles on Fe_3O_4 NPs, which causes retention of analytes by strong hydrophobic and electrostatic interactions. The SPE method combines the advantages of mixed hemi-

micelles and magnetic nanoparticles. The main factors affecting the adsolubilization of analytes, such as the amount of Fe_3O_4 NPs and surfactants, the type of surfactants, the solution pH, the sample loading volume, and the desorption conditions, were investigated and optimized. The advantages of this new SPE method include high extraction yields, high breakthrough volumes, short analysis times, and easy preparation of sorbents. Coupling this novel SPE technique with high-performance liquid chromatography separation and fluorescence detection, a highly selective SPE-HPLC-FLD analytical method was established. The reliability of this method was proven by the extraction and analysis of the three target compounds in environmental water samples.

4.2. Carbonaceous Nanomaterials (CNMs)

4.2.1. Carbon Nanotubes (CNTs). Carbon nanotubes, especially SWNTs, hold great promise for advanced applications in aerospace, electronics, and medicine. However, these industries require materials that have been subjected to rigorous quality controls. There are currently no generally accepted standards for quality assurance or quality control among the commercial suppliers of carbon nanotubes. Therefore, the study of these materials as an analytical target is a subject of great interest. The main applications of carbon nanotubes are given in Figure 9,[240] which shows that carbon
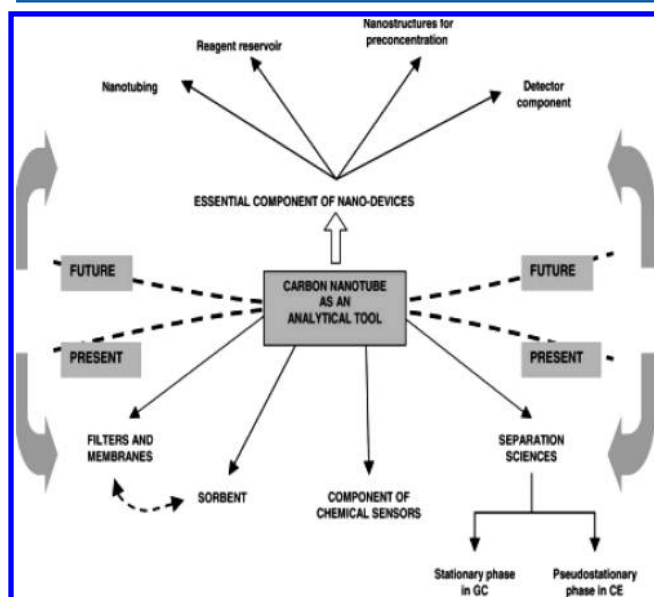

Figure 9. Present and potential future applications of carbon nanotubes as an analytical tool.[240] Reprinted from ref 240 with kind permission from Springer Science and Business Media. Copyright 2005.

nanotubes have been used as a stationary phase in gas chromatography and as a pseudostationary phase in capillary electrophoresis. Currently, however, carbon nanotubes are most widely used as a component in electrochemical sensors. Their use in sample cleanup procedures or analyte preconcentration via either filters/membranes or a sorbent packed material is also shown in this figure. In recent years many applications of MWCNTs for the preconcentration of heavy metal ions, rare earth elements, and organometallic compounds were reported.[542] CNTs were also exploited in analytical chemistry and the preconcentration of trace amounts of organic materials.[543]

4.2.1.1. Metal Ions. Recently, Baena and co-workers[544] explored the analytical potential of C_{60} fullerene, a carbon nanotube-related structure, as a solid phase adsorbent for chelates or ion pairs of metal ions from aqueous solution. Stemming from this, the potential of MWNT to preconcentrate rare earth[545] and trace amounts of Cd, Mn, and Ni[210] has been pointed out in the literature. Shamspur and Mostafavi[546] studied the application of multiwalled carbon nanotubes as a sorbent for simultaneous separation and preconcentration of trace amounts of Au(III) and Mn(II). The surface of the carbon nanotubes was modified with the analytical reagent N,N'-bis (2-hydroxybenzylidene)-2,2'-(aminophenylthio)ethane. Various parameters, such as the effect of pH, flow rate, type and amount of eluent, breakthrough volume, and interference of a large number of anions and cations on the recovery of the selected ions, were studied. The method was successfully applied for separation and determination of gold and manganese ions in water and standard samples by FAAS. Liang et al.[545] examined the determination of trace rare earth elements (REEs) by inductively coupled plasma atomic emission spectrometry (ICP-AES) after preconcentration with multiwalled carbon nanotubes. The method was based on preconcentration of elements like La, Sm, Eu, Gd, Tb, Yb, and Ho with a microcolumn packed with MWNTs. The optimum experimental parameters for preconcentration of REEs, such as pH of the sample, sample flow rate and volume, elution solution, and interfering ions, were investigated. The method was validated using a certified reference material, and was successfully applied for the determination of trace rare earth elements in lake water and synthetic seawater with satisfactory results.

4.2.1.2. Organic Compounds. The characteristic structures and electronic properties of carbon nanotubes allow them to strongly interact with organic molecules. The surface, made up of hexagonal arrays of carbon atoms in graphene sheets, strongly interacts with the benzene ring of aromatic compounds. In 2001, Long and Yang observed that dioxins, which present two benzene rings, were strongly adsorbed on MWNTs. In fact, the authors suggest that MWNTs are an ideal adsorbent for dioxin removal.[547] MWNTs have also been used for solid phase extraction of three endocrine disruptors: bisphenol, 4-*n*-nonylphenol, and 4-tertoctylphenol. These three analytes were quantitatively isolated from environmental water samples on a MWNT-packed cartridge and further eluted with convenient amounts of methanol.[548] In addition to external surfaces, carbon nanotubes appear to act as benign hosts that can encapsulate protein molecules in their internal tube cavities.[549]

Carbon nanotubes can also remove and preconcentrate volatile organic compounds. Mitra and co-workers[550] described a microtrap operating as a nanoconcentrator and injector for gas chromatography. A thin layer of carbon nanotubes was deposited by catalytic chemical vapor deposition on the inside wall of a steel capillary in order to fabricate the microtrap. The carbon nanotube film provides an active surface for fast adsorption/desorption of small organic molecules such as hexane and toluene. The sorption of toluene was much stronger than that of hexane, which can be attributed to the $\pi-\pi$ interaction between the carbon nanotube sidewall and the aromatic ring.[550] Pyrzynska et al.[551] studied sorption behavior of acidic herbicides on carbon nanotubes. In this research, carbon nanotubes and graphitized carbon were investigated as adsorbents for solid phase extraction of dicamba and 2,4,5-T,
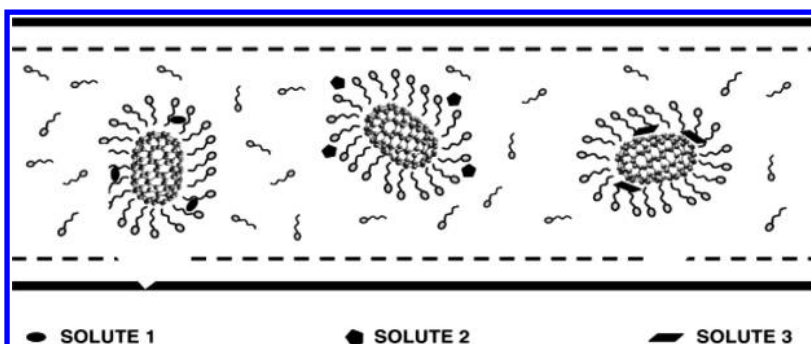
Figure 10. Principle behind separation in micellar carbon nanotube electrokinetic chromatography. Solute 1 interacting as a cosurfactant, solute 2 interacting on the surface, and solute 3 interacting on the carbon nanotube surface.[240] Reprinted from ref 240 with kind permission from Springer Science and Business Media. Copyright 2005.

two phenoxyalkanoic acid herbicides coupled to an HPLC system. The adsorption capacity increases remarkably at lower pH of the sample solution, and Freundlich isotherms were applied to analyze the data. To evaluate the analytical potential of carbon nanotubes and graphitized carbon black as solid phase extraction adsorbents for enrichment of acidic herbicides, dicamba and 2,4,5-T were used as model compounds due to their different chemical structure and hydrophobicity. Adsorption experiments were carried out at different pH values. For comparison, the study was conducted also with C_{18} silica, frequently used for isolation and preconcentration of organic compounds. CNTs have much greater herbicide adsorption capability than that of GCB and C_{18} adsorbents. The absorption capacity increases remarkably at lower pH of sample solution. The decrease of pH leads to decrease in ionization of the analytes and, simultaneously, to neutralization of the surface charge of carbon sorbents. Hence, the adsorption properties were the highest at strong acidic media. These conditions are very suitable for natural water samples, which have to be acidified after sampling.

The behavior of purified MWNTs as column packing material for gas chromatography has been described previously.[552] Satisfactory results were obtained when compared with graphitized carbon black (carbopack B) for the same active surface area: MWNT had stronger retention, a more homogeneous surface, and a smaller theoretical plate number. By studying the chromatographic separations of aromatic hydrocarbons, alkanes, halogenated hydrocarbons, alcohols, ketones, esters, and ethers, it was established that MWNTs are an interesting alternative stationary phase for volatile compounds with relative low boiling points.

Carbon nanotubes have also been used as a component of the background separation electrolyte in capillary electrophoresis. In this case, the carbon nanotubes present in the buffer act as a pseudostationary phase. The various partitions of analytes between the buffer and the nanotube surface, together with the different migration velocities of the nanotubes and the free analytes, are responsible for the electrophoretic separation. To use carbon nanotubes in this way, the first step is to solubilize them in the background electrolyte. Wang et al.[553] proposed the use of soluble carboxylic-SWNTs and observed distinct changes in the electrophoretic parameters of homologous molecules such as caffeine and theobromine. The authors also observed changes for structural isomers of catechol and hydroquinone. Such changes were attributed to the functional groups on the carboxylic-SWNT, which form intermolecular hydrogen bonds with analytes. The use of carbon nanotubes

dispersed with surfactant is another interesting route toward increasing resolution in capillary electrophoresis. Preliminary results obtained by Wang et al. indicate that dispersing SWNTs with surfactant also provides a reliable pseudostationary phase, opening the door to new advances in electrokinetic chromatography that may supersede results from MEKC and MEEKC.[240] The use of this pseudostationary phase will permit the separation and resolution of compounds by three different types of interactions (Figure 10): (i) interaction with the alkyl chain of the surfactant (ii) interaction with the micelle surface or polar groups of the surfactant, and (iii) adsorption on the carbon nanotube surface.

4.3. Silicon Nanomaterials (SiNMs)

4.3.1. Silicon Dioxide Nanoparticles (SiO_2 NPs). Besides sorbent application, the most promising role of nanosilica is being a supporting substrate for other kinds of adsorbents in separation processes. Among many types of solid phase extractors, silica gel presents the advantages of no swelling, fast kinetics, and good mechanical as well as thermal and chemical stability.[554,555]

4.3.1.1. Metal Ions. The chemical modification of silica's surface by immobilization of functional groups has been reported for extractive concentration of metal ions.[556,557] Zhang et al.[555] investigated the determination of trace metals in natural samples after preconcentration on modified silica gel and on modified silica nanoparticles. Silica gel and nanometer SiO_2 modified with 4-(2-aminoethylamino)-N-(2-amino-ethyl amino)ethyl) butanamide (SG-AAEB and nanometer SiO_2-AAEB), which were prepared based on chemical immobilization, were used as sorbents for the solid phase extraction of Cu(II), Fe(III), and Pb(II) prior to their determination by inductively coupled plasma optical emission spectrometry (ICP-OES). Adsorption efficiencies of the two sorbents toward metal ions were investigated by batch and column procedures. For both sorbents the preconcentration conditions of analytes including effects of pH, shaking time, sample flow rate, and adsorption capacity were investigated and compared. The application of SG-AAEB and nanometer SiO_2-AAEB for simultaneous preconcentration of trace Cu(II), Fe(III), and Pb(II) from natural samples was performed with satisfactory results.

4.3.1.2. Organic Compounds. Silica nanoparticles have been employed also for extracting organic materials and pollutants. Chen et al.[558] evaluated the fluoroimmunoassay application of dye-doped silica nanoparticles and successfully extracted tetracarboxy aluminum phthalocyanine as an organic dye for

fluorescent labeling of biological materials. Bagheri et al.[268] evaluated nanosilica as an adsorbent for needle trap extraction of PAHs from water samples. An inexpensive modifier, *cis*-9-octadecenoic acid (oleic acid), was selected to be grafted on the surface of the nanosilica particles as the support. In order to increase the extraction efficiency, influencing parameters including extraction time and temperature, flow rate of analyte through the needle trap, ionic strength, desorption temperature, and time were optimized. The modifier was linked to a solid surface by a covalent bond. The choice of the support depends on the intended objectives. Hence, SiO_2 was selected as a solid surface due to its cost and accessibility; moreover, the hydrolysis condition of SiO_2 can easily be controlled. On the other hand, octadecenoic acid (OA) was selected as a good choice for grafting on nanosilica because it has a double bond carbonyl group along with alkyl chain and, therefore, has good hydrophobic, $\pi-\pi$, van Der Waals, and steric interactions with PAHs. The authors performed validation procedures of the developed method under optimized conditions for the quantitative analysis of PAHs by GC−MS in a spiked distilled water sample.

4.3.2. Silicon Nanotubes (SiNTs). Recently, several attempts have been made to employ silicon nanotubes as solid phase in analytical separations. However, only a few studies have successfully implemented the hydrogen adsorption on SiNTs.[559−561] Balilehvand et al.[562] investigated the hydrogen and methane adsorption/separation on silicon nanotubes. They found that the capacity of hydrogen adsorption on SiNTs is considerably higher than that on CNTs.

4.3.2.1. Metal Ions. Zhuqing et al.[471] synthesized an ion imprinted sol−gel silicon nanotubes membrane for selective separation of copper ion from aqueous solution. Silica nanotubes are ideal vehicles for such proof-of-concept experiments because they are easy to make, have a cross-linked structure, and are highly suitable for the formation of a delicate recognition site. The prepared imprinted nanotube membrane showed several unique characteristics, such as obvious fast adsorption and desorption kinetics, mild imprinting reactive condition, low price, and proper selectivity for Cu(II). This membrane can be potentially used, when coupled with other instrumental methods like FAAS, as the solid phase extraction material for selective preconcentration and separation, and then determination of trace Cu(II) in environmental samples.

4.4. Nanofibers (NFs)

4.4.1. Metal Ions. Several articles published reports on the use of nanofibers in analytical separations, especially solid phase extraction. Rammika et al.[563] encapsulated Ni(II)-dimethyl-glyoxime ion-imprinted polymer (Ni(II)-DMG IIP) in polysulphone and electrospun into nanofibers for the determination of Ni(II) ions from aqueous samples by ICP-OES. Electrospinning increased the specific surface area of the Ni(II)-DMG encapsulated-IIP nanofiber mats, as was evidenced by the low masses of the Ni(II)-DMG encapsulated-IIP nanofiber mats used. The accuracy of the method was validated by analyzing a custom solution of certified reference material (SEP-3); the concentration of Ni(II) obtained was close to the certified one. Though the time for rebinding was not reduced relative to Ni(II)-DMG IIP, the study was successful in that nanotechnology (electrospun nanofibers) was combined with imprinted polymers, opening a wider window for application of imprinted nanofiber mats for enriching metal ions in complex aqueous matrices. High Ni(II) recoveries with good relative

standard deviation (RSD%), enrichment factors (EFs), limit of quantitative (LOQ), and limit of detection (LOD) were obtained with lesser masses of Ni(II)-DMG encapsulated-IIP nanofiber mats relative to Ni(II)-DMG IIP. It was also found that the nanofibers were more recyclable than the IIPs. Ni(II)-DMG encapsulated-IIP nanofiber mats were successfully used to trap Ni(II) ions from sea, river, and sewage water samples. From the results presented in this work, the Ni(II)-DMG encapsulated-IIP nanofiber mats offer a good possibility for use as sorbent in solid phase extraction from aqueous samples. This is mainly due to their high surface-to-volume ratio, which improves the accessibility to analytes of the imprinted cavities in polymers. Chen et al.[564] developed a solid phase extraction adsorbent based on carbon nanofibers (CNFs) and used it for a microcolumn preconcentration method attached to ICP-MS for the determination of trace elements (Mn, Co, and Ni). The effects of various experimental parameters, such as pH, sample flow rate and volume, elution solution, and interfering ions, on the retention of the studied ions were investigated systematically. In order to validate the proposed method, two certified reference materials of human hair (GBW 07601) and mussel (GBW 08571), and water sample, were analyzed with satisfactory results.

4.4.2. Organic Compounds. Kang et al.[565,566] packed polystyrene nanofibers tightly into a tip as SPE columns, but only small volume samples (2 mL) were handled because of the existence of high column pressure. This novel extraction technique was based on the solid phase material, nanofiber, prepared by electrospinning using polystyrene. Experimental optimization of the technique was carried out using seven representative drugs: edaravone, cinchonine, quinine, voriconazole, chlordiazepoxide, verapamil, and rutonding. The advantageous aspect of the technique encompasses high throughput, high sensitivity, simplicity, low cost, and green chemistry. The performance of electrospun nanofibers for determination of drugs was evaluated in both biological and water samples. Qi et al.[567] prepared electrospun polymer nanofibers as a solid phase extraction sorbent for the determination of trace pollutants. The authors describe the novel preparation of three kinds of nanofibers [poly(styrene-*co*-methacrylic acid), poly(styrene-*co*-p-styrene sulfonate), and polystyrene] to extract seven kinds of aromatic hydrocarbon compounds (nitrobenzene, 2-naphthol, benzene, *n*-butyl, *p*-hydroxybenzoate, naphthalene, and *p*-dichlorobenzene) in environmental water by HPLC. SEM images of these three nanofibers are shown in Figure 11. Some factors that could affect the sorption efficiency, such as functional groups of the polymer, medium pH, ionic strength of the sample matrix, and volume of the desorption solvent, were optimized during the extraction process. Validation of the extensive applicability of nanofiber sorbents was carried through the extraction of six organic pollutants in real water samples. The results highlighted the importance of functional groups and the polarity of nanofibers in controlling sorption of target compounds, and clearly showed that the method could be a viable and environmentally friendly technique for analyzing pollutants in environmental samples.

Xu et al.[282] investigated a nylon6 nanofibers mat-based solid phase extraction method for the determination of phthalate esters in water samples. Many polymers with sufficiently high molecular weight can be electrospun according to the characteristics of the object samples. Nylon6 is interesting here because the primary chemical structure of nylon consists
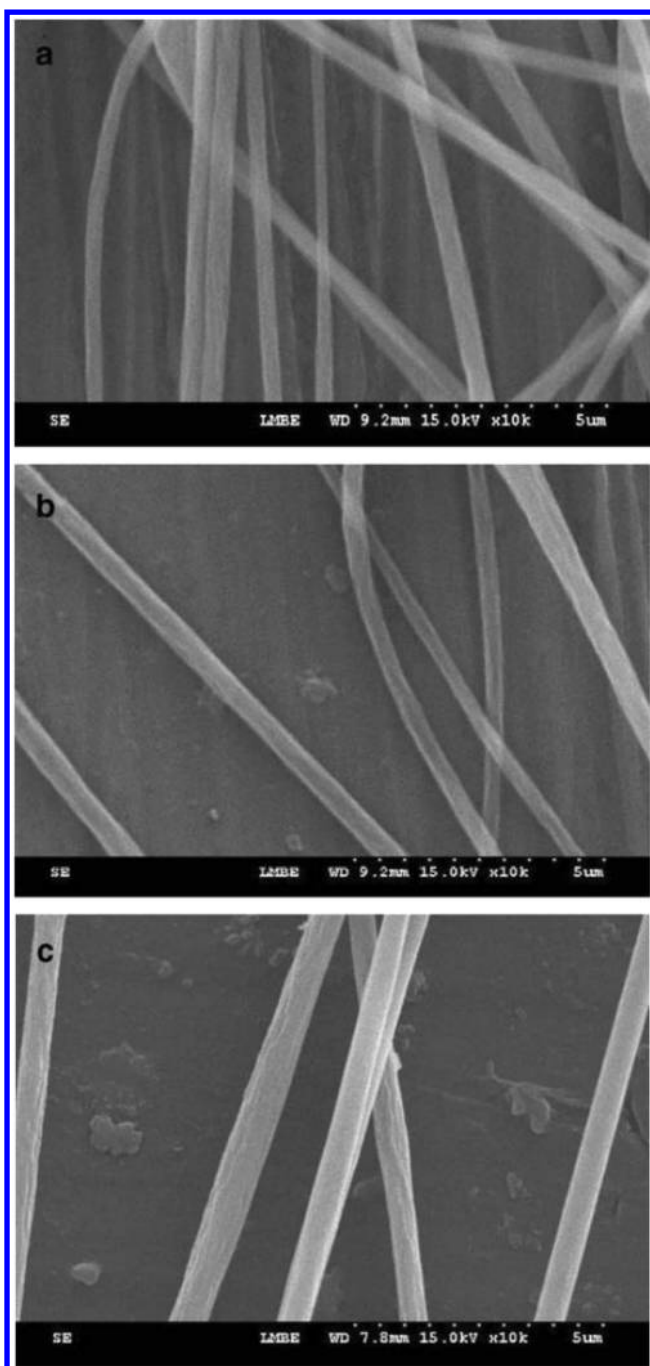
Figure 11. Scanning electron microscope images of three kinds of nanofibers: (a) polystyrene (PS), (b) poly(styrene-*co*-methacrylic acid) (PS-COOH), (c) poly(styrene-*co-p*-styrene sulfonate) (PS-SO₂OH).[567] Reprinted from ref 567 with kind permission from Springer Science and Business Media. Copyright 2008.

of amide groups separated by methylene sequences. The amide group is essentially planar due to the partial double-bond character of the C−N bond. The chains are oriented in such a way as to maximize hydrogen bonding between the amino and carbonyl groups.[568] The aqueous phase used to carry the hydrophobic analyte through the nylon nanofibers is one of the main factors in determining the successful extraction. Due to the hydrophobic nature of phthalate esters, nonpolar interactions are expected between these compounds and the methylene chains of nylon. On the other hand, the hydrophilic

amide groups are expected to enhance the water movement into the sorbent, improving mass transfer and making it more effective.[569] At the same time, in recent years, some researchers have investigated various parameters affecting electrospun nylon6 nanofibers.[570−572] These electrospinning parameters include solution concentration, tip-to-collector distance, and flow rate. It is therefore very interesting to explore the use of the electrospun nylon6 nanofibers mat as sorbent for SPE. The five phthalate esters targeted in the works of Xu et al. were dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), di-(2-ethylhexyl) phthalate (DEHP), and dioctyl phthalate (DOP). The electrospun nylon6 nanofibers mat was used as sorbent for the preconcentration of these five phthalate esters by high performance liquid chromatography coupled with UV detector (HPLC UV) from environmental water samples for the first time. Important parameters influencing the extraction efficiency, such as eluant and its volume, amount of adsorbent, pH, ionic strength, sample volume, flow rate of sample, and reusability of the nylon6 nanofibers mat, were investigated and optimized.

4.5. Nanoclays

These modified organo-clays are used in a wide range of particular applications, such as adsorbents for organic pollutants[573] and metal ions,[574] reinforcing materials for filler plastics,[575] and catalysts.[576] Because of their small particle size, the specific surface area (external and internal) of clays and clay minerals extends to a few hundred m² g⁻¹. The nanosize dimension, extensive surface area, and peculiar charge characteristics of nanoclay materials lie behind their large propensity for taking up ions and organic compounds.[577] Thus, nanoclays may be suitable for preconcentration in solid phase extraction.

4.5.1. Metal Ions. Clay has been widely used for preconcentration and separation of metal ions. Solid phase extraction for copper, cadmium, silver, nickel, and lead ions on modified clays was investigated by Krikorian and Martin.[578] Akcay and Kurtulmus[579] studied adsorption conditions for uranium on Turgulu a Kula clays. Dias et al.[580] used 2-mercaptobenzothiazole loaded on clays for solid phase extraction of Hg(II), Pb(II), Zn(II), Cd(II), Cu(II), and Mn(II) from an aqueous solution. Mohamed et al.[581] utilized Aswan clay from Egypt for speciation and preconcentration of Cr(III) and Cr(VI) from synthetic solution and tannery wastewater. Khajeh[474] employed organo-nanoclays as solid phase adsorbent for determination of zinc by FAAS in water and biological samples. A column filled with nanoclay modified with morin used for this purpose. The sample solution was passed through the modified nanoclay column, and the adsorbed zinc was subsequently eluted from the column with nitric acid solution. Influential parameters such as pH, amount of morin, and concentration of eluent were investigated and optimized, and the results showed that the mentioned factors were significant. Afzali et al.[473,582] evaluated the application of organo-nanoclay as a solid sorbent for rhodium complex and gold ion separation and preconcentration. The Rh(III) ion was first complexed with 2,3,5,6-tetra(2-pyridyl) pyrazine (TPPZ) at the desirable and optimized pH values, and then the complex was adsorbed onto the nanoclay. The rhodium ions were eluted from the sorbent with HCl. The rhodium in the effluent was determined by FAAS. Experimental parameters including the pH, eluent type, interference by other ions, and breakthrough volume were optimized. The method was applied to the

determination of rhodium in water, road dust, and synthetic samples. In addition, the authors modified organo nanoclay with 5-(4′-dimethylamino benzyliden)-rhodanine and used it as a sorbent for separation of Au(III) ions. The influences of the experimental parameters including sample pH, eluent volume and type, sample volume, and interference of some ions on the recoveries of the gold ion were investigated, and the proposed method was successfully applied for preconcentration and determination of gold in different water samples.

4.5.2. Organic Compounds. Yang et al.[583] used the nanoclay, montmorillonite, and some modified nanoclays as sorbents for anionic, cationic, and nonionic dyes. From the sorption differences among the different dye and clay structures, both chemical and morphological, the sorption forces that played important roles were identified. Dye sorption is an important parameter for coloration and wastewater control. Measurement of the dye concentrations was followed by UV−vis spectrophotometry. Materials with good dye sorption capacity usually have good dyeability, good colorfastness, less cost in dyeing, and fewer problems in wastewater treatment. The reasons for selecting montmorillonite in this research were that this clay is commercially available on a large scale with consistent properties and it is used in the preparation of various polymer nanocomposites. Furthermore, polymer composites made from montmorillonite have demonstrated the capability of improving the modulus, strength, UV absorbance, and fire resistance of the composite materials. In other words, using nanoclay as a sorbent will improve not only the dye sorption capability, but also the mechanical and service ability of the material. CI names of dyes used for sorption on nanoclays were Acid Red 226, Direct Red 80, Reactive Blue 19, Basic Red 2, and Disperse Red 65. The nanoclays treated with quaternary ammonium had a very strong sorption capability to acid, direct, and disperse dyes, a relatively low sorption of the reactive dye, and very low sorption of the basic dye. This result was due to the effects of different quaternary ammonium structures and dye structures on dye sorption indicating that the major contributive forces to dye sorption onto clay were van der Waals forces and hydrophobic interaction. Ionic attraction also played an important role. This study on dye sorption isotherms indicated that the very strong sorption ability of nanoclays is due to their high surface area and strong van der Waals, hydrophobic, and ionic interactions with dyes.

Sonawane et al.[584] combined the effects of ultrasonic irradiation and organophilic bentonite (nanoclay) surface on the adsorption of phenol. Tetrabutyl ammonium chloride (TBAC), N-acetyl-N,N,N-trimethyl ammonium bromide (CTAB), and hexadecyl trimethyl ammonium chloride (HDTMA) were used as intercalating agents. Nanoclay was synthesized using the sonication technique, and phenol concentration was determined by using UV−vis spectrophotometry at ambient temperature. TBAC modified nanoclay showed an amorphous exfoliated nature, while CTAB and HDTMA modified nanoclay showed an intercalating crystalline nature. Due to sonication, adsorption equilibrium was achieved within a short period of time, and also intraparticle diffusion resistance was overcome. The results showed that HDTMA modified nanoclay have higher adsorption parameter values for phenol.

4.6. Polymer-Based Nanomaterials (PNMs)

4.6.1. Metal Ions. Ferric-oxide-loaded polymer hybrid sorbents were used by Kaya et al.[291] to survey sorption

behaviors for chromium removal from waters. They prepared and assayed two polymers, namely, GMD and nanosized ferric-oxide-loaded GMDFe, to examine the effect of ferric oxide loading on chromium sorption from aqueous solution from the equilibrium and kinetic points of view. These two adsorbents were tested in a series of batch and continuous flow systems, and the solutions were analyzed for chromium concentration in the solution using UV−vis spectrophotometry. Langmuir and Freundlich isotherms were used for sorption processes showing a higher adsorption capacity of ferric-oxide-loaded hybrid sorbent than that of GMD. Their investigation showed that the elution of adsorbed chromate species from GMDFe was more efficient and fast compared to that from GMD sorbent. This is attributed to the relatively weak interaction force between the Fe oxides and Cr(VI) anions, as the Cr(VI) adsorption onto Fe-oxides is considered a reversible physical process by the authors. Compared to conventional separation, the linked magnetic separation and polymer supported adsorption demonstrates advantages of rapidness, efficiency, and simplicity.

4.6.2. Organic Compounds. Ganigar et al.[585] utilized polymer−clay nanocomposites for the removal of trichlorophenol and trinitrophenol from water. Two nanosized clay minerals, MMT and sepiolite (SEP), were loaded on two polycations, namely, polydiallyl dimethylammonium chloride (PDADMAC) and poly-4-vinylpyridine-co-styrene (PVPcoS). These formed polycation−clay mineral nanocomposites that were used to detect two priority phenolic pollutants, trinitrophenol (picric acid, PA) and trichlorophenol (TCP), in rivers, lakes, and water reservoirs. The concentrations of PA and TCP were determined by UV−vis spectroscopy. The adsorption kinetics of PDADMAC and PVPcoS on MMT was significantly faster (2−4 h) than on sepiolite (3−4 days), which was explained by the latter's porous structure. Consequently, PDADMAC−MMT and PVPcoS−MMT were chosen as optimal adsorbents for the removal of phenol derivatives from water. Both PA (anionic) and TCP (nonionic) showed higher affinity to the less charged polycation PVPcoS (40% of the monomers charged) than to the highly charged polycation PDADMAC. However, PA removal by the PVPcoS−MMT composite was nearly complete while TCP removal reached 40−60% of the added amounts. The adsorption isotherms of the pollutants suggested that the binding to PVPcoS−MMT was driven mainly by hydrophobic interactions, but also by electrostatic interactions in the case of PA. Differences were also seen in the binding kinetics of PA and TCP to dried and wet composites. The hydration properties of PA enhanced its binding to wet composites, whereas the hydrophobic properties of TCP enhanced its binding to dehydrated composites. The results of this study emphasize the importance of better understanding pollutant−adsorbent interactions to enable more efficient tailoring of polymer−clay mineral composites for water treatment.

4.7. Xerogels and Aerogels

The excellent mechanical properties induced by the sol−gel method along with innate surface features make xerogels and aerogels very suitable for the formation of fluidized bed and other applications including the separation and purification process for food, healthcare products, water, and wastewater samples that have very strict regulations on sorbent power contamination.[483] Besides, further functionalization of the surface and doping with proper ions also enhance their applications. Pietron and Rolison[586] demonstrated the impact

of surface modification on the performance of titania–silica composite aerogel films as a photoanode in water-splitting reactions. They stated that the efficiency of titania aerogel-based photovoltaic electrodes could be improved by electrochemically grafting isopropyl moieties on the titania's surface. Durable electrochemical modification of nanocrystalline titania aerogels may prove to be an effective means of increasing the efficiency of their surface area.

4.7.1. Metal Ions. Sol–gel-derived metal oxide xerogels have been investigated for water adsorption because most of these metal oxides are good sorbent candidates for desiccant applications. Significant research has been carried out to study the adsorption/complexation properties of different sol–gel-derived xerogels (like silica xerogel) for heavy metal ions, including mercury, Cu(II), $CdCl_2$, etc., in wastewater.[587–589] Moreover, several studies have reported the use of aerogels as destructive sorbents for toxic gases and radionuclide removal from contaminated environments.[590] Carbon aerogels can also be made from carbon materials under supercritical carbon dioxide drying conditions; these carbon aerogels were studied for removing uranium and other inorganic ions from contaminated water.[591,592]

4.7.2. Organic Compounds. Sol–gel-derived xerogel sorbents have been investigated for gas separation, purification, and environmental applications. γ-Alumina sorbents and membranes doped with cuprous and silver ions have been studied for selective adsorption or transfer of ethylene through π-complexation.[593] Metal oxide composite xerogels can also adsorb methyl orange.[594]

4.8. Quantitative Capacity

One of the most important and critical parameters that must be considered for every adsorption process is the quantitative capacity of a nanoadsorbent. The adsorption capacity is an important factor because it reflects how much sorbent is required to quantitatively concentrate the analytes from a given solution.[595] By moving toward the nanometric scale, porosity of the surface appears as an advantageous outcome, along with many other features differing from those of bulk materials. The porous surface structure should be considered as a factor providing an increase in surface area. These pores decrease the mass transfer resistance and assist in the diffusion of metal ions because of high internal surface area with low diffusion resistance, which ultimately provides high adsorption capacity and rate.[291] Table 2 compares the quantitative capacity of nanoadsorbents with conventional resins/adsorbents as a means to evaluate the use of nanosized adsorbents.

4.9. Online/Offline Recycling of the Nanoadsorbents

Besides the numerous advantages of utilizing the mentioned nanoadsorbents for various sample pretreatment applications, prolonged exposure to these materials might elicit environmental problems, and the recycling of nanoadsorbents is usually difficult. Hence, discharges of nanoadsorbents into various compartments must be quantified, and for the same reason, there is a need to develop sample pretreatment and separation technologies in order to retain and better regenerate and recycle nanomaterials in systems where their functions and reuse are desired. The nanoadsorbents cannot be separated easily from an aqueous solution by filtration or centrifugation. Regeneration and reuse of nanoadsorbent materials, along with their recycling, becomes increasingly difficult with increasing sorption capacity as the adsorbed compounds need to be released from an intricate network of nano- and mesopores.

Table 2. Comparison between Adsorption Capacity of Nanosized Materials and Conventional Adsorbents

adsorbent	analyte	adsorption capacity	detection technique	ref
Al_2O_3 NPs	Cu, Hg, Au, Pd	10.4, 16.3, 15.3, 17.4 g kg^{-1}	ICP-MS	161
TiO_2 NPs	Cr^{3+}, Cr^{6+}	7.5 g kg^{-1}	ETAAS	161
NHITBMO[a]	As^{3+}, As^{5+}	80.0, 14.6 mg g^{-1}		179
Fe_3O_4 NPs	Hg^{2+}	220 μmol g^{-1}	CVAAS	596
MWCNTs	La, Eu, Gd, Ho, Sm, Tb, Yb	8.30, 9.43, 9.93, 7.23, 9.70, 8.0, 8.57 mg g^{-1}	ICP-AES	545
SiO_2 NPs	Pb^{2+}	22.3 mg g^{-1}	ICP-OES	555
Si NTs	Cu^{2+}	0.58 mmol g^{-1}	FAAS	471
CNFs	Mn^{2+}, Co^{2+}, Ni^{2+}	0.73, 0.90, 0.86 mg g^{-1}	ICP-MS	564
organo-nanoclay	Au^{3+}	3.9 mg g^{-1}	FAAS	582
GMDFe[b]	Cr^{6+}	157.52 mg g^{-1}	UV–vis	291
anilinepropylsilica xerogel	Zn^{2+}, Cu^{2+}	0.34, 0.11 mmol g^{-1}	ASV[c]	587
amberlite XAD-7	Pb^{2+}	3.14 mg g^{-1}	FAAS	597
activated carbon	Cu^{2+}, Pb^{2+}	0.63, 0.45 mg g^{-1}	FAAS	598
silica gel	Cu^{2+}, Fe^{3+}, Pb^{2+}	12.2, 14.5, 9.8 mg g^{-1}	ICP-OES	555

[a]Nanostructured hydrous iron–titanium binary mixed oxide. [b]Nanosized ferric-oxide-loaded glycidyl-methacrylate-based polymer. [c]Anodic stripping voltammetry.

Petrik et al.[599] claimed that nonporous carbonaceous and nanostructured adsorbent materials can be regenerated using mechanical force or thermal or electromagnetic energy such that adsorption capacity is restored to at least 70–90%, and higher. Mechanical force could be performed for this purpose using simple pressure or centrifugation, even if the adsorbed material is present in a 20-fold and even higher amount relative to the weight of the adsorbent materials. As an alternative, the adsorbed compound can also be destroyed by ballistic electrons emitted from the nonporous carbonaceous and nanostructured adsorbent material using microwave irradiation.

The application of magnetic adsorbent technology to solve environmental problems has received considerable attention in recent years. Magnetic nanoadsorbents can be manipulated by an external magnetic field to facilitate this goal. Fan et al.[600] evaluated the possibility of regeneration and reusability of cross-linked magnetic modified chitosan (CMMC) as an adsorbent for Zn^{2+} uptake from aqueous solutions. For this purpose, they performed desorption experiments of Zn^{2+} from the adsorbent (Fe_3O_4, chitosan) and noted that in all samples no residual adsorbents were observed during experimentation, as evidenced by the fact that no Fe was detected in the concentrated resulting wastewater after treating with HCl. This is another important characteristic of magnetic separation techniques. The authors also surveyed the effect of recycling times on the adsorption process, which was repeated 6 times. They concluded that the uptake capacity of Zn^{2+} on the adsorbents decreased slowly with increasing cycle number. The percentage adsorption remained steady at about 90% in the first five cycles, and then the uptake capacity of Zn^{2+} decreased.

5. CONCLUSION AND OUTLOOK

This review outlines the potential of nanomaterials as nanoadsorbents and the many advances they have afforded in the separation and preconcentration of a variety of analytes. Over the past decade, nanomaterials have been the subject of

great interest. These materials, notable for their extremely small size, have the potential for wide-ranging applications. In this review, we have explained the classification, properties, applications, and several procedures to prepare nanoadsorbents including (a) nanoparticles, such as metallic oxide nanoparticles (Al_2O_3, ZnO, and TiO_2 NPs), metallic nanoparticles (Au NPs), nanostructure mixed oxides (Fe−Ti mixed oxide), and magnetic nanoparticles; (b) carbonaceous nanomaterials, such as carbon nanotubes; (c) silicon nanomaterials, such as silicon dioxide nanoparticles and silicon nanotubes; (c) nanofibers; (d) nanoclays; (e) polymer-based nanoadsorbents; (f) xerogels and aerogels; and (g) destructive nanoadsorbents.

This review systematically highlights the use of nano-adsorbents for the purpose of characterization and application. The demands of chemical analysis in modern biology, environmental science, chemistry, medicine, and industry need very high sample throughput and parallel analytical strategies. While the increasing role of NPs in separation and preconcentration science is evident, the future will need greater control over the NPs' size, composition, and self-assembly. As a result of recent improvement in technologies to see and manipulate nanomaterials, these material fields have seen a huge increase in funding from private companies, and academic research centers and governments have formed many partnerships.

Unpolluted water is essential for human health. It is a critical feedstock in a great variety of key industries, such as electronics, pharmaceuticals, and food. The world is facing enormous challenges in meeting rising demands for unpolluted water as the freshwater supplies available are decreasing due to (i) population growth, (ii) extended droughts, (iii) competing demands from a variety of users, and (iv) more stringent health-based regulations. Nanomaterials have a number of key physicochemical properties that make them particularly attractive for use as separation media for water treatment: (a) they have much large surface areas than bulk particles; (b) they can be functionalized using different chemical groups to enhance their affinity to a given compound; and (c) they can also be used as high selectivity/capacity recyclable ligands for toxic elements and organic and inorganic solutes/anions in aqueous media. We envision that nanomaterials will become critical components of public water treatment and industrial systems.

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ABBREVIATIONS

AAEB	4-(2-aminoethylamino)-*N*-(2-(2-aminoethyl amino)ethyl)butanamide
AFS	atomic fluorescence spectrometry
BET	Brunauer−Emmett−Teller
BPA	bisphenol A
CE	capillary electrophoresis
CEC	capillary electrochromatography
CMMC	cross-linked magnetic modified chitosan
CNM	carbonaceous nanomaterial
CNP	carbon nanoparticle
CNS	carbon nanosheet
CNT	carbon nanotube
CPC	cetylpyridiniumchloride
CRM	certified reference material
CSD	chemical solution decomposition
CTAB	cetyltrimethylammonium bromide
CUS	coordinatively unsaturated surface
CVD	chemical vapor deposition
DAE	direct anionic exchange
DAMAB	*N,N*-didecylaminomethylbenzene
DBP	di-*n*-butyl phthalate
DEHP	di-(2-ethylhexyl) phthalate
DEP	diethl phthalate
DMG	dimethylglyoxime
DMP	dimethyl phthalate
DNPH	dinitrophenylhydrazine
DOP	dioctyl phthalate
DP	deposition precipitation
EGDMA	ethylene glycol dimethacrylate
EOF	electroosmotic flow
ETAAS	electrothermal atomic absorption spectrometry
FA	formaldehyde
FAAS	flame atomic absorption spectrometry
FI	flow injection
FID	flame ionization detector
FLD	fluorescence detection
FTIR	Fourier transformed infrared
GC	gas chromatography
GCB	graphitized carbon black

GMD	glycidyl methacrylate-based polymer
HDTMA	hexadecyl trimethyl ammonium chloride
HGD	hot gas desulfurization
HPLC	high performance liquid chromatography
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
IEP	isoelectric point
IGCC	integrated gasification combined cycle
IIP	ion-imprinted polymer
LBL	layer-by-layer
LOD	limit of detection
LOQ	limit of quantification
MCC	metal containing compound
MEEKC	microemulsion electrokinetic chromatography
MEKC	micellar electrokinetic chromatography
MMT	montmorillonite
MNP	magnetic nanoparticle
MOCVD	metal organic chemical vapor deposition
MPN	monolayer-protected NPs
MSPE	magnetic solid phase extraction
MVM	metal vapor method
MWCNT	multiwalled carbon nanotube
MWCO	molecular weight cutoff
NHITBMO	nanostructure hydrous iron−titanium binary mixed oxide
NIR	near-infrared
NF	nanofiber
NMP	nanosized magnetic polymer
NPs	nanoparticles
NP	nonylphenol
NTC	nontubular carbon
OA	octadecenoic acid
OP	octylphenol
OTCEC	open tubular capillary electrochromatography
PA	picric acid
PAH	polycyclic aromatic hydrocarbons
PD	photocatalytic deposition
PDADMAC	polydiallyl dimethylammonium chloride
PLA	polylactide
PLGA	poly-D,L-lactide-*co*-glycolide
PNM	polymer-based nanomaterial
PVA	poly(vinylalcohol)
PVPcoS	poly-4-vinylpyridine-*co*-styrene
PZC	point of zero charge
REE	rare earth element
RLS	resonance light scattering
RSD	relative standard deviation
SAAMS	self-assembled mercaptan on mesoporous silica
SDBS	sodium dodecylbenzene sulfonate
SDS	sodium dodecyl sulfate
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SEP	sepiolite
SESD	spontaneous emulsification solvent diffusion
SiNM	silicon nanomaterial
SiNP	silicon nanoparticle
SiNT	silicon nanotube
SiNS	silicon nanosheet
SMAD	solvated metal atom dispersion
SPE	solid phase extraction

SPME	solid phase microextraction
SPNE	solid phase nanoextraction
STPF	stabilized-temperature platform furnace
SWNT	single walled carbon nanotube
TBAC	tetrabutyl ammonium chloride
TCP	trichlorophenol
TEM	transmission electron microscopy
TEOS	tetraethyl-ortho-silicate
TEPA	tetraethylenepentamine
TMA−POSS	tetramethylammonium−polyhedral oligomeric silsesquioxane
TPPZ	tetra(2-pyridyl) pyrazine
TTIP	titanium tetraisopropoxide as the precursor
UV−vis	ultraviolet−visible

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