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Silver nanoparticles for separation and preconcentration processes

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ABSTRACT

There is a great deal of interest in the application of nanomaterials, nanotechnology and nanocrystalline inorganics, such as silver nanoparticles (AgNPs), whose intriguing physical and chemical properties have been topics of many scientific research projects. Notable for their extremely small size, AgNPs have been seen in wide-ranging fields, such as optical probes, optical sensors, and plasmonic and biomedical applications. Since AgNPs show different properties, such as surface-plasmon resonance, large surface area, catalysis, and quantum size effects, they can be used for bioassays based on electrochemistry, silver-enhanced fluorescence, surface-enhanced Raman scattering, colorimetry and chemiluminescence. In this review, we highlight the potential of AgNPs as nanoadsorbents for the analytical processes of extraction, separation and sample pretreatment.

Contents

1. Introduction

Nanoscience and nanotechnology offer new opportunities for making superior materials for use in industrial, health, and environmental applications [1–5]. Nanoparticles (NPs), the primary building blocks of many nanomaterials, are of particular interest in various studies, as the fate of NPs in aqueous environments will depend on their extraordinary properties and widespread range of applications in different scientific and industrial backgrounds. NPs (i.e., particles with structures ~1–100 nm in size) have a significant impact in many scientific fields, including chemistry, electronics, medicine, biology, and material sciences [6–15]. The physical, material, and chemical properties of NPs are directly related to their intrinsic composition, apparent size, and extrinsic surface structure [16–21], so the design, the synthesis, the characterization, and the applications of nanostructures are critical aspects of the emerging field of nanomaterials. One of their important properties is that most of the atoms that have high chemical activity and

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adsorption capacity for many metal ions are on the surface of nanomaterials [22,23]. The surface atoms are unsaturated, so they are subject to combination with the ions of other elements by static electricity [24], so nanomaterials can strongly adsorb many substances, including trace metals [25] and polar organic compounds [26].

Sample-pretreatment methods, such as separation and/or preconcentration prior to instrumental detection, have developed rapidly due to the increasing need for accurate, 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 limits of detection (LODs) of many analytical methods. The concept of NP-assisted sample separation and preconcentration plays important roles in many analytical methods. While primarily associated with increasing the concentration of analytes, the approach provides a number of benefits, ranging from the removal of interfering species to potentially beneficial changes in matrix composition [27]. The potential of NPs was extensively studied in separation science in recent years, and many advances were achieved.

Recently, NPs were used as a sorbent due to their intrinsic properties, such as chemical activity and fine grain size, being better than those of classical substances, including normal-scale titanium dioxide and alumina [28,29]. NPs were chemically modified by a reagent to obtain a new selective solid-phase extractant for the preconcentration of metal ions [30–32].

As novel materials, NPs play a critical role in removal of environmental pollution as adsorbents, several separation and preconcentration methodologies, which utilize NPs as solid phases, such as solid-phase extraction (SPE), solid-phase microextraction (SPME), μ-solid-phase extraction (μSPE). NPs are also used in chromatographic techniques, including gas chromatography (GC) and high-performance liquid chromatography (HPLC) with columns covered with NPs as stationary phases. These uses of NPs are very important in environmental clean-up.

The aim of this article is to review different applications of AgNPs, used as adsorbents for environmental, water, biological and other samples.

2. Silver nanoparticles as adsorbents in separation and preconcentration

As mentioned above, despite the wide-ranging applications of AgNPs in different fields of science and technology, the aim of this article is to review those that have been used for analytical purposes and investigated the role of AgNPs as adsorbents in preconcentration and clean-up processes. Accordingly, we proceed to the effects of AgNPs in analytical preconcentration and removal of some organic, trace-metal and gaseous species from aqueous, biological and environmental samples.

2.1. Organic species

2.1.1. Preconcentration of pyrene

Olenin et al. [33,34] used adsorption-luminescence methods to combine the preconcentration of polyaromatic hydrocarbons (PAHs), such as pyrene, on the adsorbent surface and their subsequent luminescence determination directly in the adsorbent matrix. For this purpose they used hydrophobic AgNPs with an average size of 4 nm, which were synthesized in two-phase water-organic emulsions. Through the characterization procedure by the instruments, such as molecular spectroscopy and electron microscopy, the physical properties of these AgNPs were evaluated and it was found that they had a specific surface area of 60–110 m^2/g.

The adsorption-luminescence analysis of PAHs has been an issue of great interest. For this purpose, nanosized organized media, such as AgNPs, deserve special attention in order to improve the accuracy of predicting the conditions of quantitative extraction, and the sensitivity and the specificity of determination in dilute solutions. In this work, CTAB was a surfactant and phase transfer catalyst. CTAB molecules stabilized the surface of AgNPs and transferred them into the organic phase in order to form the organosols of AgNPs. Surfactants are most frequently used in the synthesis of AgNPs for their stabilization, which modifies not only the properties of the test solution, but also those of the adsorbent surface, so the use of CTAB-stabilized AgNPs as adsorbents of pyrene during its determination by the adsorption-luminescence method can radically change the adsorption of pyrene and optimize the spectral parameters of the analytical signal. Eventually, Olenin et al. tested the preconcentration procedures in both organic (n-hexane) and aqueous (water) solutions and showed that the resulting AgNPs could successfully serve as adsorbent and preconcentrate pyrene molecules from both dilute (10^{-8}–10^{-6} g/mL) and concentrated (10^{-4} g/mL) n-hexane solutions.

2.1.2. Analysis of olefins

Sherrod et al. [35] utilized AgNPs in a laser desorption/ionization (LDI) procedure to show selectively ionization of the olefinic compounds [e.g., cholesterol, and 1-palmitoyl-2-oleoyl-sn-glycero-3-hosphocholine (POPC)] and carotenoids, and finally to analyze them by mass spectrometry (MS). This started with complex mixtures without addition of an organic matrix, sample clean-up, or prefractionation. LDI using NPs differs from matrix-assisted laser desorption/ionization (MALDI) in several ways:

1 less complicated mass spectra in the low mass region due to a decrease in matrix-derived chemical noise (matrix ions and adducts);
2 flexible, relatively simple sample-preparation conditions;
3 higher tolerance to specific chemical additives, such as those commonly used in biological analysis (e.g., surfactants);
4 the ability to tailor the chemical properties of NPs using relatively simple derivatization schemes, which can be exploited; and,
5 modify NPs (metal and silicon based) to capture and to ionize analytes selectively on the basis of specific chemical properties (i.e., functional groups).

The ability to control size, composition, and electronic properties of AgNPs provides a basis for this procedure. This effect was attributed to π-cation interactions between olefinic compounds and AgNPs.

Sherrod and co-workers exploited the silver-olefin interaction to ionize selectively specific carotenoids, a sterol, and a lipid from complex mixtures in the presence of AgNPs without additional washing or extraction procedures. The silver-olefin interaction has long been used for chemical analysis. For example, silver-olefin interactions enhance silver cationization by electrospray ionization [36–39], facilitate olefin transport in supported membranes [40], and separate and quantitate lipids, fatty acids, and triacylglyecerols. [41–44] Moreover, thin silver films have been used to image cholesterol in thin tissue sections of rat kidneys [45] and polymorphonuclear leucocytes [46,47].

Fig. 1 illustrates the selectivity of the process for ionization of olefinic compounds. The priority of nanosized silver is apparent, as shown in Fig. 1b, in obvious contrast with silver-nitrate solution (Fig. 1a) [35].

2.1.3. Removal of methylene blue

Khajeh et al. [48] developed a simple, fast method for preconcentration and determination of trace amounts of methylene Blue (MB) from water samples by an AgNP-based solid-phase