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Use of gold nanoparticle-coated sorbent materials for the selective preconcentration of sulfonylurea herbicides in water samples and determination by capillary liquid chromatography

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A B S T R A C T

Two new gold nanoparticle (NP) coated materials (silica supported on gold NP with and without ionic liquid) were synthesized for solid phase extraction of sulfonylurea herbicides (SUHs), such as bensulfuron-methyl (BSM), metsulfuron-methyl (MSM), pyrazosulfuron-methyl (PSM), thifensulfuron-methyl (TFM) and triasulfuron (TS), from water samples, followed by capillary liquid chromatography coupled to diode array detection (CLC–DAD). Several factors influencing the preconcentration efficiency of SUHs and its subsequent determination, such as pH of the sample, eluent and reusability of sorbents, have been investigated. Under the optimum conditions, the developed method allowed the determination of BSM, MSM, PSM, TFM and TS in a linear range between 0.05 and 1.00 $\mu g\ mL^{-1}$, with relative standard deviation values lower than 4.5% ($n=10$), in all cases. Detection limits within 0.002–0.009 $\mu g\ mL^{-1}$ range were achieved. The usefulness of the proposed method was demonstrated by the analysis of river water samples, in which recoveries between 83.9 and 105.0% were obtained. The Au–NP-ionic liquid-functionalized silica sorbent showed higher recoveries (selectivity) for the SUHs than the commercially available C_{18} sorbents.

1. Introduction

Sulfonylureas are a family of herbicides used for crop protection. They efficiently control broad-leafed weeds and some grasses in cereals, and are widely used for a variety of crops because of their high herbicidal activity and low toxicity for mammals [1]. However, due to their high mobility and increasing use, sulfonylurea herbicides (SUHs) are now being detected in environment [2,3]. On the other hand, and despite their low toxicity to mammals and their high herbicidal activity, concerns have been raised by the public and by regulatory authorities regarding potential adverse environmental impacts, since SUH residues could stop cell division in plants and lead to yield reduction in sensitive crops [4,5]. As compared with other herbicides, SUHs have much lower use ranges (10–100 g of active ingredient/ha). Therefore, the concentration of these herbicides usually found in environmental soil and water is very low [6]. Then, new sample enrichment and purification techniques are needed for monitoring these herbicides in environmental samples.

Analytical methods related to series of these herbicides generally include a combination of solid phase extraction (SPE) and highly sensitive instruments to detect trace-level residues in water and soil samples. Because of their low volatility and thermal instability [7], the SUHs cannot be directly detected by gas chromatography (GC) without time-consuming derivatization procedures. In this respect, the analytical mode of SPE coupled with liquid chromatography (LC) has great potential to provide both high sensitivity and high selectivity for trace analysis of multiresidue SUHs. Different nonspecific materials, such as octadecyl-bonded silica [8–14], polystyrene divinylbenzene polymeric phase [8,11,13], a co-polymer of polydivinylbenzene-co-N-vinyl pyrrolidone [12,13], polystyrene polymer [14], magnesium silicate [15], graphitized carbon black [16] and more recently the use of a N-methylimidazolium ionic liquid (IL)-functionalized silica sorbent [17] have been reported in the SPE procedure for the extraction of SUHs from water, soil or plant samples. In addition to this, other adsorbents used in SPE for SUH extraction from environmental samples are the well-known molecularly imprinted polymers (MIPs) [18–20]. Recently, there have been increasing publications describing the success of the

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molecularly imprinted solid-phase extraction (MISPE) due to the selectivity and sensitivity of MIPs. However, some drawbacks of MISPE have restricted its widespread application, since MISPE is normally used in cartridge mode, which often results in a tedious column packing procedure, high backpressure and a low flow-rate.

The concept of nanoparticle (NP)-assisted sample preparation and preconcentration plays an important role in many analytical procedures. Whilst primarily associated with increasing the concentration of analytes, the approach provides a number of benefits, ranging from the removal of interfering species to a potentially beneficial change in the matrix composition [21]. The potential capability of NPs has been extensively studied in separation science during recent years, and many advances have been achieved toward chromatographic and electrophoretic systems for a couple of separation components and preconcentration media. Among those NPs are polymers, silica, fullerenes, carbon nanotubes, titanium oxide, silver NPs and gold NPs. Gold NPs are gradually attracting a great deal of attention for their use in future technologies, including catalysis, optical materials, electronic devices, biosensors, drug carriers, and high contrast cell imaging [22–27]. On the other hand, gold NPs have been widely used in analytical procedures because of their size dependent electrical properties, high electrocatalytic activity, and functional compatibility with molecules and polymers [28]. Besides, biomolecules containing thiol (SH) or amino (NH_2) groups can be adsorbed spontaneously onto gold surfaces to generate well-organized, self-assembled monolayers [22]. Although 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. Moreover, gold NPs are characterized by a high surface-to-volume ratio, long-term stability, easy synthesis and favorable chemical modification.

In this work, two gold NP-coated solid phase extraction sorbents have been synthesized and used to preconcentrate SUHs from water samples, which will be determined by capillary liquid chromatography (CLC). The inherent chemical stability of gold provides a high stability and durability to these sorbent materials. Moreover, the affinity that exists between SUHs and gold NPs will be used to improve the analytical figures of merit of the SPE–CLC method.

2. Experimental

2.1. Reagents and materials

The following analytical grade reagents were used: gold (III) chloride hydrate ($HAuCl_4 \cdot H_2O$, 99.99%), tetraoctylammonium bromide, dodecanethiol (98%), cetyltrimethylammonium bromide (CTAB, 99%), tetraethylorthosilicate (TEOS), 3-(trihydroxysilyl)propyl methylphosphonate (42% solution in water), ammonium nitrate, silica gel (60–100 mesh), methanesulfonic acid, N-methylimidazole (99%), 3-chloropropyltriethoxysilane, potassium hexafluorophosphate (KPF_6), toluene, chloroform, methanol (MeOH) and acetonitrile (ACN), which were from Sigma-Aldrich (St. Louis, MO, USA).

Sodium borohydride ($NaBH_4$) was from Fluka (Buchs, Switzerland) and sodium hydroxide (NaOH), acetic acid glacial and absolute ethanol from Panreac (Barcelona, Spain). Ultrapure water was obtained with a Milli-Q system (Millipore).

Standards of bensulfuron-methyl (BSM), metsulfuron-methyl (MSM), pyrazosulfuron-methyl (PSM), thifensulfuron-methyl (TFM) and triasulfuron (TS) were from Sigma (St. Louis, MO). Stock solutions of the analytes (ca. 1000 $\mu g\ mL^{-1}$) were prepared in ACN and stored at 5 °C in amber vials. Working solutions were prepared daily by dilution of the stock solutions with water.

A 200 mg of sorbent, packed into an empty polypropylene cartridge, were used to pre-concentrate the 5 studied SUHs in solution. At both ends of the cartridge, polyethylene frits (Omnifit) were fixed to prevent material losses. The commercially available C_{18} cartridges (MFE®-PAK, 200 mg/3 mL, Análisis Vínicos, Tomelloso, Spain) were also used for comparison with the synthesized sorbents.

2.2. Instrumentation and working conditions

A 1200 series liquid chromatograph provided with a degasser, a nanopump, an automatic injector and a diode array detector with a micro flow cell (Agilent Technologies, Palo Alto, CA) was used. Separation was carried out with a Luna C18 (2) capillary column ($250 \times 500\ \mu m$ i.d., 5 μm, Phenomenex, Torrance, CA, USA). Mobile phases were prepared by mixing ACN and water containing 0.01% acetic acid. Elution was performed isocratically with 35% ACN for 10 min, followed by a linear gradient from 35 to 95% ACN for 5 min, and by isocratic elution with 95% ACN for 10 more minutes. Detection was performed at 230 ± 4 nm (450 ± 10 nm as reference). The column temperature was kept at 30 °C, and the flow rate was 10 $\mu L\ min^{-1}$. The injection volume was 5 μL.

FTIR spectra were obtained using a Jasco 4100 type A spectrophotometer (Jasco, Easton, MD) fitted with a single reflection attenuated total reflectance (ATR) accessory. The ATR accessory (ATRPRO410-S, Jasco) was equipped with a ZnSe reflection crystal. All analyses were carried out at room temperature. Measurements were obtained using 50 scans at 4 cm^{-1} resolution. Spectra were recorded in the absorbance mode from 4000 to 400 cm^{-1}. Data handling was performed with the Spectra Manager version 2.07.00 software (Jasco).

Transmission electron microscopy (TEM) images of sorbents were obtained using a Jeol (Tokyo, Japan) model JEM-1010 microscope operated at 100 kV. For this purpose, materials were dispersed in EtOH by sonication. A 0.05 mL aliquot of this suspension was placed on 200 mesh Cu grids coated with an amorphous holey carbon film, and EtOH was evaporated. Images were obtained using a MegaView III camera and the AnalySIS image data acquisition system.

2.3. Preparation of Au NPs

Gold NPs (see Fig. 1A) were synthesized by following the Brust method [29]. This method is based on a two-phase synthesis that uses a thiol ligand that strongly binds gold due to the soft character of both Au and S (which protect the metallic core by a covalent Au/S bond). First, 180 mg of $HAuCl_4 \cdot H_2O$ was dissolved in 15.3 mL of water and mixed with 40.6 mL of toluene solution containing 1.1 g of tetraoctylammonium bromide. The gold salt ($AuCl_4^-$) is transferred from a water solution to toluene. The solution was stirred vigorously for 30 min before addition of 102.3 μL of dodecanethiol (Aldrich, 98%). Next, a 12.7 mL of aqueous solution of 192.1 mg of $NaBH_4$ was added slowly to the mixture. The organic phase changes color from orange to deep brown within a few seconds upon addition of $NaBH_4$. After further stirring for 3 h, the aqueous layer was removed using a separatory funnel, and the toluene was removed using rotary evaporation. This method allows the easy synthesis of thermally and air-stable gold NPs of reduced dispersion and controlled size. The solids were dissolved in a minimal amount of toluene, precipitated with absolute ethanol, and collected by centrifugation. After the process was repeated two more times, the solids were dried under vacuum [30]. The dried gold NPs were dissolved in chloroform. Two milliliters (10–20 $mg\ mL^{-1}$) of the NP solution were