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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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ABSTRACT

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 μg mL^{-1}, with relative standard deviation values lower than 4.5% (n=10), in all cases. Detection limits within 0.002–0.009 μg 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 (250×500 μm 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

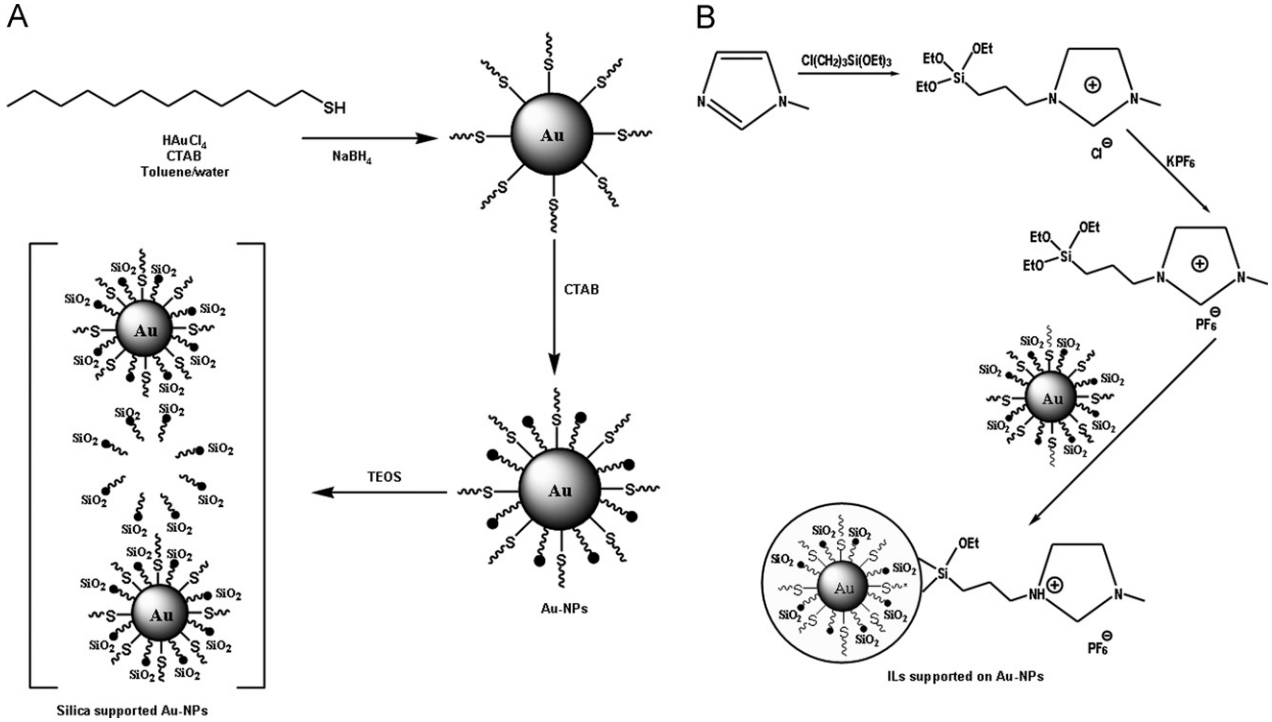

Fig. 1. Scheme of the synthesis of the silica supported Au-NPs (A) and of Au-NP–IL-functionalized silica sorbent (B).

mixed with 0.4 g of CTAB and 20 mL of water. The mixture was then sonicated and stirred [30].

2.4. Preparation of silica supported Au NP (Au–TEOS)

Silica supported Au-NPs were synthesized according to the scheme represented in Fig. 1A. Briefly, 10 mL of the Au-NPs–CTAB solution was adjusted to pH 11 with NaOH 1 M. Then, 2.1 mL of TEOS was added and stirred overnight, and the resulting solution was heated at 50 °C during 30 min. Then, 127 μL 3-(trihydroxysilyl)propyl methylphosphonate was added into the mixture, and the solution was stirred for another 2 h. The synthesized materials were centrifuged and washed with MeOH. The CTAB surfactants were removed from the mesopores by dispersing the as-synthesized materials in a solution of 160 mg of ammonium nitrate and 60 mL of 95% ethanol and heating the mixture at 60 °C for 15 min. The materials were then centrifuged, washed with ethanol and dried under vacuum at 80 °C for 8 h.

2.5. Preparation of Au-NP–IL-functionalized silica sorbent

The synthesis process represented in Fig. 1B was carried out in the presence of ACN with three steps. 15 mM of N-methylimidazole (1.2 mL) was mixed with 16.5 mM of 3-chloropropyltriethoxysilane (silane-coupling agent, 4.0 mL) in a 500 mL round bottomed flask, and the mixture was refluxed with stirring for 48 h. After the reaction had cooled to room temperature, 2.8 g of KPF_6 dissolved in 50 mL ACN was slowly added and the anion-exchange reaction was allowed to take place over the next 26 h. 0.25 g of the Au NP-mesoporous silica sorbent (Au–TEOS) previously synthesized was mixed with the silane-coupling agent attached with N-methylimidazolium IL and the mixture was refluxed with stirring for 24 h, after which the product was recovered by filtration and consecutively rinsed with ACN and deionized water. The obtained Au-NP–IL-functionalized silica was dried under vacuum at 80 °C for 8 h.

3. Results and discussion

3.1. Optimization of the chromatographic conditions

In preliminary studies, and as it is recommended in the literature for the chromatographic separation of SUHs [14,17], various types of C_{18} columns of different lengths and different diameters of particle, such as Luna C18 reverse phase Phenomenex (250 mm × 500 μm i.d., 5 μm), Jupiter C18 reverse phase Phenomenex (250 mm × 500 μm i.d., 4 μm), and C18 reverse phase Ascentis Express (150 mm × 500 μm i.d., 2.7 μm) were used. However, the best separation of the five analytes was obtained with a Luna C18 reverse phase Phenomenex (250 × 500 μm i.d., 5 μm). Moreover, different mobile ternary phases, containing ACN/MeOH/water, or binary phases with MeOH and water at different ratios, and with different concentrations of acetic acid were tested. As a compromise between adequate retention times for these compounds and a good sensitivity when peak areas are measured, ACN (solvent A) and acetic acid (0.01%) (solvent B) mobile phase was selected in a gradient mode, combining solvents A and B as follows: 35% A (10 min); 35–95% A (5 min); 95% A (10 min). The CLC system was re-equilibrated with the initial composition for 5 min prior to the next injection.

The effect of injection volume was investigated over the range from 0.01 to 40 μL. In general, the peak area of all SUHs increased with increasing injection volume. Thus, a volume of injection of 5 μL was chosen as a compromise between pressures detected in the system, sensitivity, and peak resolution. On the other hand, the effect of the mobile phase flow rate was tested in the 5–20 $\mu L\ min^{-1}$ range. As expected, both retention time and peak width decreased as the flow rate increased for all the compounds. However, a lower resolution of TS and MSM was observed for the higher flow rates. Therefore, as a compromise, a flow rate of 10 $\mu L\ min^{-1}$ was chosen for further work. The UV–DAD detector was set at 230 nm.

Under the established capillary chromatographic conditions, standard mixture solutions were injected into the CLC–DAD system obtaining efficient, reproducible, and sensitive separation and detection of the five SUHs evaluated in less than 25 min.

3.2. Characterization of the synthesized AU–TEOS and AU-NP–IL-functionalized silica sorbents

The FTIR spectra of both AU–TEOS and Au-NP–IL-functionalized silica sorbents (see Fig. 2) were measured to confirm the immobilization reaction of the IL onto the Au–TEOS material. As it can be observed in Fig. 2, no significant differences were observed between the spectra of both sorbents, which is in agreement with Fang et al. [17]. However, the band observed at ~2360 nm, which could be attributed to the Si–H bond, showed a lower absorbance for the Au-NP–IL sorbent. This fact could be explained taking into account the bonds formed between Si and the IL [17].

On the other hand, TEM images were also recorded to observe the presence of gold NP in both sorbents. As observed in the images of Fig. 3, the presence of gold NP in both sorbents was corroborated. However, TEM images corresponding to

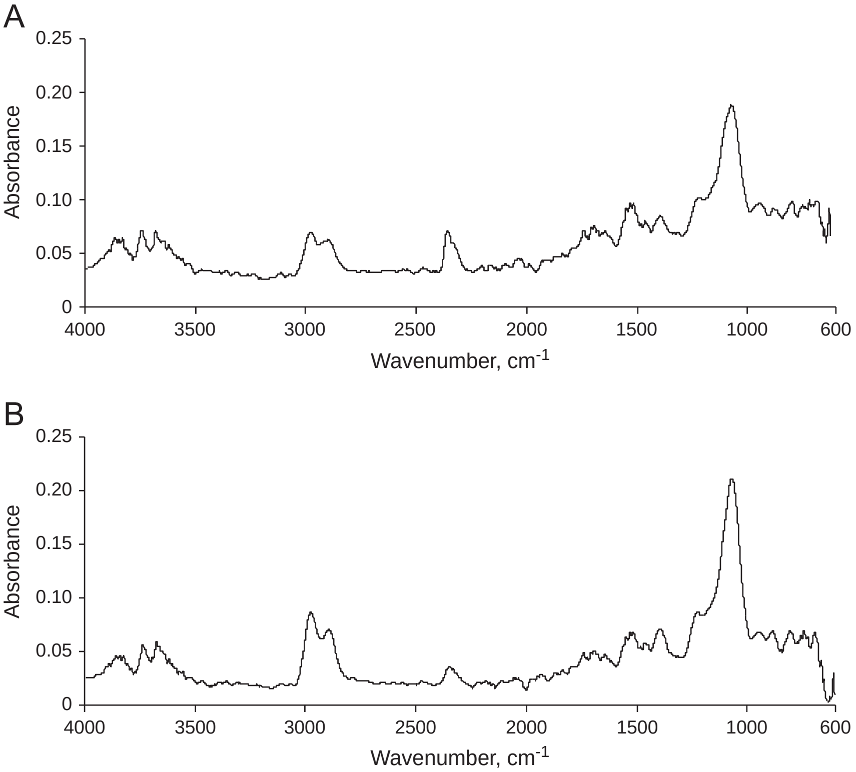

Fig. 2. FTIR spectra of Au–TEOS (A) and Au-NP–IL-functionalized silica (B) sorbents.

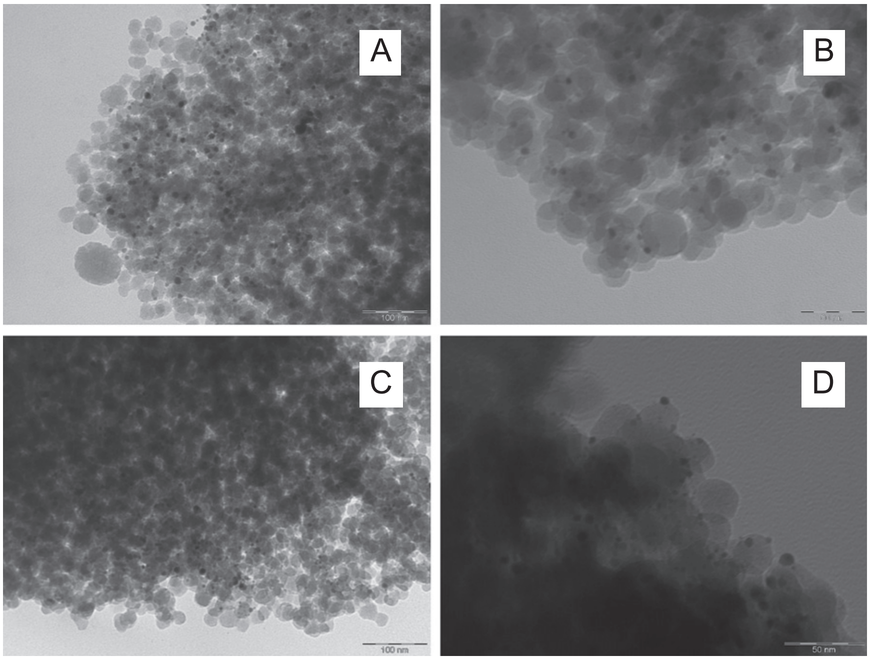

Fig. 3. TEM images of Au–TEOS (A and B) and Au-NP–IL-functionalized silica (C and D) sorbents.

Au-NP–IL showed a lower concentration of gold NPs, which is in agreement with the FTIR spectra, since in this sorbent there are several Si–IL bonds thus the number of gold NP engaged to Si were lower.

3.3. *Optimization of SPE conditions*

To evaluate the capability of the sorbents for the selective preconcentration of SUHs from water samples, different parameters such as pH, amount of sorbent and elution conditions were optimized. A factor by factor method was used for the optimization of the parameters affecting the extraction efficiency. The recovery percentage was calculated from the amount of SUHs present in the starting sample and the amount of SUHs eluted from the cartridge. Three replicates were performed for each experiment by initially passing 2 mL of a 1 mg mL^{-1} SUH standard aqueous solution through the cartridge, and by eluting them using 2 mL MeOH–acetic acid (9:1 v/v) mixture.

3.3.1. *Effect of sample pH*

The fate of SUHs in environmental samples is directly related to their chemical structure and mainly to the ionization of the sulfonylurea bridge (SO_2NHCON). SUHs are weak acids with pK_a from 3 to 5, and in waters they exist mainly in the ionized (anionic) form. This explains their low sorption coefficients, which are pH-dependent. Thus, and in order to evaluate the pH dependence of the SUH retention, the pH values of sample solution were adjusted to a range of 3–6 with a minimum volume of 0.01 mol L^{-1} acetic acid and/or NaOH. The effect of pH value on analyte recovery is shown in Fig. 4 for Au–TEOS (A) and Au-NP–IL-functionalized silica (B) sorbents. It was observed that at low pH values, the adsorption capacity was low for most analytes, reaching in all cases its maximum recovery value at a pH=5. Thus, pH=5 was selected for further studies.

3.3.2. *Optimization of elution conditions*

Elution solvent and elution volume are essential parameters to be investigated in SPE procedures. First, mixtures of MeOH–acetic acid with different proportions (acetic acid percentage varied between 1 to 15%) were tried as elution solvent (see Fig. 4C and D). For the Au–TEOS sorbent (Fig. 4C), recoveries of about 100% were obtained for all analytes when acetic acid percentage ranged from 1 to 10%, being recovery value lower for a 15% acetic acid percentage. For the Au-NP-IL-functionalized silica sorbent (Fig. 4D), recovery decreases when acetic acid percentage was increased. Then, a 1% acetic acid was selected for the following studies. Then, the effect of elution volume (0.5–3 mL) on the recovery after passing 10 mL MeOH with 1% acetic acid was also investigated. As observed in Fig. 4E and F, at least 2 mL were necessary to obtain at about 100% recovery. Then, and in order to improve the enrichment factor, 2 mL of sample containing SUHs were evaporated to dryness, and the extract was redissolved in 0.5 mL of water.

3.3.3. *Reusability of sorbents*

The potential regeneration and stability of sorbents were also investigated. Sorbents could be reused after regenerating with 5 mL of deionized water. Moreover, it was observed that both sorbents were stable up to at least 350 retention–elution cycles and could be repeatedly used without significant loss of their uptake capacity.

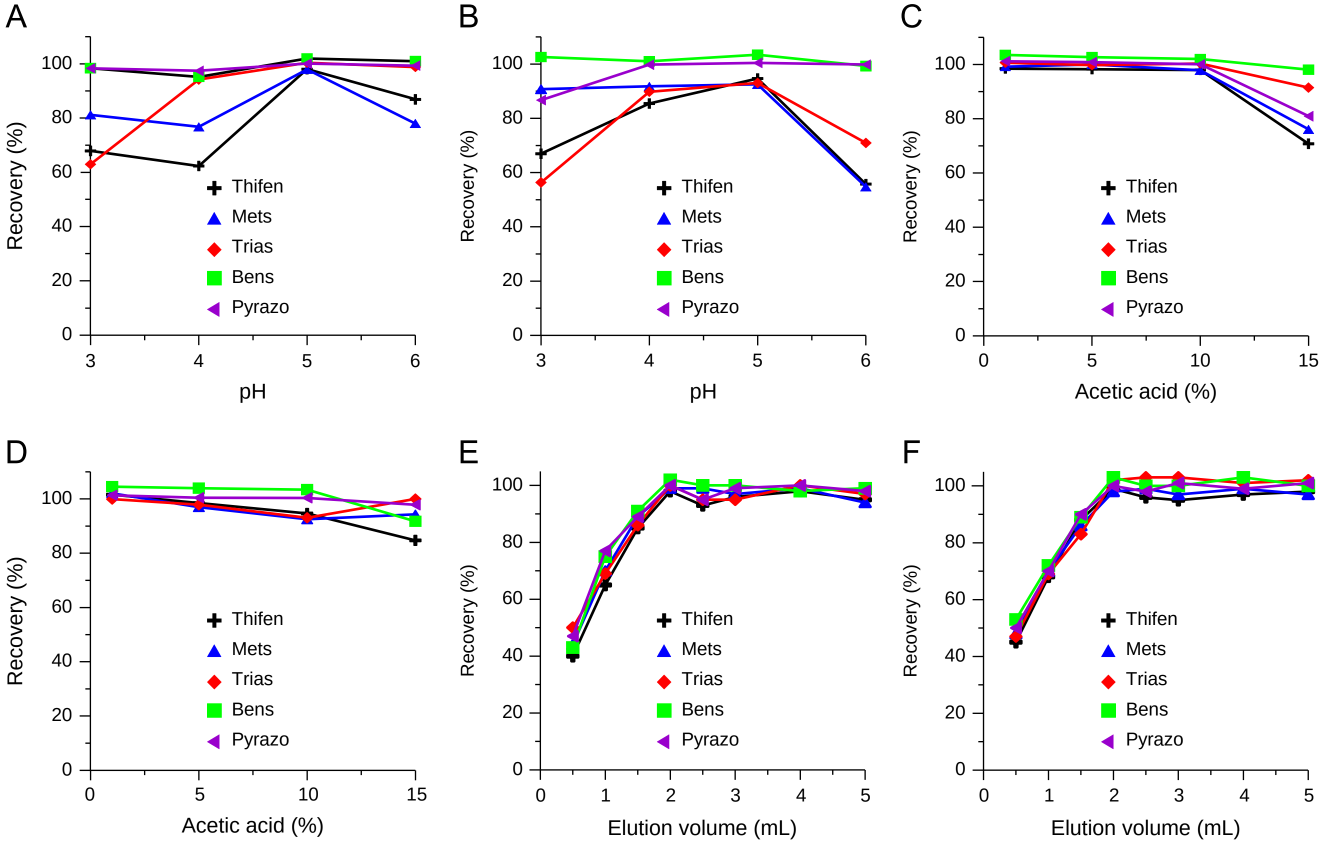

Fig. 4. Effect of sample pH (A and B), acetic acid percentage (C and D) and eluent volume (E and F) on the retention of SUHs on the Au–TEOS and Au-NP–IL-functionalized silica sorbents, respectively. Experimental conditions for A and B: SU concentration, 1 mg mL^{-1}; elution solvent, MeOH/ 10% acetic acid; elution volume, 2 mL; sample volume, 2 mL. Experimental conditions for C and D: SUH concentration, 1 mg mL^{-1} at pH 5; elution volume, 2 mL; sample volume, 2 mL. Experimental conditions for E and F: SUH concentration, 1 mg mL^{-1} at pH 5; elution solvent, MeOH/ 1% acetic acid; sample volume, 10 mL.

3.4. Analytical performance and application to the determination of SUHs in water samples

The performance of the proposed SPE method was evaluated under the optimized extraction conditions using spiked water samples. Additionally, the analytical features of the proposed sorbents were also compared with those obtained by using the commercial C_{18} sorbents. The preconcentration conditions used when the C_{18} sorbent was employed were the same than those employed with the other two sorbents, except to the elution solvent, which was ACN in this case, since it has been reported to elute SUHs absorbed on C18 sorbents [11–14]. In first place, external calibration curves of peak areas were constructed by injecting standard solutions in the range 0.05–1.5 μg mL^{-1} range after the AU–TEOS, the Au-NP–IL-functionalized silica and the C_{18} preconcentration step. At least three replicates were performed at each concentration level. The linear range, linearity curve and other figures of merit are summarized in Table 1 for the Au–TEOS, the Au-NP–IL–silica and the C_{18} sorbents. Repeatabilities of peak areas and retention times were obtained by injecting a mixture containing 0.5 μg mL^{-1} of each standard 10 times per day during 3 days. Repeatability values ranging from 2.1 to 4.5% and from 0.1 to 0.3% were found for peak area and retention time, respectively. The limits of detection (LODs) and limits of quantification (LOQs) were estimated for signal-to-noise ratios of 3 and 10, respectively. For the Au–TEOS sorbent, LOD and LOQs were comprised between 0.002–0.009 and 0.005–0.030 μg mL^{-1}, respectively, whereas for the Au-NP–IL–silica sorbent LOD and LOQ values were comprised between 0.002–0.006 and 0.008 and 0.020 μg mL^{-1}, respectively. These values were similar to those obtained by the C_{18} sorbent, which were comprised between 0.003–0.006 and 0.009–0.019 μg mL^{-1} for LOD and LOQ values, respectively.

The applicability of the proposed method was evaluated in the analysis of SUHs in river water samples coming from different effluents of river Guadiana (Ciudad Real), that were found to contain none of the five above mentioned SUHs. Thus, water samples were spiked with the 5 SUHs at different levels. The concentration of SUHs in the spiked samples was calculated from the calibration equations. A chromatogram showing the spiked water sample preconcentrated by the Au-NP–IL–silica sorbent is shown in Fig. 5. The retention times (min ± SD, $n=10$) were: 12.85 ± 0.08 min (TFM), 14.10 ± 0.07 min (MSM), 17.20 ± 0.08 min (TS), 20.1 ± 0.09 min (BSM) and 21.10 ± 0.09 min (PSM). The recovery results obtained are summarized in Table 2. As it is observed in this table, depending on the sorbent material used and the analyte extracted, different recovery values were obtained. Higher recovery values were obtained for all the analytes with the Au-NP–IL–silica sorbent when compared with the Au–TEOS and C_{18} sorbents. For the latter sorbents, recoveries ranged between 70.0–96.1% and 73.5–107.2%, respectively, being the recoveries comprised between 83.9 and 105% for the Au-NP–IL–silica sorbent.

4. Conclusions

In this work, two new gold NP coated materials (silica supported on Au-NP with and without ionic liquid) have been successfully prepared and applied for the preconcentration of SUHs in water samples, followed by their separation and quantification by CLC–DAD. Different factors that influenced preconcentration efficiency, such as pH of the sample and elution conditions, were optimized. As a result of this study, it was demonstrated that pH is a critical variable in the adsorption process of the SUHs onto the two proposed sorbents. On the other hand, and by using both sorbents, the proposed method has demonstrated good recoveries and precisions in terms of repeatability and reproducibility by SPE; however, better recoveries

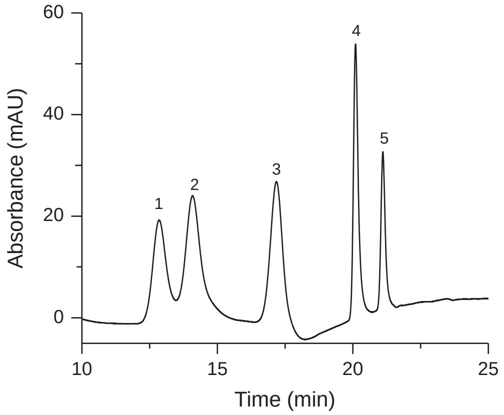

Fig. 5. Chromatogram of a SPE of 20 mL of 0.1 μg mL^{-1} SUHs using Au-NP–IL-functionalized silica sorbent coupled to CLC–DAD. Peak identification: 1, TFM; 2, MSM; 3, TS; 4, BSM; and 5, PSM. Experimental conditions as described in Section 2.2.

Table 1
Linear range, linearity curve and other figures of merit for the determination of SUHs in water samples using the Au–TEOS and the Au-NP–IL–silica sorbents.

Sorbent	Analyte	Linear range (μg mL^{-1})	Linearity curve	r^2	Repeatability, RSD[a] (%)		LOD (μg mL^{-1})	LOQ (μg mL^{-1})
					Peak area	t_R		
Au–TEOS	TFM	0.05–1.0	$y=799.9x-38{,}213$	0.989	3.7	0.2	0.009	0.030
	MSM	0.05–1.5	$y=1621.8x+424.65$	0.998	3.9	0.1	0.006	0.019
	TS	0.05–1.0	$y=4496.2x+710.92$	0.996	4.5	0.2	0.002	0.005
	BSM	0.05–1.0	$y=3283.7x+158.97$	0.993	2.5	0.3	0.003	0.009
	PSM	0.05–1.5	$y=1322.2x+78.431$	0.997	2.1	0.2	0.005	0.017
Au-NP–IL–silica	TFM	0.05–1.5	$y=1549x+10.52$	0.993	3.1	0.1	0.005	0.016
	MSM	0.05–1.5	$y=1954.2x+10.896$	0.988	4.0	0.2	0.005	0.016
	TS	0.05–1.0	$y=2359.3x+483.37$	0.999	3.9	0.2	0.003	0.009
	BSM	0.05–1.0	$y=3698.2x+405.79$	0.994	3.3	0.3	0.002	0.008
	PSM	0.05–1.5	$y=1117x+248.68$	0.989	2.8	0.2	0.006	0.020
C_{18}	TFM	0.05–1.5	$y=3383.5x+142.82$	0.999	3.5	0.1	0.006	0.019
	MSM	0.05–1.5	$y=1146.9x+40.79$	0.994	3.8	0.2	0.005	0.017
	TS	0.05–1.0	$y=8320.9x+119.13$	0.996	4.1	0.1	0.004	0.013
	BSM	0.05–1.0	$y=1320.2x+420.59$	0.994	3.0	0.3	0.003	0.009
	PSM	0.05–1.5	$y=1632.8x+174.02$	0.998	2.6	0.2	0.005	0.017

[a] For a SUH concentration of 0.5 μg mL^{-1} ($n=30$).

Table 2
Recovery results of the determination of SUHs in water samples spiked at different levels using the Au–TEOS, the Au-NP–IL–silica and the C_{18} sorbents.

Analyte	Au–TEOS			Au-NP–IL–silica			C_{18}		
	Spiked level (μg mL^{-1})	Concentration found (μg mL^{-1})	Recovery (%)	Spiked level (μg mL^{-1})	Concentration found (μg mL^{-1})	Recovery (%)	Spiked level (μg mL^{-1})	Concentration found (μg mL^{-1})	Recovery (%)
TFM	0.05	0.035	70.0	0.05	0.042	83.9	0.05	0.038	75.4
	0.1	0.072	72.5	0.1	0.085	84.8	0.1	0.076	76.4
	0.4	0.32	79.2	0.4	0.34	84.1	0.4	0.31	77.8
	0.7	0.54	77.6	0.7	0.63	89.5	0.7	0.51	73.5
	1.0	0.72	71.5	1.0	0.87	87.2	1.0	0.77	77.2
MSM	0.05	0.036	72.9	0.05	0.043	86.5	0.05	0.040	80.3
	0.1	0.073	73.4	0.1	0.084	84.4	0.1	0.083	82.5
	0.4	0.30	75.4	0.4	0.36	89.4	0.4	0.34	84.3
	0.7	0.55	77.8	0.7	0.63	90.0	0.7	0.58	82.8
	1.0	0.74	74.4	1.0	0.87	86.8	1.0	0.84	83.5
TS	0.05	0.046	91.2	0.05	0.048	95.5	0.05	0.044	88.4
	0.1	0.090	90.1	0.1	0.098	97.7	0.1	0.090	89.9
	0.4	0.37	93.4	0.4	0.39	98.0	0.4	0.37	91.3
	0.7	0.63	89.4	0.7	0.68	96.9	0.7	0.65	92.4
	1.0	0.91	90.7	1.0	0.97	97.0	1.0	0.91	90.7
BSM	0.05	0.047	94.7	0.05	0.05	100.0	0.05	0.054	107.2
	0.1	0.095	95.0	0.1	0.105	105.0	0.1	0.090	90.4
	0.4	0.38	96.1	0.4	0.40	99.9	0.4	0.38	94.2
	0.7	0.67	95.9	0.7	0.71	101.4	0.7	0.67	95.3
	1.0	0.95	95.0	1.0	1.01	101.2	1.0	0.94	94.4
PSM	0.05	0.039	78.9	0.05	0.048	95.1	0.05	0.040	80.1
	0.1	0.080	79.5	0.1	0.091	91.1	0.1	0.080	80.4
	0.4	0.32	80.1	0.4	0.38	94.3	0.4	0.35	88.7
	0.7	0.56	79.4	0.7	0.65	92.4	0.7	0.63	89.5
	1.0	0.81	80.7	1.0	0.95	94.7	1.0	0.88	88.4

(83.9–105.0% in comparison to 70.0–96.1%) and lower LODs and LOQs were obtained when the Au-NP–IL–silica sorbent was used, although its synthesis is longer due to the addition of the IL. In addition to this, the use of the Au-NP–IL-functionalized silica sorbent as SPE material is, in some cases, a better option than the use of conventional SPE materials such as C_{18} sorbents. The use of these type of materials could be expanded to the extraction of other compounds for clean-up/preconcentration processes prior to a chromatographic or electrophoretic separation method.

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