

Determination of bisphenols in sewage based on supramolecular solid-phase extraction/liquid chromatography/fluorimetry

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Abstract

Supramolecular sorbents (hemimicelles/admicelles) are proposed for the extraction/preconcentration of bisphenols from aqueous environmental samples prior to their liquid chromatography/fluorimetric determination. A comparative study on the use of cetyltrimethylammonium bromide (CTABr)-coated silica and sodium dodecyl sulphate (SDS)-coated γ -alumina as sorbent materials, is presented. Bisphenol A (BPA) and bisphenol F (BPF) were quantitatively retained on CTABr admicelles. Addition of tetrabutylammonium chloride (TBAC) to water samples was required to completely retain bisphenols on SDS- γ -alumina. Retention on both sorbents occurred through hydrophobic and pi-cation interactions between the quaternary ammonium head group of the cationic amphiphile (CTABr or TBAC) and the aromatic rings of the target analytes. TBAC-SDS- γ -alumina was the sorbent selected for the SPE of bisphenols on the basis of the lower elution volume required (1 ml of methanol) and the greater breakthrough volume allowed (400 ml), which permitted to reach practical detection limits of 10 and 15 ng/l for BPF and BPA, respectively. The proposed method was used to quantify bisphenol A and bisphenol B in wastewater samples from four sewage treatment plants. Recoveries obtained ranged between about 99 and 105% for raw wastewater and between 96 and 106% for treated wastewater.

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1. Introduction

Supramolecular assemblies (hemimicelles/admicelles) have recently emerged as an efficient sorbent material for the extraction and preconcentration of inorganic [1–5] and organic [6–11] substances. They are formed from adsorption of surfactants on the surface of metal oxides such as alumina, silica, titanium dioxide and ferric oxyhydroxides. Attractive electrostatic interactions between the head group of ionic surfactants and oppositely charged groups on the oxide result in the formation of monolayers of adsorbed surfactant termed hemimicelles. After saturation of the oxide surface, hydrophobic interactions between hydrocarbon chains of surfactant molecules result in the formation of admicelles. These aggregates have been traditionally described as surfactant bilayers, although recent studies have brought forward evidences of the formation of discrete surface aggregates, similar to aqueous micelles [12].

Adsorbing characteristics of supramolecular sorbents can be easily modified on the basis of both the nature of surfactant (hydrophobicity of its non-polar moiety and charge of its polar groups) and the type of assembly formed: hemimicelles, whose outer surface is hydrophobic in nature or admicelles, able to provide both hydrophobic and electrostatic interactions with analytes. The unique features of surfactant-coated mineral oxides make them especially suitable for the extraction of amphiphilic substances based on the formation of mixed aggregates [6,7]. Excellent results have been also obtained for the extraction of polar ionic organic compounds by using admicelles of surfactants bearing opposite charge to that of the target analytes [8].

In this paper, a comparative study on the capability of cationic and anionic hemimicelles/admicelles for the extraction and preconcentration of bisphenols [bisphenol A (BPA) and bisphenol F (BPF)], from environmental aqueous samples is presented. Bisphenols are synthesized in high quantities to be used in the manufacture of thermoset plastics which have numerous applications (lacquer coatings in food-stuffs cans, structural steel coating, floor varnishes, etc. [13,14]). The release of these toxic and estrogenic phenolic compounds into the environment

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occurs through wastewater from manufacturing processes and by leaching from final products. Effluent from cities and industrial wastewater treatment plants frequently contain bisphenols, because of the incomplete removal of these contaminants during treatment.

The low concentrations at which bisphenols are present in aqueous environmental samples and the complex and potential different composition of these samples make necessary the use of preconcentration and clean up steps prior to their chromatographic analysis. GC/MS is the technique most commonly used to determine bisphenols at the ng/l level in water samples [15–18], its main drawback being the complex and time-consuming sample treatments required, which comprise at least three steps: extraction of the target analytes, evaporation of the extract to dryness and derivatization. A number of methods based on liquid chromatographic separation and mass spectrometric [19,20], fluorimetric [21] and electrochemical [21,22] detection, using simpler and faster sample treatments, have been recently reported.

Solid-phase extraction is the technique commonly used for bisphenols extraction from environmental aqueous samples prior to LC analysis because of its advantages over liquid–liquid extraction: high preconcentration factors, low consumption of organic solvents, elimination of emulsions and easy automatization. C₁₈-silica is the most widely used sorbent material, but it provides relatively low recoveries (about 80% for bisphenol A at the ng/l level from 500 ml of water [19]), and, requires evaporation of eluates to reach the preconcentration factors demanded in environmental analysis (which greatly increases analysis time). Other sorbents such as polystyrene–divinylbenzene polymers present similar drawbacks [22]. Quantitative recovery of bisphenol A has been reported by using molecularly imprinted polymers (MIPs) [20,23] and multiwalled carbon nanotubes (MWNTs) [21], their main disadvantages being the no commercial availability of MIPs and the high cost of MWNTs.

The aim of this work was to develop a simple and rapid sample treatment approach based on the use of supramolecular sorbent materials that permits the quantitative extraction of bisphenols at the low concentration levels present in environmental water samples. With this purpose, hemimicelles and admicelles formed by adsorption of SDS on γ -alumina and cetyltrimethylammonium bromide (CTABr) on silica were tested. Experimental variables affecting recoveries and preconcentration factors achieved for bisphenols were studied, analytical features of the SPE-LC/fluorimetric method were established and the proposed approach based on the use of tetrabutylammonium (TBAC)-coated SDS hemimicelles was applied to the determination of the target analytes in sewage samples.

2. Experimental

2.1. Chemicals and materials

Commercially available highest-grade chemicals were employed without further purification. Alumina (γ -form, for column chromatography) and silica (Davisil, grade 646) were purchased from Sigma (St Louis, MO, USA) and Aldrich

(Steinheim, Germany), respectively. The physical properties of these mineral oxides were as follows: alumina—surface area, 155 m²/g; point of zero charge (pzc), 8.5; particle diameter range, 50–200 μ m; mean pore size, 58 Å. Silica—surface area, 300 m²/g; point of zero charge; pzc, 2.9; mean pore size, 150 Å; particle diameter range, 250–500 μ m. Bond Elut Jr. cartridge columns with 500 mg alumina were obtained from Varian (Vic., Australia) and cartridge columns with 500 mg silica were obtained from Analisis Vinicos (Tomelloso, Spain). The surfactants sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTABr) were supplied by Aldrich. A 0.5 M aqueous solution of tetrabutylammonium chloride (TBAC, Fluka, Buchs, Switzerland) was prepared by dissolving 16.22 g of the reagent in 50 ml of distilled water. Bisphenol A [BPA; 2,2'-bis(4-hydroxyphenyl)propane] and bisphenol F [BPF; bis(4-hydroxyphenyl)methane] were obtained from Fluka. A stock solution containing a 2 g/l concentration of each bisphenol was prepared in acetonitrile and stored under dark conditions at 4 °C. This stock solution was stable for at least 1 month. Working solutions containing a 10 mg/l concentration of each bisphenol were prepared weekly by appropriate dilution with acetonitrile. HPLC-grade acetonitrile and methanol were supplied by Pan-reac (Sevilla, Spain).

2.2. Sample collection and preservation

Water samples were collected from four different sewage treatment plants (STPs), all of them in the region of Andalusia (south of Spain), located at Linares, Lucena, Puente Genil and Arahal. Linares STP receives the same level of both domestic and industrial wastewaters (mainly from the car and engineering industries), Lucena and Puente Genil STPs receive mainly industrial effluents (from the furniture and bronze factories and from the food industry, respectively) and Arahal STP receives mainly domestic sewage. Raw sewage and final effluent samples from the four STPs investigated were taken in June 2004. After their collection in brown glass bottles, samples were adjusted to pH 2 by the addition of concentrated hydrochloric acid, filtered through 0.45 μ m HNWP nylon membranes (Millipore, Bedford, MA, USA) in order to remove suspended soils, and stored under dark conditions at 4 °C.

2.3. Recommended procedure for the determination of bisphenols in sewage

2.3.1. SDS hemimicelle-based extraction

Extractions were performed using a Supelco Visiprep (Bellefonte, PA, USA) vacuum manifold attached to a Rikakikai Eyela A35 (Tokyo, Japan) vacuum pump. The Bond Elut Jr. cartridge columns were conditioned with 5 ml of Milli-Q water. Then, hemimicelles were formed on the alumina by passing a 25 ml 0.01 M hydrochloric acid solution containing 42.5 mg of SDS. Afterwards, 400 ml of sewage (influent or effluent) sample containing bisphenols and 5 mM TBAC were passed through the hemimicelle extraction column at a rate of less than 10 ml/min by adjusting the vacuum to ca. 70 kPa. Finally, after drying the column under vacuum, bisphenols were eluted with 1 ml methanol

at a rate of less than 1.5 ml/min by adjusting the vacuum to ca. 4 kPa. An aliquot (20 μ l) of the eluate was injected into the liquid chromatographic system.

2.3.2. Liquid chromatographic analysis

The liquid chromatographic system used consisted of a TermoQuest Spectra System (San José, CA, USA) furnished with a P4000 quaternary pump, a SCM 100 vacuum membrane degasser and a FL3000 fluorescence detector. The column was a 15 cm \times 3.9 mm I.D. Waters Nova-Pack C₁₈ column (Milford, MA, USA) of 4 μ m particle diameter. In all experiments a Rheodyne 7725 injection valve (Rohnert Park, CA, USA) furnished with a 20 μ l sample loop was used. Bisphenols were separated by using a mobile phase consisting of 70:30 (v/v) water–acetonitrile (flow rate = 0.8 ml/min). Fluorimetric detection of analytes was performed at 278–306 excitation-emission wavelengths (in nm).

3. Results and discussion

3.1. Hemimicelle/admicelle extraction

A comparative study on the ability of CTABr-coated silica and SDS coated- γ -alumina to extract bisphenols (BPA and BPF) from environmental aqueous samples was performed. With this purpose, different variables affecting adsolubilization of bisphenols (amount of surfactant and short chain quaternary ammonium salts, sample loading volume and flow rate) and their desorption from adsorbent materials (volume of organic solvent and eluent flow rate) were investigated.

3.1.1. Factors affecting adsolubilization of bisphenols

The knowledge of the adsorption isotherms of the surfactants used as sorbents (i.e. SDS or CTABr), under the experimental conditions investigated, is essential to understand the mechanisms of adsolubilization of analytes and to correctly optimize the parameters affecting the SPE sequence. Fig. 1 shows the experimental isotherms obtained for the adsorption of CTABr on silica at pH 6 (Fig. 1A) and SDS on γ -alumina at pH 2 (Fig. 1B).

Two factors determine the surfactant load on the oxide surface, namely, the charge density of the mineral oxide, which is a function of the amount and surface area of the oxide and pH, and the amount added of surfactant. In order to maximize the

surfactant load on the oxide and, in consequence, the adsolubilization capability of supramolecular sorbents, the pH value for the formation of surfactant aggregates should be selected to ensure maxima charge density on the mineral oxide surface. Thus, taking into account that the point of zero charge (pzc) is 2.9 for silica and 8.5 for γ -alumina, basic and acid pHs should be selected, respectively, for the adsorption of CTABr on silica and SDS on alumina. However, because method development was intended to determine bisphenols in wastewater and undesirable precipitations can occur at basic pHs, an acid pH value (about 6) was selected for the adsorption of CTABr on silica. This explains the difference in the maximum surfactant load obtained for CTABr and SDS (compare Fig. 1A and B).

Both isotherms show the three regions suitable for SPE methods (hemimicelles, mixed hemimicelles/admicelles and admicelles). In these regions, the surfactant aggregates are in equilibrium with surfactant aqueous monomers. Above the critical micellar concentrations (CMCs) of CTABr and SDS, aqueous micelles of these surfactants are in equilibrium with admicelles, which causes partition of analytes between both types of surfactant aggregates and makes this isotherm span unsuitable for SPE.

The effect of the amount of surfactant on the adsolubilization of bisphenols was studied in the batch mode by adding 50 μ l of an aqueous solution containing 3 g/l of each bisphenol to a 25 ml aqueous solutions of surfactant (CTABr, pH 6.0 or SDS, pH 2.0) containing 0.5 g of silica or γ -alumina, respectively. The surfactant amount was varied in the intervals 0–55 mg CTABr/g silica and 0–290 mg SDS/g alumina to give adsorbed surfactant concentrations comprised in the hemimicellar, hemimicellar/admicellar, and admicellar regions. The aqueous suspension was vigorously stirred for 5 min, and then centrifuged at 4000 rpm for 5 min, and the concentrations of bisphenols were determined in the supernatants by LC/fluorimetry, as specified in Section 2. At the bisphenol concentrations used in this experiment (6 mg/l), percentages of adsolubilization up to 99.8% could be determined by direct measurement of the remaining analyte in the supernatants.

The retention capability of supramolecular sorbents (hemimicelles and admicelles) for bisphenols highly depended on the nature of the surfactant used to form the surface aggregates (Fig. 2). Both analytes were hardly retained on hemimicelles

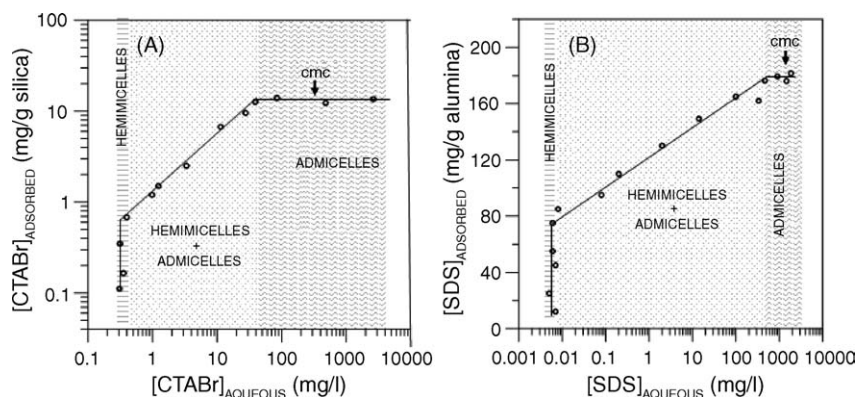


Fig. 1. Experimental adsorption isotherms for (A) CTABr on silica at pH 6 and (B) SDS on alumina at pH 2.

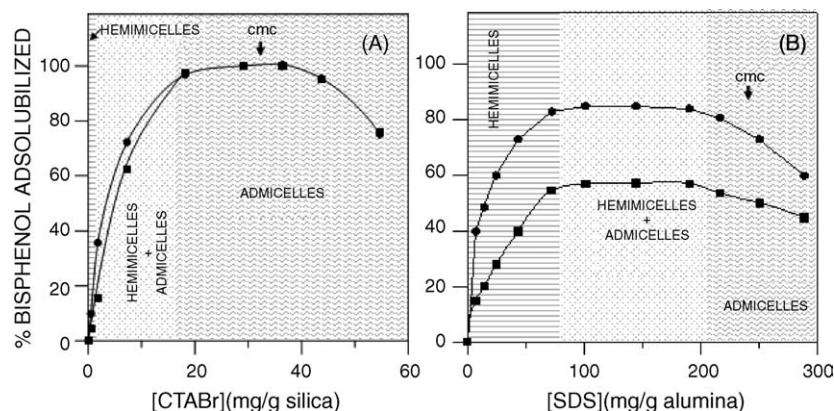


Fig. 2. Influence of the amount of (A) CTABr and (B) SDS on the adsolubilization of bisphenols: (●) BPA and (■) BPF. Operation in the batch mode. Amount of metal oxide: 0.5 g of (A) silica and (B) alumina. pH: (A) 6 and (B) 2.

of CTABr; their retention increased with the formation of admicelles and total adsolubilization occurred at the maxima surfactant coverage density (Fig. 2A). On the contrary, adsorption percentages of about 85% BPA and 57% BPF were obtained for SDS hemimicelles and these percentages were hardly modified in the presence of admicelles (Fig. 2B). The differences in the adsolubilization capability of SDS and CTABr in the hemimicellar region, where retention of analytes is mainly governed by hydrophobic interactions, could be explained on the basis of the differences in the amount of cationic and anionic surfactant adsorbed on the oxide mineral surface (compare Fig. 1A and B). In the admicellar region, pi-cation interactions between the quaternary ammonium head group of the cationic surfactant and the aromatic rings of analytes, in addition to hydrophobic interactions, were responsible for the quantitative retention of bisphenols on CTABr. Phenolic compounds have been previously reported to associate with quaternary ammonium salts via a pi-cation interaction [24,25]. These pi-cation interactions were decisive to reach quantitative recoveries of bisphenols, as it can be derived from the fact that analytes adsolubilization on SDS was scarcely modified when admicelles were formed on the oxide surface. For both, SDS and CTABr, adsolubilization of bisphenols decreased at surfactant concentrations above the CMC due to the formation of aqueous micelles where analytes were solubilized.

In order to get the benefits of working at high surfactant load (e.g. higher breakthrough volumes), we tested the possibility of obtaining pi-cation interactions on SDS hemimicelles. For this purpose, the effect of adding tetrabutylammonium chloride (TBAC) on the retention of bisphenols was investigated. The experiment was carried out in two steps. First SDS hemimicelles were yield on alumina (0.5 g) by passing 25 ml 0.01 M hydrochloric acid solution containing 42.5 mg of SDS. Afterwards, a 25 ml solution containing the bisphenols and different TBAC concentrations at pH 2 were percolated through the SDS hemimicelles. Fig. 3 shows the results obtained. As it was expected, TBAC molecules were retained on SDS hemimicelles through hydrophobic interactions, which resulted in the change of the nature of the outer surface of the supramolecular sorbent from hydrophobic to cationic. The percentage of bisphenols

retained on hemimicelles of SDS greatly increased with the concentration of ammonium salt. The amount of TBAC required to achieve quantitative retention of the most polar bisphenol (BPF) was that necessary for saturation of SDS hemimicelles, assuming that each TBAC molecule interacted with two SDS molecules.

The breakthrough volume for each bisphenol on both sorbents (CTABr admicelles and TBAC-coated SDS hemimicelles) was studied by passing increasing volumes (25–500 ml) of aqueous solutions containing 25 μ g of each bisphenol at pH 6 or 2, respectively, through cartridges filled with the supramolecular sorbent, and then, determining the amount of BPA and BPF eluted with methanol. Breakthrough was considered to occur when the amount eluted decreased about 5%. Quantitative recovery of BPA was achieved in the interval studied using TBAC-coated SDS hemimicelles, while a breakthrough volume of 400 ml was obtained for the most polar bisphenol (i.e. BPF). The breakthrough volume was reduced to 400 and 200 ml for BPA and BPF, respectively, when CTABr-coated silica was

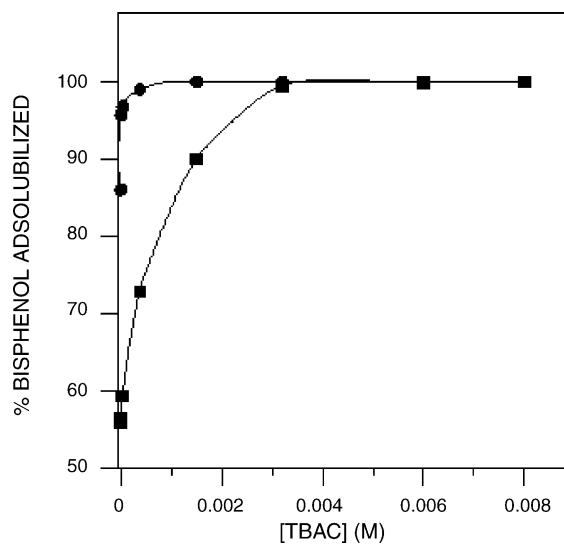


Fig. 3. Effect of the concentration of TBAC on the adsolubilization of bisphenols on hemimicelles of SDS at pH 2: (●) BPA and (■) BPF. Operation in the SPE mode. Amount of alumina: 0.5 g. Amount of SDS: 85 mg/g. Sample loading volume: 25 ml. [BPF] = [BPA] = 1 mg/l.

used, probably due to the lower amount of cationic surfactant adsorbed on silica compared to that of SDS on alumina (compare isotherms A and B in Fig. 1). Experiments were performed at the sample flow rates obtained (2 and 10 ml/min for CTABr admicelles and TBAC coated SDS hemimicelles, respectively) by adjusting the vacuum to the maximum value recommended by the vacuum system supplier (ca. 70 kPa). No increased breakthrough volumes were obtained by reducing the sample flow rates to 1 and 5 ml/min for CTABr and TBAC-SDS coated mineral oxides, respectively.

3.1.2. Factors affecting desorption of bisphenols

Organic solvents are known to cause disruption of hemimicelles/admicelles and, therefore, to permit desorption of organic compounds from supramolecular sorbents [6–8]. Elution of bisphenols from CTABr admicelles and TBAC-coated SDS hemimicelles was studied using different volumes (1–4 ml) of methanol, acetonitrile and tetrahydrofuran. All elution experiments were performed after passing 25 ml of aqueous sample containing 5 µg/l of each bisphenol at pH 6 or 2 through the supramolecular column (CTABr-silica or TBAC-SDS-γ-alumina, respectively). Quantitative recovery of bisphenols from CTABr admicelles and TBAC-coated SDS hemimicelles was obtained by using 2 and 1 ml of methanol, respectively. Higher solvent volumes were required to completely elute bisphenols using acetonitrile or tetrahydrofuran.

The eluent flow rate was a determining factor to reach complete desorption of bisphenols, its effect being more pronounced when analytes were retained on CTABr admicelles. Thus, the elution rate should not be superior to 0.2 and 2.0 ml/min for CTABr-silica and TBAC-SDS-alumina, respectively, in order to get quantitative recoveries.

3.2. Analytical features

Linear calibrations were obtained in the interval 0.2–40 ng for BPF and 0.3–40 ng for BPA (correlation coefficient = 0.9997 and 0.9993, respectively). The sensitivities, expressed as the slope of the calibration curves, were $392 \pm 5 \text{ ng}^{-1}$ for BPF and $365 \pm 3 \text{ ng}^{-1}$ for BPA. The instrumental detection limits were calculated from blank determinations by using a signal-to-noise ratio of 3 (the ratio between the peak areas for each bisphenol and peak area of noise). They were estimated to be about 0.08 ng for BPF and 0.12 ng for BPA. From these values and considering the maximum preconcentration factor achieved for each of the supramolecular sorbent tested, the detection limits that could be achieved for bisphenols in environmental water samples are shown in Table 1. The practical detection limits [26] were

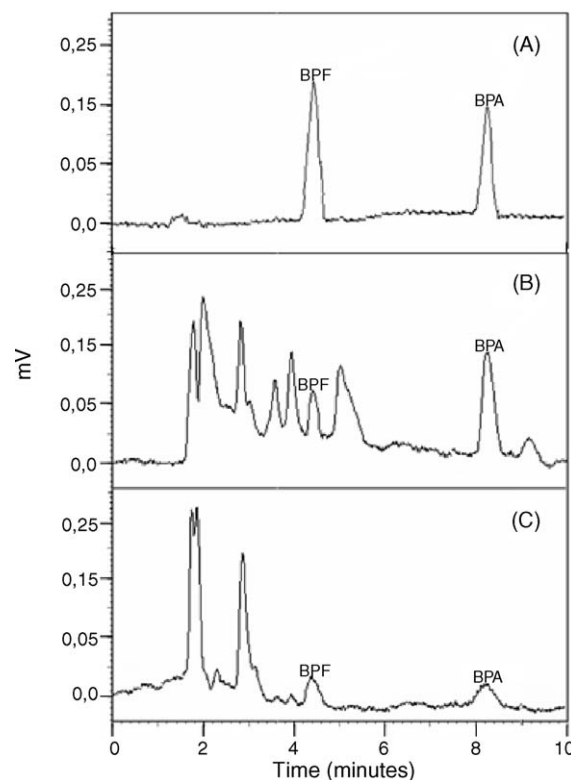


Fig. 4. Chromatograms obtained from (A) a standard solution containing 0.4 mg/l BPA and 0.4 mg/l BPF and from (B) a influent and (C) a effluent sample obtained from the Linares sewage treatment plant in Córdoba, Spain.

estimated from six independent complete analyses of a typical matrix low-level material. The matrix of sewage samples was found not to have any effect on the detection limits achieved for the determination of bisphenols, because of the high selectivity of both the supramolecular solid phase extraction and fluorimetric detection. Because of the higher sample loading volume permitted and the lower volume of eluent required to quantitative recovery of bisphenols, TBAC-coated SDS hemimicelles provided the lowest detection limits and it is the recommended sorbent.

3.3. Analysis of sewage samples

Influent and effluent samples from four different sewage treatment plants (STPs) were analysed using TBAC-SDS hemimicelles extraction/LC/fluorimetry (experimental conditions are given in Section 2.3). Fig. 4 shows the chromatograms obtained from a standard solution (A) and sewage samples taken from the Linares STP (B and C). The concentrations obtained for BPF and

Table 1
Preconcentration factors and limits of detection (LOD) of bisphenols in environmental water samples achieved using the two supramolecular sorbents tested

Supramolecular sorbent	^a Sample volume (ml)	Elution volume (ml)	Preconcentration factor	LOD (ng l ⁻¹)	
				BPF	BPA
TBAC-SDS-alumina	400	1	400	10	15
CTABr-silica	200	2	100	40	60

^a Breakthrough volume.

Table 2
Recovery of bisphenols from influent and effluent water samples from four sewage-treatment plants

Sample	Concentration ($\mu\text{g l}^{-1}$)					
	Added		Found ^a \pm SD ^b		Recovery (%)	
	BPF	BPA	BPF	BPA	BPF	BPA
Linares influent	0	0	0.25 ± 0.02	1.62 ± 0.04		
	1.0	1.0	1.27 ± 0.06	2.8 ± 0.2	102 ± 4	105 ± 6
Linares effluent	0	0	0.16 ± 0.01	0.30 ± 0.02		
	0.2	0.2	0.37 ± 0.02	0.49 ± 0.02	102 ± 6	98 ± 4
Lucena influent	0	0	<LOD ^c	0.36 ± 0.04		
	1.0	1.0	1.03 ± 0.05	1.37 ± 0.03	103 ± 5	101 ± 2
Lucena effluent	0	0	<LOD ^c	0.28 ± 0.01		
	0.2	0.2	0.212 ± 0.007	0.476 ± 0.008	106 ± 6	100 ± 2
Puente Genil influent	0	0	<LOD ^c	<LOD ^c		
	1.0	1.0	1.00 ± 0.05	0.94 ± 0.09	99 ± 2	100 ± 1
Puente Genil effluent	0	0	<LOD ^c	<LOD ^c		
	0.2	0.2	0.197 ± 0.004	0.203 ± 0.008	98 ± 2	102 ± 4
Arahal influent	0	0	0.060 ± 0.004	1.146 ± 0.005		
	1.0	1.0	1.085 ± 0.03	2.16 ± 0.03	102 ± 3	101 ± 1
Arahal effluent	0	0	0.047 ± 0.001	0.11 ± 0.02		
	0.2	0.2	0.24 ± 0.01	0.309 ± 0.003	96 ± 6	99 ± 1

^a Mean of two independent determinations.

^b Standard deviation.

^c Lower than the detection limit; sample volume = 400 ml.

BPA, expressed as the mean value of three independent determinations and their corresponding standard deviations, are listed in Table 2. Because of the higher use of BPA compared with BPF, the concentration of the former in sewage samples was higher. Although biodegradation treatment process used in all the STPs tested were found to reduce the amount of bisphenols in treated wastewaters, they were unable to effectively remove these compounds from sewage (a total concentration of bisphenols up to about $0.5 \mu\text{g/l}$ were found in effluent samples).

The accuracy of the proposed method was evaluated from recoveries studies performed by spiking influent and effluent samples with 1.0 and $0.2 \mu\text{g/l}$ of each bisphenol, respectively. Results obtained are shown in Table 2. Recoveries ranged between 96 and 106% for BPF and between 98 and 105% for BPA, respectively, which demonstrated the validity of the proposed method to analyze sewage samples.

4. Conclusions

Supramolecular assemblies (hemimicelles/admicelles) have been demonstrated to be an advantageous alternative to the sorbent materials proposed up to date for the extraction/preconcentration of bisphenols from environmental aqueous samples. They permit the quantitative extraction of these organic contaminants at the low ng/l level, reaching preconcentration factors of 400 without the need of reducing the volume of eluate by evaporation, which is usually proposed when other solvents (e.g. C_{18} -silica, polystyrene–divinylbenzene polymers, etc.) are used due to the volume of eluent required (typically 6–10 ml). The low volume of eluent necessary when hemimicelles/admicelles are used results in shorter analysis times,

beside of avoiding analytes losses during organic solvent evaporation.

This research greatly extends the scope of application of hemimicelles/admicelles based SPE. The use of ammonium surfactant-based supramolecular sorbents, able to provide pication interactions with analytes bearing aromatic structures, has proven to give high extraction yields. So, these sorbents are expected to find wide application in environmental analysis where most pollutants are aromatic.

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References

- [1] J.L. Manzoori, M.H. Sorouraddin, A.M.H. Shabani, J. Anal. At. Spectrom. 13 (1998) 305.
- [2] M. Hiraide, J. Hori, Anal. Sci. 15 (1999) 1055.
- [3] A.M.H. Shabani, S. Dadfarnia, K. Dehghan, Talanta 59 (2003) 719.
- [4] G. Absalan, M.A. Ayatollahi Mehrdjardi, Sep. Purif. Technol. 33 (2003) 95.
- [5] J. Nan, X.P. Yan, Anal. Chim. Acta 536 (2005) 207.
- [6] F. Merino, S. Rubio, D. Pérez-Bendito, Anal. Chem. 75 (2003) 6799.
- [7] M. Cantero, S. Rubio, D. Pérez-Bendito, J. Chromatogr. A 1067 (2005) 161.
- [8] F. Merino, S. Rubio, D. Pérez-Bendito, Anal. Chem. 76 (2004) 3878.
- [9] T. Saitoh, Y. Nakayama, M. Hiraide, J. Chromatogr. A 972 (2002) 205.
- [10] T. Saitoh, S. Matsushima, M. Hiraide, J. Chromatogr. A 1040 (2004) 185.

- [11] T. Saitoh, S. Matsushima, M. Hiraide, *J. Chromatogr. A* 1069 (2005) 271.
- [12] R. Atkin, V.S.J. Craig, E.J. Waules, S. Biggs, *Adv. Colloid Interface Sci.* 103 (2003) 219.
- [13] J.E. Biles, K.D. White, T.P. McNeal, T.H. Begley, *J. Agric. Food Chem.* 47 (1999) 1965.
- [14] P. Paseiro Losada, C. Pérez Lamela, M.F. López Fabal, P. Sanmartín Fenollera, J. Simal Lozano, *J. Agric. Food Chem.* 45 (1997) 3493.
- [15] J.L. Vílchez, A. Zafra, A. González-Casado, E. Hontoria, M. Olmo, *Anal. Chim. Acta* 431 (2001) 31.
- [16] T. Suzuki, Y. Nakagawa, I. Takano, K. Yaguchi, K. Yasuda, *Environ. Sci. Technol.* 38 (2004) 2389.
- [17] H. Fromme, T. Kuchler, T. Otto, K. Pilz, J. Müller, A. Wenzel, *Water Res.* 36 (2002) 1438.
- [18] R. Liu, J.L. Zhou, A. Wilding, *J. Chromatogr. A* 1022 (2004) 179.
- [19] S. Rodríguez-Mozaz, M.J. López de Alda, D. Barceló, *J. Chromatogr. A* 1045 (2004) 85.
- [20] W. Yoshiyuki, H. Ken, T. Nobuo, K. Takuya, M. Masatoshi, K. Takuya, *Anal. Bioanal. Chem.* 381 (2005) 1193.
- [21] Y. Cai, G. Jian, J. Liu, Q. Zhou, *Anal. Chem.* 75 (2003) 2517.
- [22] K. Inoue, Y. Yoshie, S. Kondo, Y. Yoshimura, H. Nakazawa, *J. Chromatogr. A* 946 (2002) 291.
- [23] Y. Watabe, T. Kondo, M. Morita, N. Tanaka, J. Haginaka, K. Hosoya, *J. Chromatogr. A* 1032 (2004) 45.
- [24] A. McCurdy, L. Jiménez, D.A. Stauffer, D.A. Dougherty, *J. Am. Chem. Soc.* 114 (1992) 10314.
- [25] A. Dalla Cort, M. Nissinen, D. Mancinetti, L. Mandolini, C. Pasquini, K. Rissanen, *Supramol. Chem.* 16 (2004) 59.
- [26] M. Thompson, S.L.R. Ellison, R. Wood, *Pure Appl. Chem.* 74 (2002) 835.