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Polymeric and silica sorbents on endocrine disruptors determination

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ABSTRACT

Endocrine disrupting determination at low concentration levels comprises one of the most important targets in environmental analytical chemistry. In spite of inherent high sensitivities obtained for HPLC, these techniques have some limitations depending on the contaminants. As a result, interest in preconcentration using solid—phase extraction (SPE) still continues increasingly for endocrine disrupting determinations by HPLC due to the high accuracy of this method. In this work, we evaluated three different adsorbents in preconcentration of endocrine disruptors in three different categories: pharmaceuticals (sulphamethoxazole, trimethoprim and diclofenac), hormones (estrone, 17β-estradiolacetate and 17β-estradiol) and plastic materials (bisphenol A) in multicomponent aqueous solution using the combination SPE -HPLC. The adsorbents investigated were such as modified silica (octadecylsilane)—DSC-18 (Supelco) and two polymers, a divinylbenzene-N-vinilpirolidona —Oasis® HLB (Waters) and a styrene-divinylbenzene modified with butyrolactone—Strata-X™ (Phenomenex). The parameters selected to evaluate the best adsorbent were sample loaded, breakthrough volume, recovery and adsorption capacity. The results showed that the polymeric sorbents Oasis and Strata presented good separation and selective ability, then the most efficient sorbent for the described test was applied to the determination of endocrine disruptor (ED) in a wastewater real sample. Almost all endocrine disruptors studied in the present work were found and quantified in the effluent sample, suggesting the selected cartridge could be useful for preconcentration technique of endocrine disruptors in environmental analytical applications. Correlation analysis identified the adsorption parameters which had the most influence in efficiency of SPE adsorbents, such as initial ED concentration, breakthrough volume and recovery.

Keywords: SPE; Breakthrough volume; Endocrine disruptors

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1. Introduction

Endocrine disruptors (EDs) are a heterogeneous group of substances that can disrupt the synthesis, circulating levels and peripheral action of hormones. They are also characterized by their potential to interfere with the function of the endocrine system in wildlife and humans [1]. A wide range of substances, both natural and man-made, are thought to cause endocrine disruption, including, hormones, pharmaceuticals, dioxin and dioxin-like compounds, polychlorinated biphenyls, DDT and other pesticides, and components of plastics such as bisphenol A (BPA) and phthalates [2]. The concentration of EDs detected in the environment is quite low (ng L^{-1}—μg L^{-1}) [3,4].

However, the low limit of detection of these compounds in aqueous wastes requires the development of highly efficient and reliable extraction procedures. Various techniques have been used for EDs extraction in aqueous matrices, such as liquid-liquid extraction and solid-phase extraction (SPE) [5].

In recent years, SPE has become a well-established preconcentration technique in environmental analytical applications of different samples, e.g. environmental, biological and medical, amongst others. This technique has spread very fast and found interest in different domains of research. The analytical procedures using SPE are applied very often in both science and industry. SPE, due it capacity for allows the isolation of different compounds, sample preconcentration, change of the sample matrix and sample clean-up, is one of the most common techniques used for EDs preconcentration in waters, although the use of SPME is also well documented [6—10].

The efficiency of SPE depends on the physicochemical properties of the compounds, sorbents and the solvents used in the extraction process, like: polarity, acidity, basicity and hydrophobicity. Extracting pollutants with a wide range of physical and chemical structures requires a variety of sorbents to be used in order to trap properly all the target compounds present in the samples. For extraction system selection it is very important to establish the relations/interactions between compounds, sorbent and elution solvents. Thus, the sorbent selection depends basically on the nature matrix and analyte properties, as well as sample loaded, breakthrough volume, recovery and adsorption capacity which are important stage for the analytical method elaboration [6,7,11—15].

The physical characteristics of the sorbents such as surface area, particle size, and pore volume are crucial sorbent properties [16,17]. However, the extraction ability of sorbents in the SPE bed depends also on the bed capacity; the volume of sample loaded on the bed, the nature and volumes of conditioning solvents and eluents.

The breakthrough volume, V_b, sample volume which can be loaded on the sorbent bed without the loss of the analytes, is the most important characteristic parameter of a sampling device for isolating the analytes of interest, mainly SPE sorbent bed. It depends on the sorbent kinetic parameters, retention parameters and sample flow rate. In this context, selection of the appropriate sorbent is an important stage in the elaboration of the analytical method [6,18].

Several studies have investigated the detection of EDs in wastewater using SPE analysis with different SPE adsorbents, such as Oasis HLB [13,15,19,20]; C-18 [21,22] and Strata-X [6].

Currently, no standardized analytical methods are available for the analysis of EDs in environmental waters. Owing to the diversity of physicochemical properties exhibited by the various classes of organic micropollutants, the majority of established analytical methods described in the literature focus on a specific class of compounds, with few methods applicable to multi-class compound analysis.

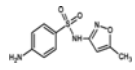
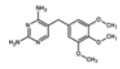
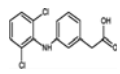
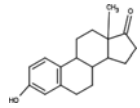
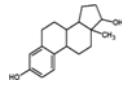
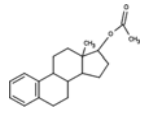
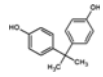
The aim of this paper was to evaluate three different adsorbents, commonly used in the literature, in preconcentration of EDs in three different categories: pharmaceuticals (sulfamethoxazole, trimethoprim and diclofenac), hormones (estrone, 17β-estradiolacetate and 17β-estradiol) the plastic materials (BPA) in multicomponent aqueous solution in terms of the parameters sample loaded, breakthrough volume, recovery and adsorption capacity. Interaction mechanisms between EDs-sorbents also were discussed.

2. Experimental

2.1. Chemicals

A stock solution of 1,000 mg L^{-1} of compounds was prepared in methanol (HPLC grade, VETEC-Brazil), and the standards for pharmaceuticals (sulfamethoxazole, trimethoprim and diclofenac), hormones (estrone, 17β-estradiolacetate and 17β-estradiol) the plastic materials (BPA) were purchased from Sigma—Aldrich-USA. Then, working solutions were prepared in dilutions with deionized water to a concentration of 1.5 mg L^{-1} (17β-estradiolacetate) and 5 mg L^{-1} (sulfamethoxazole, trimethoprim, 17β-estradiol, BPA, diclofenac and estrone) for adsorption test. The physicochemical properties for the EDs selected are shown in Table 1.

Table 1
Physicochemical properties for the endocrine disruptors studied

Category	Compounds	Molecular Formula	Molecular weight ($g\,mol^{-1}$)	Solubility ($mg\,L^{-1}$ at 25°C)	log K_{ow}	p*Ka*	Molecular Structure
Pharmaceuticals	Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	253.28	610	0.89	5.5	
	Trimethoprim	$C_{14}H_{18}N_4O_3$	290.3	400	0.9	7.12	
	Diclofenac	$C_{14}H_{11}Cl_2NO$	296.14	2.4	0.7	4.2	
Hormones	Estrone	$C_{18}H_{22}O_2$	270.37	0.8—12.4	3.43	10.4	
	17β-estradiol	$C_{18}H_{24}O_2$	272.39	3.9–13.3	3.94	10.4	
	17β-estradiolacetate	$C_{20}H_{26}O_3$	314.42	1.37	4.95	10.4	
Plastic materials	BPA	$C_{15}H_{16}0_2$	228.1	120	3.32	9.6—10.2	

2.2. Sorbents

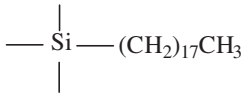
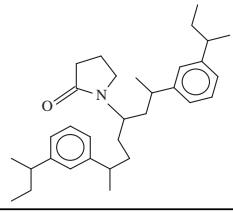
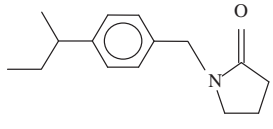
Three commercial adsorbents were tested: modified silica (octadecylsilane)—DSC-18 (Supelco) and polymers, a divinylbenzene-N-vinilpirolidona—Oasis® HLB (Waters) and a styrene-divinylbenzene modified with butyrolactone—Strata-X™ (Phenomenex). Physical and chemical sorbents characteristicsare shown in Table 2.

2.3. SPE experiments

The SPE experiment was carried out as follows: 1 L of solution (concentration of $5\,mg\,L^{-1}$ and flow rate of $1.0\,mL\,min^{-1}$) was introduced into SPE sorbent conditioned with methanol (10 mL). For each compound, frontal analysis was carried out as follows.

The solute was put in contact with the sorbent in a downward flow and aliquots of 10 mL were collected

Table 2
Physical and chemical sorbents characteristics

Parameter	DSC-18	Oasis® HLB	Strata™-X
Surface area ($m^2\,g^{-1}$)	463	823	818
Pore diameter (Å)	73.0	82.0	88.0
Pore volume ($mL\,g^{-1}$)	0.850	1.34	1.26
Particle size (μm)	53	30,3	28
Sorbent mass (mg)	500	200	200
Sorbent nature	Silica	Polymeric	Polymeric
Functional group			

every 10 min, after which 20-μL effluent sample was taken and the compounds were determined using HPLC-DAD. The calibration curves followed the external standard methodology.

Breakthrough curves were determined as the relationship between concentration in the water sample passed through the sorbent and initial synthetic solution (C/C_0). For each sorbent-analyte system, the retention parameters were determined from the appropriate curve [6,18,23,24].

In a breakthrough curve, C_0 is the adsorbate concentration in the effluent and V_e is the effluent volume that percolates through the SPE sorbent. The breakpoint, chosen arbitrarily as C_b, occurs when the effluent concentration reaches 5% of the initial concentration C_0. The SPE sorbent achieves complete saturation, when the concentration C_x approaches C_0. The total effluent amount, V_b, is passed through the SPE sorbent until the breakpoint is reached [25]. The part between C_x (exhaustion point) and C_b (breakpoint) is called primary adsorption zone (PAZ) and the time needed to establish PAZ in the SPE sorbent is calculated by Eq. (1) [24—27]:

$$t_x = \frac{V_x}{F_m} \tag{1}$$

where t_x is the time to establish PAZ (min), F_m is the flow rate (mL/min) and V_x is the exhaustion volume (mL).

The time required for movement of PAZ down the column is given by Eq. (2) [26,27]:

$$t_\sigma = \frac{V_x - V_b}{F_x} \tag{2}$$

where t_σ is the time required for movement of PAZ down the column (min), V_b is the breakthrough volume (mL), Fm is the flow rate (mL min^{-1}) and V_x is the exhaustion volume (mL). Thus, for depth D of the adsorbent, the depth and time ratios are given by Eq. (3) [26,27]:

$$U = \frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} \tag{3}$$

where δ is the length of PAZ (cm), D is the adsorbent depth (cm), t_f is the PAZ formation time. The time required to achieve PAZ is given by Eq. (4) [26,27]:

$$t_f = (1 - F)t_\delta \tag{4}$$

where F is the SPE adsorbent fractional capacity in the adsorption zone characterized by solute preconcentration from the solution under limiting conditions.

The SPE adsorbent fractional capacity is given by Eq. (5) [26,27]:

$$F = \int_{V_b}^{V} \frac{C_0 - C \times d_v}{C_0(V_x - V_b)} \tag{5}$$

The SPE sorbent saturation percentage is obtained by Eq. (6) [26, 27]:

$$\%S = \left[1 - \left(\frac{\delta(F-1)}{D}\right)\right] \times 100 \tag{6}$$

The maximum ED preconcentration capacity in the SPE sorbent is given by Eq. (7) [23,24]:

$$Q = \frac{C_0 x F_m}{m_S} \int_{t=0}^{t=x} \left(1 - \frac{C}{C_0}\right) dt \tag{7}$$

Recovery was determined considering the ratio of analyte mass introduced to the sorbent bed and analyte mass determined in the eluent, multiplied by 100%.

2.4. Chromatographic analysis

Qualitative and quantitative analyses of effluent samples were carried out with the use of a liquid chromatograph HPLC Shimadzu (20A prominence) with UV-DAD detector (SPD-M20A) (230 nm), C18, 5-μm column, 250 × 4.6 mm i.d (Hichrom5), acetonitrile/HCl 0.1% as mobile phase. Analyses were carried out in a programmed gradient: increase of 10—100% acetonitrile in 10 min, returning to 10% in four minutes. The initial flow was 1.4 mL min^{-1}; and after five minutes, the flow was increased to 2.0 mL min^{-1}.The column was thermostated during analysis at 35°C.

2.5. Correlation analyses

Correlation analysis was used for identifying the linear relationship between the adsorption parameters with adsorbate and adsorbents properties. Pearsons correlation coefficients (r) stranded for the bivariate correlation.

Data were elaborated by means of Spearman's test analysis using the SPSS 17.0 statistics program (SPSSfor Windows, Chicago, IL). Differences were considered to besignificant for $p < 0.05$.

3. Results and discussion

Extraction process of pharmaceuticals, hormones and plastic materials from water samples by means of

SPE with the use of series sorbents might be characterized by the parameters collected in Tables 3—5. Significant similarities were found when these data were analysed. For all analytes, better efficiency of SPE adsorbents given by the adsorption capacity corresponded to the highest recovery.

The adsorption capacity of the column was determined by Eq. (7) for $C/C_0 = 0.5$. The values of the adsorption capacities of the sorbents are shown in Table 3. The adsorption capacities of Oasis and Strata-X sorbents were better than those found for C-18 sorbent.

Strata-X sorbent was found to be the most efficient sorbent for pharmaceuticals. The adsorption capacities ($mg\,g^{-1}$) found were: 2.85 (sulphamethoxazole), 18.35 (trimethoprim) and 17.09 (diclofenac); the recoveries (%) found were: 21.11 (sulphamethoxazole), 51.74 (Trimethoprim) and 72.25 (diclofenac).

The most efficient sorbent for hormones was also Strata-X where the adsorption capacities ($mg\,g^{-1}$) were 6.59 (estrone), 2.79 (17β-estradiolacetate) and 3.5 (17β-estradiol); the recoveries (%) found were 77.39 (estrone), 8.51 (17β-estradiolacetate) and 61.49 (17β-estradiol) (Tables 3 and 4).

According to the adsorption capacity ($6.34\,mg\,g^{-1}$) and recovery (34.76%), the Strata-X was also the most efficient sorbent for BPA as shown in Tables 3 and 4.

Table 3
Parameters obtained from breakthrough curves

SPE sorbent	Compound	C_0 ($mg\,L^{-1}$)	V_b (mL)	V_x (mL)	Q ($mg\,g^{-1}$)
C18	Sulfamethoxazole	3.085	100	250	0.771
	Trimethoprim	11.840	160	800	6.867
	Diclofenac	7.120	160	800	6.052
	Estrone	4.250	190	1,000	4.208
	17β-estradiolacetate	3.380	140	710	0.980
	17β-estradiol	4.250	140	220	1.233
	BPA	4.610	150	800	3.919
Oasis	Sulfamethoxazole	3.085	130	800	4.165
	Trimethoprim	11.840	260	700	20.424
	Diclofenac	7.120	160	1,000	17.266
	Estrone	4.250	170	810	9.244
	17β-estradiolacetate	3.380	150	690	2.620
	17β-estradiol	4.250	150	240	3.294
	BPA	4.610	140	810	9.681
Strata	Sulfamethoxazole	3.085	130	710	2.854
	Trimethoprim	11.840	180	700	18.352
	Diclofenac	7.120	150	1,000	17.088
	Estrone	4.250	160	810	6.588
	17β-estradiolacetate	3.380	160	260	2.789
	17β-estradiol	4.250	160	230	3.506
	BPA	4.610	140	800	6.339

Table 4
EDs recovery efficiency (%)

Compound	Recovery (%), $n = 3$		
	C-18	Oasis	Strata-X
Sulfamethoxazole	0.12	15.79	21.11
Trimethoprim	13.25	46.13	51.74
Diclofenac	7.60	67.08	72.25
Estrone	22.01	73.66	77.39
17β-estradiol	16.67	59.82	61.49
17β-estradiolacetate	3.53	8.48	8.51
BPA	2.53	33.91	34.76

According to results in Table 3, adsorption capacity of all the compounds follows the order:

For C-18 sorbent: trimethoprim > diclofenac > estrone > BPA > 17β-estradiol > 17β-estradiolacetate > Sulphamethoxazole.

For Oasis sorbent: trimetoprim > diclofenac > BPA > estrone > sulphamethoxazole > 17β-estradiolacetate > 17β-estradiol.

For Strata-X sorbent: trimetoprim > diclofenac > estrone > BPA > 17β-estradiol > sulphamethoxazole > 17β-estradiolacetate.

On the other hand, the adsorption capacity of pharmaceuticals and plastic materials in sorbents follows the order Oasis > Strata-X > C18 and for hormones the order was Strata-X > Oasis > C18.

The recovery (desorption) of EDs was carried out by a methanol/acetone (8:4 v/v) elution method (Table 5). The analytes analysed on Strata sorbent showed good recovery results (35—77%), except for sulphamethoxazole (21.11%) and 17β-estradiolacetate (8.5%). The recovery for DSC-18 cartridge (0.12—22%) was inefficient for preconcentration of the studied compounds (Table 4).

According to the AOAC manual for the Peer-Verified Methods program [28], which calculates the estimated recovery data as a function analyte concentration, for concentrations between 1 and $10\,mg\,L^{-1}$, its expected recovery range is 80—110%. Liu et al. [19] found recovery levels between 63% and 116% using Oasis HLB for preconcentration of estrogens (at levels up to 500 ng/L).

It was observed that some recoveries are below 80% even for Strata-X, however the efficiency of Strata-X cartrige was confirmed to complex matrices.

Huang et al. [20] studied several types of SPE cartridges (LC-18, Oasis HLB, Sep-Pak C18 and ENVITM-18) for the evaluation of extraction efficiency of steroids (estrone, 17β-estradiol 17α-ethinylestradiol

Table 5
Parameters t_x, t_δ, t_f, f, δ and saturation in the SPE sorbents for a multi-component aqueous solution

SPE sorbent	Compound	t_x* (min)	t_δ* (min)	t_f* (min)	f*	δ* (cm)	% SAT*
C18	Sulfamethoxazole	250.0	150.0	60.1	0.599	0.553	131.6
	Trimethoprim	800.0	640.0	218.5	0.659	0.770	137.6
	Diclofenac	800.0	640.0	218.5	0.659	0.770	137.6
	Estrone	1000.0	810.0	276.8	0.658	0.784	138.3
	17β-estradiolacetate	710.0	570.0	191.4	0.664	0.769	136.9
	17β-estradiol	220.0	80.0	36.3	0.546	0.305	119.8
	BPA	800.0	650.0	216.4	0.667	0.780	137.1
Oasis	Sulfamethoxazole	800.0	670.0	209.9	0.687	0.795	135.6
	Trimethoprim	700.0	440.0	180.8	0.589	0.593	134.8
	Diclofenac	1000.0	840.0	268.3	0.681	0.804	136.7
	Estrone	810.0	640.0	222.7	0.652	0.763	137.9
	17β-estradiolacetate	690.0	540.0	187.8	0.652	0.753	137.4
	17β-estradiol	240.0	90.0	40.8	0.547	0.316	120.5
	BPA	810.0	670.0	216.0	0.678	0.790	136.4
Strata-X	Sulfamethoxazole	710.0	580.0	188.9	0.674	0.779	136.2
	Trimethoprim	700.0	520.0	192.0	0.631	0.717	137.8
	Diclofenac	1000.0	850.0	264.1	0.689	0.809	135.9
	Estrone	810.0	650.0	221.1	0.660	0.773	137.6
	17β-estradiolacetate	260.0	100.0	45.2	0.548	0.326	121.1
	17β-estradiol	230.0	70.0	32.5	0.536	0.248	116.5
	BPA	800.0	660.0	213.6	0.676	0.788	136.4

*t_x is is the time to establish PAZ (min); t_δ is the time required for movement of PAZ down the column (min); t_f is the PAZ formation time; f is the SPE adsorbent fractional capacity in the adsorption zone; δ is the length of PAZ (cm)

and estriol) in water, which were spiked at $1\,\mu g\,L^{-1}$ using 10 mL of acetone as elution solvent. The results showed poor recoveries (13.6—38.6%) for all the analytes studied on C-18 cartridges, due to the fact that white-suspended matters produced in eluents caused adverse influences on subsequent derivatization procedure. On the other hand, Oasis HLB cartridges showed the best recoveries (82.—94.9%).

Fig. 1 shows the oasis cartridge recovery chromatogram. It is possible to observe a good separation for the compounds. The peaks are numbered as: (1) trimethoprim; (2) sulphamethoxazole; (3) BPA; (4) 17β-estradiol; (5) estrone; (6) diclofenacand; and (7) 17β-estradiolacetate. A memory-effect peak could be noticed before peak 1. Peak 2 is not as intense as the other peaks observed, probably because of the low-recovery values obtained for the sulphamethoxazole compound.

According to results in Table 3, the removal efficiencies of the studied sorbents were in the order Oasis > Strata-X > C-18. By correlation analysis, it was possible identified that recoveries are directly related to the adsorption capacity Q ($r_s = +0.536$, $p = 0.012$ ($p < 0.05$)) and corresponds to surface area also ($r_s = +0{,}501$, $p = 0.021$ ($p < 0.05$)).

These results were expected, since a requirement of a good adsorbent is for there to be a high surface area to mass ratio as it assures a large amount of sites where molecules can attach to the surface of the adsorbent. This high surface area typically results in a higher adsorption capacity. C-18 has the lower surface area, as the lower adsorption capacity and recovery.

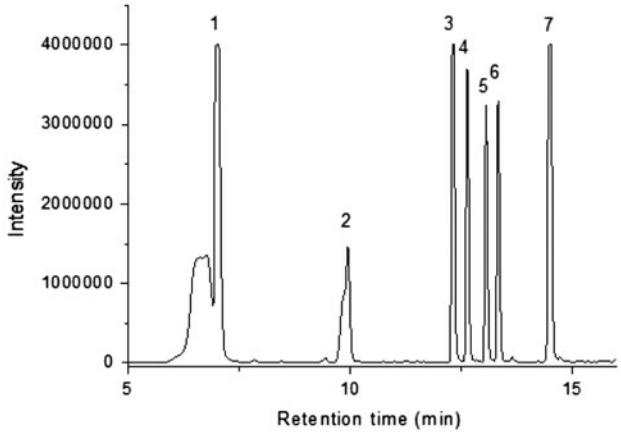


Fig. 1. Oasis cartridge recovery chromatogram. (1) Trimethoprim; (2) sulfamethoxazole; (3) BPA; (4) 17β-estradiol; (5) estrone; (6) diclofenac and (7) 17β-estradiolacetate.

The values obtained from the breakthrough curves were used to calculate parameters t_x, t_δ, t_f, f and the

percentages of saturation of the SPE sorbents, as shown in Table 5.

The breakthrough volume (V_b) is another important parameter to determine the suitability of a sampling device for isolating the analytes of interest and is established from a breakthrough curve. The point on the curve at which some arbitrary amount of sample is detected at the outlet of the sampling device is the breakthrough volume [18]. Examples of the breakthrough curves for adsorption of EDs on SPE sorbents are shown in Figs. 2 and 3.

The curves for all the studied compounds were used to obtain the parameters breakthrough and exhaustion volumes and the adsorption capacities for each compound which are summarized in Table 3. The results of the breakthrough volumes (V_b) for C-18 sorbent are higher than 100 mL for all compounds. A similar trend was also observed for Oasis and Strata-X sorbents. However, the breakthrough and exhaustion volumes came later for most EDs with those sorbents (Table 3). According to correlation analysis, this behaviour can be due to the fact that breakthrough volumes depend on the concentration of analytes in the solution loaded to the sorbent [6]. Breakthrough volumes are directly related to the initial concentration ($r_s = +0.578$, $p = 0.006$ ($p < 0.05$)) and adsorption capacity ($r_s = +0.583$, $p = 0.005$ ($p < 0.05$)).

In the other words, the higher is the initial ED concentration, the higher is the breakthrough volume and adsorption capacity.

It also depends on the variety of compounds loaded in the SPE bed due to the effect of competition between them for the active sites of the sorbent.

Based on the results presented in Table 3, it can be concluded that the higher is the initial ED concentration, the higher is the breakthrough volume and consequently the exhaustion volume, especially for Trimethoprim and Estrone. But the difference between the smallest and largest breakthrough volume for each compound at each SPE sorbent was not great, being at most 130 mL.

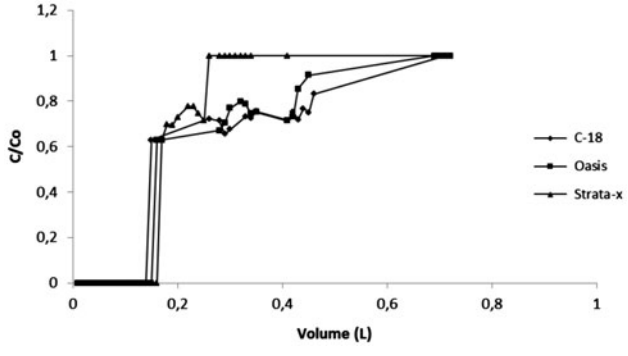


Fig. 2. Example of the breakthrough curves generated on SPE sorbents for the hormone 17β-estradiolacetate. Condition: multi-component aqueous solution 5 mg L^{-1}; pH 3.0; flow 1.0 mL min^{-1} at room temperature (28°C).

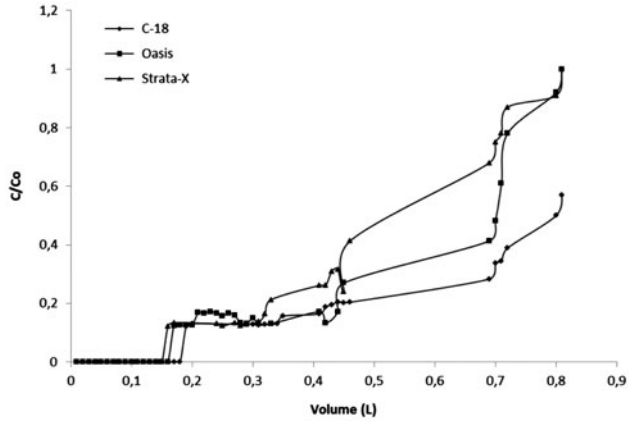


Fig. 3. Example of the breakthrough curves generated on SPE sorbents for the hormone Estrone. Condition: multi-component aqueous solution 5 mg L^{-1}; pH 3.0; flow 1.0 mL min^{-1} at room temperature (28°C).

The breakthrough volume value indicates the service time of the SPE sorbent until the first breakthrough volumes are reached. For C-18 sorbent, the service time is 100 min, while for Oasis and Strata-X sorbents is 130 min. In general, an increase in the breakthrough volumes also increases the adsorption capacity.

For C-18 sorbent, the total time to establish the PAZ (t_x) is at maximum for estrone (1,000 min) and at minimum for 17β-estradiol (220 min). The time required to move the adsorption zone down the column (t_δ) is situated between 80 and 810 min. The time required for initial formation of the PAZ (t_f) is between 36.3 and 218.5 min. For Oasis sorbent, the total time to establish the PAZ (t_x) is at maximum for diclofenac (1,000 min) and at minimum for 17β-estradiol (240 min). The time required to move the adsorption zone down the column (t_δ) is situated between 90 and 840 min. The time required for initial formation of the PAZ (t_f) is between 40.8 and 268.3 min. On the other hand, for Strata-X sorbent, the total time to establish the PAZ (t_x) is at maximum for diclofenac (1,000 min) and at minimum for 17β-estradiol (230 min). The time required to move the adsorption zone down the column (t_δ) is situated between 70 and 850 min. The time required for initial formation of the PAZ (t_f) is between 32.5 and 264.1 min.

The time required to move the adsorption zone down the column (t_δ) are directly related to the

adsorption capacity Q ($r_s = +0.510$, $p = 0.018$, ($p < 0.05$)), as well the other parameters (t_x, t_f and f), in the other words, the higher the values of t_x, t_δ, t_f and f, greater the efficiency of the cartridges in terms of adsorption capacity.

Again, Oasis and Strata-X proved to be more efficient for pharmaceuticals, hormones and plastic materials than DSC-18 sorbent.

As previously mentioned, initially, aqueous solutions containing EDs were acidified to pH 3, because it is know that pH affect the preconcentration efficiency [19,29]. Generally, the speciation of weakly acidic compounds in aqueous solutions depends on the solution properties, such as its pH value. Acidification of water solution is likely to decrease the dissociation of weakly acidic solutes, which may lead to increasing extraction efficiency of the target compounds if the non-dissociated form binds strongly to the SPE sorbents [19,29].

Pharmaceuticals and BPA in the neutral form would more readily adsorb onto silicate adsorbents, as DSC-18 sorbent, compared to those in the cationic and anionic forms, with adsorption predominately occurring via hydrophobic interactions [30—32]. The dominant mechanism was based on hydrophobic interactions between active sites from sorbents and neutral drugs and that the hydrophobicity of sorbents is significant for the adsorption process.

For polymeric sorbents, as Strata and Oasis, the π—π electron donor—acceptor interaction has been considered as one of the predominant driving forces for the preconcentration of chemicals with benzene rings, as pharmaceuticals and BPA [33,34]. The contribution of π—π bonds between the phenolics and the polymeric adsorbent with benzene rings is beyond dispute. Each carbon atom in a polymeric adsorbent has a π electron orbit perpendicular to polymeric sorbent surface. Therefore, the strength of π—π interaction is expected to scale up with the number of aromatic rings. The two benzene rings of BPA and pharmaceuticals molecules have stronger attractions with the rings on the surface of the polymeric sorbent [35].

In this work, correlation analysis was also used for identifying the linear relationship between the number of aromatic rings with adsorption capacity, and it was found that the number of aromatic rings are directly related to the adsorption capacity Q ($r_s = +0.461$, $p = 0.036$ ($p < 0.05$), so we can assume that π—π interaction was one of the predominant adsorption mechanisms.

Hydrogen bonding is also one mechanism for the preconcentration of organic compounds. The —OH substitution on the phenolics and the nitrogen-containing groups on the polymeric adsorbent surface may form hydrogen bonding; the hydrogen bonding may also form between the surface-adsorbed and dissolved phenolics. So, the existence of —OH substitution on the phenolics is advantageous to the adsorption on the aminated polymeric adsorbents [35].

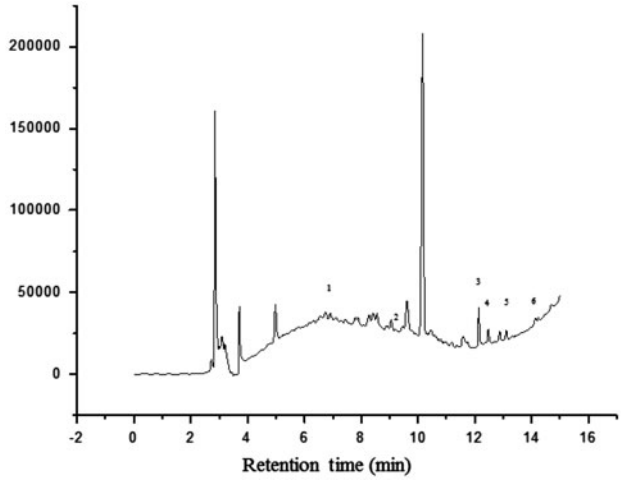


Fig. 4. Wastewater sample chromatogram—trimethoprim (1), sulfamethoxazole (2), BPA (3), 17β-estradiol (4), estrone (5) and diclofenac (6).

The log K_{ow} parameter measures the hydrophobicity of the hormones by partitioning between octanol and water. As a general rule of thumb, compounds with log $K_{ow} > 2.5$ are expected to accumulate in solid phases instead of being soluble in the aqueous phase [36]. The log K_{ow} values for the hormones described in Table 1 are above 2.5. Therefore, hormones are expected to interact with the membranes by hydrophobic interactions.

However, by correlation analysis, log K_{ow} is inversely related to the adsorption capacity Q ($r_s = -0.471$, $p = 0.31$ ($p > 0.05$), so we can assume that hydrophobic interactions are not predominant adsorption mechanisms for hormones.

3.1. Application to real sample

The most efficient sorbent for the described test, Strata-X, was applied to the determination of ED in a wastewater sample from wastewater treatment plant (WWTP) localized in Fortaleza, Brazil in order to confirm the efficiency of Strata-X cartrige also in complex matrices. Almost all ED studied in the present work was found and quantified in the effluent sample (Fig. 4): trimethoprim (1), sulphamethoxazole (2), BPA (3), 17β-estradiol (4), estrone (5) and diclofenac (6) in the concentrations of 8.2, 25.2, 39.3, 17.1, 9.1 and 0.5 μg L^{-1}, respectively.

4. Conclusion

According to results, the Oasis and Strata-X sorbents exhibited good recognition and selective ability, suggesting that it could be a useful tool for preconcentration technique in environmental analytical applications.

The DSC-18 cartridge was inefficient for preconcentration of the compounds studied and the most efficient sorbent for hormones, pharmaceuticals and plastic materials was Strata-X.

Furthermore, a method can be successfully developed to determination of EDs at low-concentration levels in wastewater samples using SPE sorbent for further analysis in HPLC system.

Correlation analysis identified the adsorption parameters which had the most influence in efficiency of SPE adsorbents, such as initial ED concentration, breakthrough volume and recovery, all these parameters are directly related to the adsorption capacity. Correlation analysis also identified the predominant adsorption mechanisms, such as π—π interactions.

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