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Potentiality of Epoxy-Montmorillonite Composite for Stir-Bar Sorptive Extraction for Determination of Atrazine

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HIGHLIGHTS

- Epoxy resin and montmorillonite were investigated to produce bars for SBSE.

- A robust PTFE support was made to hold the bars, affording adequate stirring.

- Close to 71% of atrazine extraction from aqueous medium was observed.

- The bars can be used at least for 80 times without memory effects and damages.

Abstract: A new low-cost material is presented for the first time, aiming to study the sorption process for the stir-bar sorptive extraction (SBSE) technique. The bars were made using a composition of a commercial epoxy resin and montmorillonite, under different compositions and a final ratio of 70% (epoxy) and 30% (montmorillonite) was employed, providing the best mechanical and chemical resistance. A PTFE support was developed to hold the bars permitting the magnetic stirring, without turbulent behavior even under long times of stirring at 1000 rpm. The bars were employed to study the sorption of the herbicide atrazine (ATZ), and the best extraction conditions were: sample volume 20.0 mL, pH 6.0, extraction time of 15 min, room temperature, stirring speed of 100 rpm, and 10.0% (w v^{-1}) NaCl. This preliminary evaluation suggests that the modified bars could be employed for ATZ sorption, affording close to 71% of ATZ removal, and presented robust characteristics to be used at least 80 times.

Keywords: SBSE; preconcentration; sorption; water.

GRAPHICAL ABSTRACT

Atrazine

Extraction
- ❖ 20.0 mL
- ❖ pH 6.0
- ❖ 15 min
- ❖ 100 rpm
- ❖ ≈ 25 ºC
- ❖ 10% NaCl
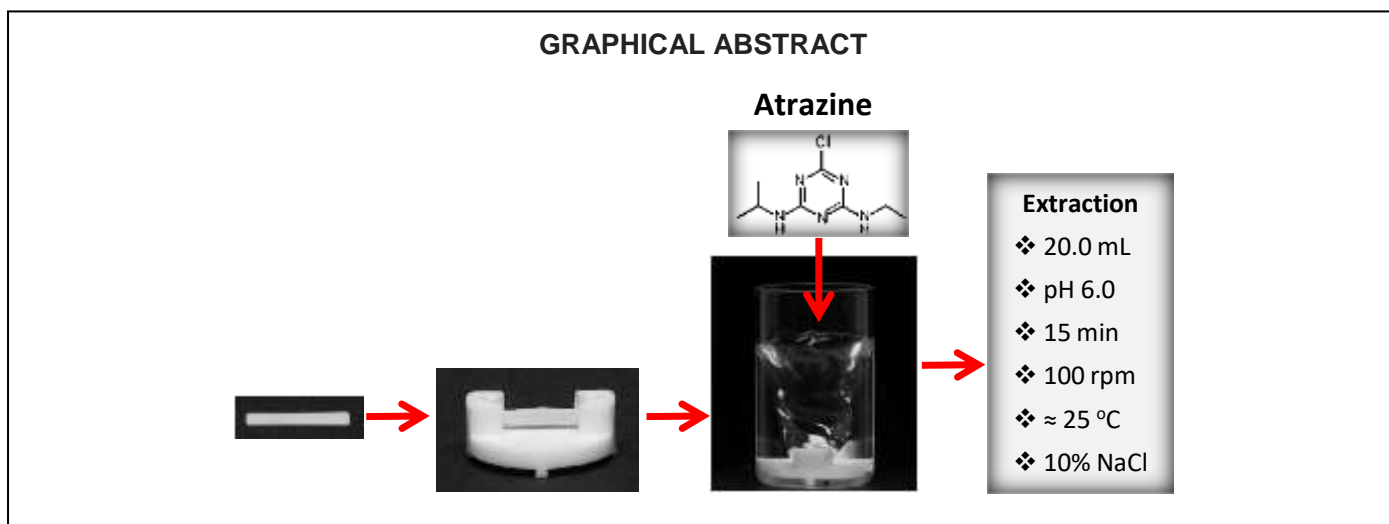
INTRODUCTION

The sample preparation is considered the most critical step in analytical chemistry, even currently is a challenge in the analytical process. During the last decades, the development of miniaturized extraction techniques for sample preparation has increased, considering the need for lower solvent and reagents consumption, as well as aiming faster analyses [1,2]. These techniques have the trend to provide the extraction and preconcentration in a unique step, affording the use of a lower volume of extraction solvent when compared to the sample volume. The development of the commercial solid-phase extraction (SPE) was in the mid-1970s, and since then, several relevant approaches have been proposed and employed [3,4]. Among them, the stir-bar sorptive extraction (SBSE) was proposed in 1999 by Baltussen et al. [5] and the principle of extraction by SBSE is considered analogous to the fiber solid-phase microextraction (SPME) [1,3,6]. SBSE is based on the partition equilibrium of an analyte between a sorbent phase in the surface of a magnetic stir bar and the solution, usually in aqueous medium. After a determined contact time under stirring, the next step is a subsequent thermal desorption of the analyte for gas chromatography (GC) determination, or the desorption in a small volume of an appropriate mobile phase, followed by liquid chromatography (LC) quantitation [1,3]. The SBSE, like the other extraction techniques, requires the evaluation of a number of variables for the optimization of the extraction process. Parameters such as pH, salting out effect, extraction time, temperature, stirring speed and sample volume must be studied to achieve the best performance [4]. Although SBSE is considered similar to SPME, the former has some advantages including the higher amount of sorbent phase, higher sensitivity, more robust, and thus it has been applied to determine ultra-traces in a lot of matrices, providing an expressive number of publications since its outset [6]. The SBSE has been employed as a very efficient technique based on the use of the commercial bars from the trademark Twister (Gerstel), using the polydimethylsiloxane (PDMS) as a coating. On the other hand, the use of this sorbent phase limits the application of SBSE, mainly for the non-polar analytes [4,6,7], although polar phases as ethylene glycol modified silicone and polymetacrylate are commercialized by Gerstel nowadays [8]. Nevertheless, a lot of recent works have been carried out in order to evaluate different approaches or materials to be used as sorbent phases [7–13], besides the publication of some specific reviews concerning SBSE [1,4,6,14].

Despite the great efforts for the developments of new materials for SBSE, the search for easier, quicker and low-cost procedures, and at the same time, the use of robust and high durability materials, are desired. In this sense, Ghani et al. [7] prepared extraction bars by using commercial epoxy glue (Araldite®), in composition with montmorillonite for extraction of four chlorophenols from water. These authors observed robustness for the bars, permitting the use at least for 50 times without the reduction of the performance, and verified good figures of merit. Recently, it was proposed the use of another kind of commercial epoxy resin (Durepoxy®) to make bars with high mechanical resistance, as well as chemical inertia to acetonitrile (ACN) under ultrasound [15]. The bars were produced using only the epoxy resin (ER) without any sorbent phase and were successfully applied to extract triclosan and methyl-triclosan from water samples. The procedure

demonstrated high simplicity with adequate figures of merit and the bars were employed around 40 times without memory effects.

Based on the attractive properties of Durepoxi®, the goal of this paper was to prepare a composite between ER and montmorillonite MTK10 from Aldrich, to evaluate the potentiality for SBSE application. In previous studies, it was demonstrated that MTK10 presents remarkable sorption process by different triazines [16–18]. Therefore, there is the hypothesis that this mineral could be employed as a sorption phase in composition with the ER, using atrazine (ATZ) as prototype analyte. Because of the square profile of the composite ER and MTK10 (ER-MTK10), a home-made PTFE support was proposed, to provide an appropriate stirring of the bars and to prevent the attrition with the surface of the glass flask. Based on the literature data, this is the first study of this specific ER-MTK10 to be evaluated as a sorbent phase for SBSE, as well as, the use of the robust PTFE support to hold the bars during the stirring time.

MATERIAL AND METHODS

Reagents, solutions and materials

The ATZ standard was purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany), and was employed to prepare the stock solution (1.00 mg mL^{-1}) in methanol (HPLC grade, Phillipsburg, USA) stored at –18°C in amber glass flask. This solution was used to prepare an additional ATZ solution at 20.0 µg mL^{-1} in ultrapure water (resistivity higher than 18 MΩ cm). This water was produced by reverse osmosis system, model Q842-210, from Quimis (Diadema, SP, Brazil) followed by purification using the Simplicity UV system, from Millipore (Molsheim, France). This ATZ solution was kept at 4°C and it was employed to prepare the diluted working solutions in ultrapure water, before the use. The acid-activated montmorillonite (MTK10), surface area of 270 m^2 g^{-1} was acquired from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). The epoxy resin (ER), commercialized as Durepoxi® (Loctite, Brazil) was purchased from a local market. Sulfanilic acid, pyridine, ACN, KCl, NaOH and HCl were of analytical grade from Merck, Carlo Erba or J.T. Baker.

Preparation of ER-MTK10 composite

The MTK10 was previously treated with KCl, in order to obtain a homoionic material as described elsewhere [16]. The homoionic MTK10 was washed three times using ultrapure water to remove the KCl excess, being used centrifugation steps (2800 rpm, 10 min) to separate the solid phase. The solid was dried at 80°C (24 h), gently ground with the aid of a pestle and a mortar to pass in a 200 mesh sieve (grain size 75 µm), and stored in a desiccator. In order to obtain the ER-MTK10, the ER was prepared using equal masses of part A (epoxy) and part B (curing agent), according to the supplier's instructions. After the formation of a homogeneous mass, the MTK10 was added at the proportion of 30% (w w^{-1}), and homogenized. This composite was pressed between small flat glass plates in order to produce the bars in square profile (Figure 1). The cure step was performed at room temperature for 24 h followed by an additional 1 h in an oven at 100°C, in order to aid the removal of the more volatile compounds. The bars were polished by using sandpaper (P500, 3M), to obtain a square profile of 3 x 3 mm, and 20 mm length, and also to obtain more homogeneous surfaces. Although this home-made process to prepare the bars was very simple, it provided to obtain the bars with an appropriate reproducibility in terms of the dimensions above mentioned. The bars were washed several times using ACN, and additional washings in ultrapure water, dried at room temperature and stored in glass vials for the further use.

(a)   (b)

Figure 1. Extraction bars. ER bar (**a**), ER-MTK10 bar in composition of 70% ER and 30% MTK10 (**b**). Dimensions: 20 mm length and 3 x 3 mm of each side.

A PTFE home-made support was made specifically to hold and stirring the bars. This support was 28 mm and 3 mm of external diameter and height, respectively, with a lateral hole of 1.5 mm external diameter

and 27 mm in deep, to insert a magnetic wire and promote the stirring. At the bottom part, a cross shape was adopted to minimize the friction with the glass flask (Figure 2a). Two parts with 11 mm of total height, 10 mm wide, and 21 mm length were made in opposite sides of the support, to accommodate the ER or the ER-MTK10 bar, and to maintain the bar about 2 mm above the support base (Figure 2b).

Extraction procedure and ATZ quantitation

The magnetic stirring was carried out using a cylindrical glass flask with 35 mm internal diameter and 65 mm height, permitting an appropriate stirring of the PTFE support with the bar (Figure 2c). This system was employed to evaluate the best extraction conditions, using a 0.50 µg mL^{-1} ATZ solution. The variables sample volume, temperature, pH, NaCl concentration, stirring speed and the extraction time were investigated, being the determinations repeated three times. After the extraction, the bar was removed from the PTFE support using a tweezers, washed two times in ACN under ultrasound (5 min), rinsed two times with ultrapure water, and dry at room temperature for the next extraction.
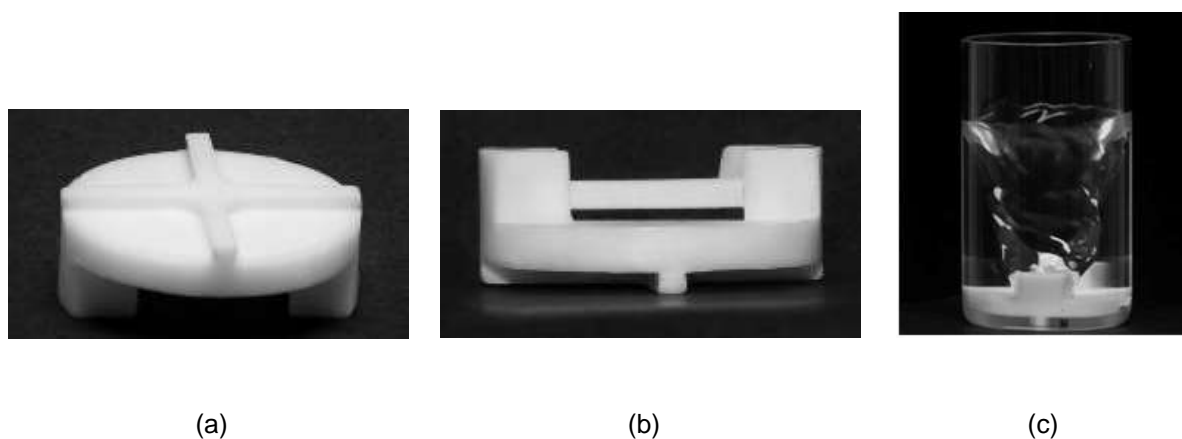

(a)   (b)   (c)

Figure 2. PTFE support. Bottom view (**a**), lateral view with the ER-MTK10 bar (**b**), extraction glass flask containing 30.0 mL of solution under stirring at 1000 rpm (**c**).

The ATZ quantitation in the aqueous phase was made using an aliquot of 1.50 mL, employing the well-established method based on the Konig reaction for ATZ determination [19], using a Femto 700 Plus spectrophotometer (São Paulo, SP, Brazil) at the wavelength of 445 nm, dotted of a 10 mm glass cell. A potentiometer from Analion, model PM 608 Plus (Ribeirão Preto, SP, Brazil), using an Ag/AgCl combination glass electrode was used for the pH adjustments to obtain the sample and the standard solutions. The analytical curves were made using five working solutions in concentrations between 0.10 and 1.00 µg mL^{-1}, affording a limit of quantitation (LOQ) of 0.08 µg mL^{-1} that is in good accordance with the literature value of 0.098 µg mL^{-1} [19].

The statistical significance (95%) of the observed differences between all the investigated extraction conditions was evaluated by one-way analysis of variance (ANOVA).

RESULTS AND DISCUSSION

Evaluation of the bars

The technique of scanning electron microscopy (SEM), using the equipment Quanta 450 FEG (USA), with resolution of 1 nm, was employed to perform a morphological evaluation of the bars surface. Figure 3a shows the surface of a bar formed only by ER, without the incorporation of MTK10. A dark surface was observed and various clear points, probably due to the partial mineral composition, previously determined for this commercial ER [15]. Although, no commented in the experimental section, the first ATZ sorption experiments were made trying to use only a deposition of MTK10 in the surfaces of ER, and not using the ER-MTK10 composite. It is important to notice, that this approach would be more appropriate, since a total coating was reached, being possible to observe the irregular mineral grains of MTK10 (Figure 3b). Despite of this, an easy releasing of the MTK10 particles was verified under the stirring, since the adhesion between the mineral particles and the ER was very weak, and as a result, the experiments were not reproducible. Based on this drawback, it was proposed to produce the ER-MTK10 composite, as employed by Ghani et al.

[7]; although in this work the authors used another kind of resin for other analytes. Figure 3c shows the SEM image for ER-MTK10 for the composition (w w^{-1}) 70% (ER) and 30% (MTK10). As it can be seen, several clear regions were verified, owing to the MTK10 distribution, as well as, the polishing marks. This polishing was necessary to provide the exposure of the sorption sites, eventually covered by ER, and for a better definition of the bars size, with good reproducibility in length and sides. Although only this composition was presented (Figure 3c), the percentage of MTK10 was evaluated between 10 and 50% (w w^{-1}), aiming a higher availability of sorption sites. However, the bars demonstrated mechanical and chemical resistance, until 30% (MTK10), under stirring at least for 1 hour followed by two cycles of 5 min in ACN and two additional cycles of 5 min in ultrapure water, both under ultrasound. Moreover, as would be expected, previous experiments using bars with lower MTK10 contents demonstrated lower ATZ sorption, and for this reason the ratio 70% (ER) and 30% (MTK10) (w w^{-1}) was adopted to produce the bars.
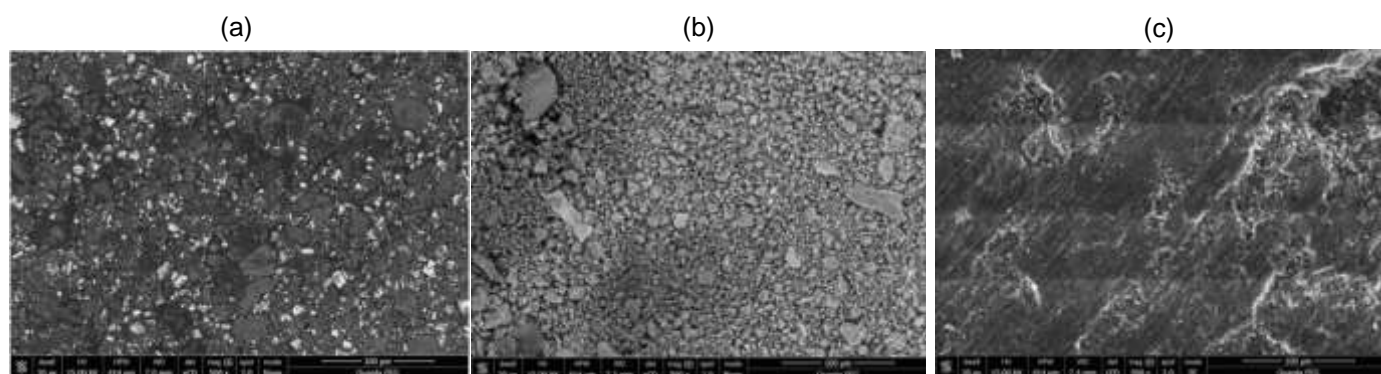
(a)   (b)   (c)

Figure 3. Scanning Electron Microscopy (SEM) images, at 500X of magnification. Epoxi resin (**a**), Epoxi resin coated by the granular MTK10 (**b**), ER-MTK10 composite - 70% ER and 30% MTK10 (**c**).

Preliminary considerations about the extractions

In a previous paper [15] it was reported the use of the commercial ER (Durepoxi®) as stir bar, and as the sorbent phase, and some characteristics of this material. Only ER was employed in this work, due to the high log K_{OW} values of 4.8 (triclosan) and 5.2 (methyl-triclosan) [15]. Thus, bars made of only ER were used for the first experiments in the present work, but no ATZ sorption was observed, probably due to the lower log K_{OW} of ATZ (2.61) [1]. As the mineral phase MTK10 presented good sorption characteristics for ATZ and other triazines, according to previous works [16–18], the use of MTK10 previously sorbed in the ER bars was proposed (Figure 3b). The pH values of the solutions were close to neutral, and the pK_a of ATZ is 1.68, and, hence, it is probable that MTK10 sorbs ATZ as neutral molecules, also due to the relatively low charge density of 2 x 10^{-3} mmol/m^2 [16]. According to Barriuso et al. [20] a higher sorption process is expected for ATZ as neutral molecules, for smectites with lower charge density values, that suggests the occurrence of physical sorption mechanism and hydrogen bonding [16,17]. In addition, the sorption/desorption process is reversible by using ACN as solvent, with satisfactory recoveries [18], that is indicative of weaker interaction between ATZ and MTK10. However, as previously discussed, it was not possible to use the bars coated with MTK10, and for this reason the ER-MTK10 composite was used to produce the bars.

Some authors have proposed the use of dumbbell format for the bars [13,15,21] during the stirring or rotating-disk [22], in order to minimize the attrition between the bars and the glass surfaces, and also to reduce the possibility of the sorbent damage. In the present work, it was proposed the PTFE support (Figure 2) that provided a robust and very appropriate system for the bars stirring.

Extraction conditions

Figure 4 shows the results for the evaluation of the extraction conditions in triplicate, expressed as the removal percentage of ATZ at initial concentration of 0.50 µg mL^{-1}. The evaluation of the extraction variables in SBSE is essential to define the conditions to accomplish the best enrichment [6]. Also, for comparison purposes, in Table 1 is presented the conditions adopted for ATZ sorption in the present work, as well as some results from the literature related to the sorption of triazines, making use of alternative materials for the SBSE technique.

Table 1. Conditions for triazines sorption and comparison with the literature using alternative materials for SBSE technique

Sorbent	Triazine	Sample volume (mL)	pH	Extraction time (min)	Stirring (rpm)	RSD (%)	Reuse[9]	Reference
MIP-MNPs[1]	Several [2]	8.0	NI [3]	60	NI [3]	< 10	3	11
PDMS/MIL-100(Fe)	Several [4]	10.0	8.0	50	800	< 6.3	> 50	13
PU [5]	Several [6]	25.0	3,7,10	3600	1250	< 7.0	NI [3]	24
PU [5]	ATZ	25.0	7.0	30	750	NI [3]	NI [3]	25
MIP [7]	Several [8]	5.0	NI [3]	60	500	< 8.8	> 50	26
ER-MTK10	ATZ	20.0	6.0	15	100	< 6.5	> 80	This work

[1] MIP-MNPs: Molecularly imprinted polymer-magnetic nanoparticles; [2] deethylatrazine, deisopropylatrazine, simazine, cyanazine, propazine, terbutylazine; [3] NI: not informed or not investigated; [4] ATZ, simazine, ametryne, prometon, prometryne, prebane; [5] PU: polyurethane foam; [6] ATZ, simazine, ametryne, propazine, prometon, prometryne, terbutryn; [7] MIP: Molecularly imprinted polymer; [8] ATZ, simazine, cyanazine, ametryne, propazine, prometryne, terbutylazine, terbutryn, simetryne; [9] The reuse represents the maximum number of extractions presented.
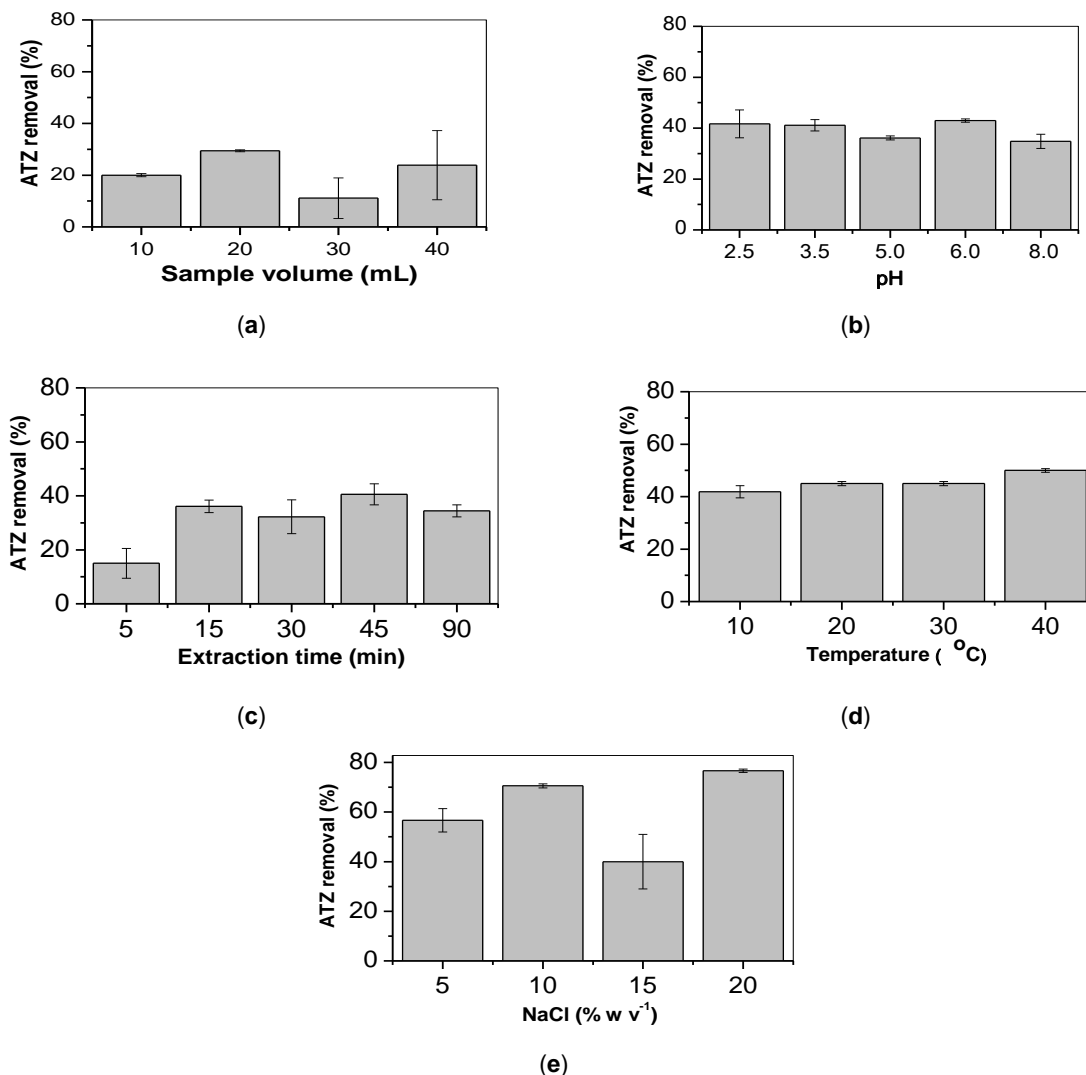

(a)

(b)

(c)

(d)

(e)

Figure 4. Evaluation of the extraction conditions, using 0.50 μg mL^{-1} ATZ solution, n = 3. (a) Sample volume: 30 min of stirring at 100 rpm, room temperature, pH 5.5, absence of NaCl; (b) pH: sample volume of 20.0 mL, 30 min of stirring at 100 rpm, room temperature, absence of NaCl; (c) Extraction time: sample volume of 20.0 mL, pH 6.0, stirring at 100 rpm, room temperature, absence of NaCl; (d) Temperature: sample volume of 20.0 mL, pH 6.0, 15 min of stirring at 100 rpm, absence of NaCl; (e) NaCl: sample volume of 20.0 mL, pH 6.0, 15 min of stirring at 100 rpm, room temperature.

The sample volume was studied between 10.0 and 40.0 mL (Figure 4a). Lower samples volumes were not evaluated, since 10.0 mL was the minimum volume appropriate to cover completely the PTFE support, and higher samples volumes were not studied due to the flask capacity. The higher ATZ removal observed was close to 29.5% for the volume of 20.0 mL. On the other hand, for the volumes of 30.0 and 40.0 mL, higher standard deviation values were verified; and also, an apparent anomalous result for 30.0 mL (only 11% of ATZ removal). In spite of this, no significant differences were verified according to ANOVA, F-value 2.968 and F-critical 4.07 (95%), considering the four volumes investigated, and, hence, 20.0 mL was adopted as the best sample volume, owing to the lower standard deviation value. Frequently, lower sample volumes are employed in SBSE (between 10 and 100 mL), and generally the best results are observed by using low sample volumes [8,10,15,21,23], probably due to the easier mass transport. On the contrary, higher sample volumes require longer times to reach the equilibrium [23], and for the present study 30 min was employed as the extraction time. Also, for ATZ or other triazines, sample volumes between 25.0 mL [24,25] and 5.0 mL [26] have been employed for the best conditions of SBSE, as depicted in Table 1, that is in good agreement with the best sample volume (20.0 mL) obtained in the present work.

The influence of pH was evaluated between 2.5 and 8.0, as presented in Figure 4b, by using diluted HCl or NaOH solutions for the pH adjustments. In this pH range, a significant difference was verified, F-value 4.478 and F-critical 3.48; however, for pH 6.0 the best result was observed, close to 43% of ATZ removal, and the lower standard deviation, and for this reason this value was chosen for the next experiments. It is important to point out that lower pH values could be desirable, since the ATZ pK_a is 1.68; therefore, a higher sorption process could occur for pH values lower than the ATZ pK_a, but this possibility was not investigated, since the ER seems to be more susceptible to the acid attack, as previously observed [15]. Thus, under the pH conditions here studied, the ATZ is present as neutral molecules, explaining the similar sorption results. Similar pH values were reported in the literature for ATZ or other triazines, but for a different sorbent phase [13]. The authors verified no influence in the pH for ATZ and SIM (lower pK_a values), whereas for the other triazines investigated, (AM, PR, PROM and PRE), with pK_a between 3.71 and 4.36 a clear enhancement in the extraction efficiency was observed at higher pH values, and the pH 8.0 was employed [13] (Table 1). In spite of this, other authors observed negligible differences using pH 3.0, 7.0 or 10.0 for several triazines, suggesting no importance for the adjustment of this parameter, at least for triazines [24].

The next step was the evaluation of the extraction time, between 5 and 90 min according to Figure 4c. After 5 min a great increase in the ATZ removal was observed, and in fact, significant differences (based on ANOVA, 95%) were observed when 5 min was compared to 15, 30, 45 or 90 min. In general, the higher the contact time, the most efficient the extraction, and frequently extraction times higher than 30 min have been reported [8–11, 13–15]. These longer extraction times have been often observed due to the larger volume of the extraction phase [3], the higher sample volume [23], and the thickness of the sorbent phase [22]; even though in some cases lower extraction times of 10 min [21] and 20 min [7,22] have been reported. In the present work, the best result was observed at 45 min, although no significant difference has been verified by comparing the times of 15 and 45 min, and, hence, an extraction time of 15 min was adopted, affording close to 36% of ATZ removal. As a double step of ACN washing, followed by a double step of ultrapure water washing, both under 5 min in ultrasound was enough, and no memory effects were observed, this suggests that there was no ATZ diffusion into the bars, despite of the high thickness of the sorbent phase that is the square profile (3 x 3 mm). Moreover, the possibility to employ only 15 min, without the trend of sorption enhancement indicates a mechanism of adsorption and not absorption. This is in good agreement with Ghani et al. [7] that employed MTK10, but using other kind of resin to produce the composite, and chlorophenols as analytes. These authors observed a slight increase of sorption between 5 and 30 min of extraction time, employing 20 min as the enough time. The commercial SBSE phase based on PDMS, provides very good results in terms of sorption. However, according to the literature [1,6,14], the theoretical efficiency is deeply dependent on the sample volume, the PDMS volume on the stir-bar, and the log K_{OW}. Therefore, low efficiency is expected for ATZ (log K_{OW} 2.61) [1], and the equilibrium is not attained up to 48 h [14], whereas some authors reported 2 h as equilibrium time, for a study involving ten triazines [27]. Because of this reason, many times the non-equilibrium condition is employed [1,6,27]. In fact, the equilibrium time represents a challenge, especially for relatively more polar compounds, and some SBSE studies involving alternative materials for triazines sorption have been carried out [11,13,24–26], (Table 1). Molecularly imprinted polymer monolith modified with magnetic nanoparticles was performed by Díaz-Álvarez et al. [11] to study six triazines, including ATZ in soil samples, and 30 min was established as an adequate time. The modified polydimethylsiloxane/MIL-100(Fe) was employed for determination of six triazines in water samples and the extraction time of 50 min was employed [13]. In other study, polyurethane foam (PU) was investigated in

order to determine seven triazinic herbicides in water, and an extraction time of 6 h was necessary to attain the equilibrium time [24]; although also using PU as sorbent, 30 min was considered an adequate extraction time for ATZ [25]. The ER-MTK10 presented a very satisfactory extraction time, since 15 min was enough to attain an apparent equilibrium (Figure 4c). As previously cited, this behavior is indicative of an adsorption process, affording an appropriate extraction time when compared to other alternative sorbent phases investigated (between 30 and 3600 min, Table 1).

Figure 4d presents the influence of the temperature in the extraction process. At first, the increase in temperature aids to speed up the mass transport [9] and to reach the equilibrium, but on the contrary, provide a higher solubility of the analytes. As a result, a decrease of the sorption is observed [4], as well as the diminution of the partition coefficient [9], even though in the present work the process is probably governed by adsorption as already described. Perhaps this antagonistic effect was the reason for the slight raise verified between 42 and 50% of ATZ sorption for 10ºC and 40ºC, respectively. The global evaluation of the differences between the temperatures, pointed out that the extraction was particularly influenced by the comparison of the temperatures of 10ºC and 40ºC, based on Least Significant Difference (LSD), F-value 19.254 and F-critical 4.07. On the other hand, between 20ºC and 30ºC no significant difference was observed, suggesting that a rigorous temperature control would be unnecessary. Perhaps, for this reason, this parameter has been employed at room temperature [24], or it has not been evaluated, and thus, it was not cited in Table 1. In addition, higher temperatures could contribute to a dilation effect, probably decreasing the life-time of the bars.

In the previous studies (Figures 4a–4d) the stirring speed was fixed at 100 rpm; thus an additional evaluation was made at 1000 rpm (figure not showed). The extraction conditions were the same employed in the temperature study (Figure 4d), but at room temperature. The ATZ removal observed for 100 rpm and 1000 rpm were $60 \pm 3\%$ and $54 \pm 8\%$, respectively, suggesting no significant difference. The stirring speed and the equilibrium time affect the extraction kinetics, since they influence the mass transfer. In this sense, a higher extraction efficiency for the higher stirring speed would be expected, as observed in the literature [6,9,13]. Therefore, an additional value of 1500 rpm was evaluated, but a significant decrease was verified ($37 \pm 5\%$). Some authors observed no influence of the stirring speed, at least between 600 and 1000 rpm [13,21]. Based on the results, 100 rpm was adopted for the next experiments, although this value is inconsistent when compared with the literature results for triazines, between 500 rpm [26] and 1250 rpm [24], according to Table 1. A possible explanation for this relatively low speed, would be due to the weak interaction between ATZ and MTK10, owing to the adsorption mechanism; and, hence, higher agitation speeds could cause a kind of ATZ self-desorption, resulting in best results for lower speeds. On the other hand, no lower stirring speeds were evaluated, due to the limitation of the magnetic stirrer.

The ionic strength is another important parameter usually investigated in extraction procedures. The influence of this parameter was tested using NaCl solution between 5.0 and 20.0% (w v^{-1}), and the results are shown in Figure 4e. The higher extraction efficiency was verified for 20.0% NaCl, although a similar result was observed for 10.0%, and an apparent anomalous result was verified for 15.0% that is, lower extraction efficiency when compared to 10.0 and 20.0%. Although this inconsistency is not clear at this moment, a similar effect was also observed in the literature for other triazines [24]. The effect of the salt addition is more pronounced particularly for more polar analytes, with log $K_{OW} < 3$ [6], due to the lower solubility of the analytes in aqueous medium under higher ionic strength; although some authors observed loss of extraction efficiency for higher ionic strength [9]. This lower extraction efficiency seems to be related to an increase in the viscosity of the solution for higher ionic strength values [9]. Although this effect of decrease in the extraction efficiency with the viscosity was not observed for ATZ in the literature, it was verified to other triazines [13], and perhaps is related with the contradictory result observed in the present work for 15.0% NaCl. The influence of ionic strength was not shown in Table 1, since from the results presented, only Lei et al. [13] employed NaCl at 20.0 (w v^{-1}), and in fact these authors verified a significant enhancement of the sorption for some triazines, including ATZ. On the other hand, some authors did not studied the influence of the ionic strength [11,25,26], while Portugal et al. [24] observed a reduction in the sorption for the most of the triazines when the NaCl concentration was evaluated at 0.0, 5.0, 10 and 15% (w v^{-1}), concluding that the best conditions would be in the absence of NaCl. In the present work, the result at 20.0% NaCl (ATZ removal of 76.6%) when compared to 10.0% NaCl (ATZ removal of 70.6%) indicate no significant difference based on ANOVA (95%), and for this reason 10.0% was adopted, affording an easier NaCl dissolution.

It is important to inform that the desorption of ATZ was not evaluated aiming the preconcentration step, and no lower initial concentrations than 0.50 μg mL^{-1} were investigated, owing to the drawbacks of the

spectrophotometric method. On the contrary in all the references cited in Table 1, it was employed liquid chromatography, or gas chromatography as the techniques for quantitation.

In spite of the recovery was not evaluated, if one considers the maximum ATZ removal, close to 70% (Figure 4E), this indicates approximately 7 μg of ATZ sorbed on the stir-bar, and this suggests a high capacity to sorbs ATZ. This result is very satisfactory in comparison with other non-commercial stir-bar [13], which presented 41% of extraction efficiency. If this ATZ mass (7 μg) was completely removed, for instance, in 2.0 mL of ACN, a relatively high ATZ concentration (3.5 mg L^{-1}) would be obtained, and according to the previous works [16–18], a relatively easy desorption from MTK10 in batch mode was observed for ATZ. Also, in the present work, the cleanup of the bars using acetonitrile indicates no memory effects that corroborate the complete ATZ desorption.

Although some anomalous results were observed, as previously commented, the relative standard deviation (RSD) for the most of the results was below 10%, and for the ATZ conditions defined for this study, the higher RSD (6.5%) was observed for the extraction time of 15 minutes (Figure 4c). These results suggest that the home-made process to produce the bars was adequate, based on the appropriate reproducibility. In spite of this, the RSD values from the references pointed out in Table 1 consider all the process (sorption and desorption), and, hence, it is probably that RSD values higher than 6.5% could be observed if the complete process was performed.

Another important aspect is that one bar was employed to study each parameter, and, hence, each bar was used between 9 times (stirring speed) and 15 times (pH and extraction time), although one of the bars was employed to study all the parameters (n = 3), that is, it was used around 80 times. It was not verified loss of efficiency, and apparently, no damage in the surfaces had been observed. These aspects suggest that ER-MTK bars presented an appropriate mechanical and chemical resistance, at least for ACN and ultrapure water under ultrasound that was employed after each use to clean the bars. Nevertheless, a more in-depth investigation would be necessary using the technique of SEM for a best evaluation, and also additional studies using new bars could be carried out, in order to confirm the possibility of reusability.

CONCLUSION

A robust home-made PTFE support was proposed to afford the use for the SBSE technique, and an adequate stability was observed even at agitation speed of 1000 rpm. It is a low-cost and simple alternative to hold the bars without attrition with the glass flask bottom, avoiding any kind of physical damage to the bars. Furthermore, any type of bar could be employed in this support, without the need to include a magnetic wire.

For the first time, it was produced a stir bar based on the use of a specific commercial ER in composition with the mineral phase MTK10, made in a square profile. Based on the results, the composite formed in the proportion 70% ER and 30% MTK10 suggests an adequate performance in terms of mechanical and chemical resistance, during the stirring in aqueous medium, as well as, in ACN under ultrasound. Six bars were employed between 9 and 15 times, and an additional bar was used around 80 times, without any apparent physical damage, suggesting a high robustness, and also presented no memory effects between each use. However, a more careful evaluation would be necessary, to confirm the preservation of the bar surfaces.

The herbicide ATZ was employed to evaluate the device composed by the PTFE support and the ER-MTK10 bars, and the main extraction conditions were evaluated in order to determine the best parameters. It was verified close to 71% of ATZ extraction, and the stirring speed and ionic strength presented a key role in the ATZ sorption. Although this study was not applied for the ATZ desorption to evaluate the enrichment factor, and for real water samples, one can infer that the proposed system could be a valuable tool to use in the SBSE technique. Besides the low cost and the ease to prepare the ER-MTK10 stir-bar, other remarkable aspects related to ATZ were the sorbed amount, and the short extraction time of 15 min. In addition to, the kind of ER here employed could be blended with other kind of sorbent materials, providing adequate mechanical and chemical resistance, to determine other analytes, and, hence, it is a promising alternative material.

Conflicts of Interest: "The authors declare no conflict of interest."

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