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New sorbents based on poly(methacrylic acid-TRIM) and poly(vinylimidazole-TRIM) for simultaneous preconcentration of herbicides in water samples with posterior determination by HPLC-DAD

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In the present study, new sorbents for solid-phase extraction (SPE) based on poly(methacrylic acid-trimethylolpropane trimethacrylate) (PMA-TRIM) and poly(vinylimidazole-TRIM) (PV-TRIM) for simultaneous extraction of tebuthiuron (TBT), hexazinone (HEX), diuron (DIU) and ametryn (AME) and posterior determination by HPLC-DAD were developed. The method was based on the preconcentration of 50.0 mL of water at pH 6.0 through 200 mg of each sorbent packed into a cartridge with further elution by 3.0 mL of methanol. The analytical curves were linear for the herbicides in the range 1.0–150.0 $\mu\text{g L}^{-1}$ with limits of detection (LOD) of 0.40, 0.31, 0.12, 0.34 $\mu\text{g L}^{-1}$ for TBT, HEX, DIU and AME, respectively, when using PMA-TRIM as the sorbent and 0.14, 0.44, 0.17 and 0.39 $\mu\text{g L}^{-1}$, respectively, when using PV-TRIM. The precision in terms of repeatability assessed as RSD (relative standard deviation, $n = 10$) for the multiresidue analysis ranged from 1.23% to 1.91% and 0.97% to 1.79% for respective concentrations of 10.0 and 100 $\mu\text{g L}^{-1}$ using the PV-TRIM polymer and 2.13% to 3.31% and 1.43% to 2.91% using PMA-TRIM. As observed, better analytical performance was achieved using PV-TRIM as the sorbent. The obtained analytical performance from the polymers, mainly PV-TRIM in terms of LOD and preconcentration factor (PF) was much higher compared to commercial sorbents octadecyl-C18-silica (C₁₈) and Amberlite® XAD4 poly(styrene-divinylbenzene) (DVB). Moreover, exceptional reusability was achieved (>161 recycles) without loss of adsorption capacity. To assess the accuracy of the preconcentration method, analyses of surface waters (well and river water), collected from an area near the cultivation of sugar cane, were carried out. From the recovery test ranging from 96% to 101%, it was concluded that the solid-phase extraction prior to HPLC-DAD analysis is appropriate and it is an alternative for multiresidue analysis in natural water.

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Introduction

Herbicides have been widely applied over the years on different crops aimed at increasing the agricultural production. However, due to their persistence in the environment and the release into environmental water bodies, these compounds may be the source of contamination affecting human beings.¹ Human

health effects related to the exposure to some herbicides include endocrine disruption, neural disorders and cancer.^{2,3}

The sugarcane industry has been one of the most important products of the Brazilian economy, where Brazil is the biggest worldwide producer of sugarcane, whose crops are concentrated mainly in the São Paulo state region.^{4,5} The herbicides widely used in weed control and other plagues in sugarcane crops include the members of the substituted urea class, tebuthiuron (TBT) (*N*-t5-(1,1-dimethylethyl)-1,3,4-thiadazol-2-yl-*N,N*-dimethylurea) and diuron (DIU) (*N'*-(3,4-dichlorophenyl)-*N,N*-dimethylurea); hexazinone (HEX) (3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4-(1*H*,3*H*)-dione) belongs to chemical group of triazinones and ametryn (AME) ((2-ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine), which belongs to the triazine family.^{6,7}

Tebuthiuron exhibits high leaching through soils and contaminates groundwater due to its high solubility in water

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(2.5 g L⁻¹) and low absorption coefficient (log K_{ow} = 1.79).⁸ Diuron, in turn, is classified by the EPA as a likely human carcinogen,⁹ and due to its low solubility in water of 42 mg L⁻¹ and relatively low adsorption coefficient (log K_{ow} = 2.68), it presents low tendency to sorb to soils and sediments. However, considering that its hydrolysis and aqueous photolysis half-lives are relatively long, diuron can be considered both mobile and relatively persistent.¹⁰ Hexazinone and ametryn have low coefficient of adsorption (log K_{ow} = 1.2 and 2.98, respectively), and due to their high toxicity and high resistance in soil and surface water, they are considered one of the most important classes of chemical pollutants.¹¹ Taking into account that these herbicides may be considered a contamination source affecting human beings, some international regulations have established the maximum allowed levels of these pesticides in treated water. The maximum allowed level of diuron is 0.5 and 10.0 µg L⁻¹ according to European Community (EC) and Environmental Protection Agency (EPA), respectively.^{12–14} In Brazil, the Brazilian Ministry of Health (BMH) has established the maximum limit of diuron in drinking water to 90 µg L⁻¹.¹⁵ Australian regulations allow a maximum level of 2.0 µg L⁻¹ and 5.0 µg L⁻¹ for hexazinone and ametryn, respectively.¹⁶ For tebuthiuron, EPA set 0.27 µg L⁻¹ as the maximum contaminant level for irrigation water.¹⁶ As observed, the regulatory agencies around the world do not follow a pattern to define the maximum amount allowed of a specific herbicide in water samples. Nevertheless, the levels are extremely low, which makes the analysis of aforementioned herbicides in water samples, mainly natural waters containing high concentrations of interfering compounds, a difficult task.¹⁷ Liquid and gas chromatography have been widely used for pesticide analysis, particularly when coupled with mass spectrometry (MS). However, even while using mass spectrometry for detection, successful analysis of residual contaminants at trace levels requires previous sample preparation in order to promote sample clean-up or enrichment.^{18–20}

Thus, the implementation of sample pretreatment based on preconcentration methods has been highly recommended for a reliable analysis. Different preconcentration methods have been reported for analysis of pesticides, such as in tube solid-phase extraction,²¹ supramolecular system-based extraction,²² dispersive liquid–liquid microextraction,²³ cloud point extraction,²⁴ single-drop microextraction,²⁵ and magnetic solid-phase extraction.²⁶ The solid-phase extraction methods are still the most employed ones due to large amount of available sorbents with different properties.²⁷

The literature reports some sorbent materials including molecularly imprinted polymers,²⁷ montmorillonite,²⁸ octadecyl-C18-silica,^{6,29} graphene,³⁰ poly(methyloctadecylsiloxane) immobilized on silica,³¹ magnetic nanoporous carbon (MNC)³² and poly(styrene-divinylbenzene) sorbent (DVB),³³ for solid-phase extraction of herbicides that are herein investigated with further determination by HPLC. Although the sorbents have been considered efficient for herbicides adsorption, in general, they are applied only in purified water samples or drinking water and are limited to environmental samples. Notwithstanding this, the reusability of some of them is much too low, mainly octadecyl-C18-silica, and to the best of our

knowledge neither of them was applied to multiresidue analysis containing tebuthiuron, diuron, hexazinone and ametryn. Therefore, considerable efforts have been made to deal with the issue of development of new sorbent materials, which present fast adsorption towards the multiresidues, high chemical stability in a wide pH range, high adsorption capacity, negligible swelling effect in different fluids, exceptional reusability and low cost of synthesis.³⁴ In this context, cross-linked polymers containing functional monomer with acid or base properties seem to be very useful for multiresidue preconcentration, due to their structural rigidity, high surface area depending upon synthesis process and the possibility to establish different interactions among binding sites of polymers.

Therefore, the aim of the current study has been the development of a new solid-phase method for the simultaneous preconcentration and detection by HPLC-DAD of tebuthiuron, diuron, hexazinone and ametryn using two cross-linked polymers synthesized with different functional monomers, methacrylic acid and 1-vinylimidazole, and trimethylolpropane trimethacrylate (TRIM) as the cross-linking reagent. These polymers have already been synthesized by our research group³⁵ and characterized using FT-IR, SEM, TGA, textural data, elemental analysis, kinetic studies and adsorption isotherms for tebuthiuron. The highlight and novelty of present study relies on the evaluation of analytical performance of poly(methacrylic acid-TRIM) and poly(vinylimidazole-TRIM) towards multiresidues column solid-phase extraction and their validated applicability in the analysis of surface water (well and river water).

Experimental

Reagents and instruments

All herbicides (tebuthiuron, diuron, hexazinone and ametryn) were used as received without further purification from Sigma-Aldrich (PESTANAL, analytical standard, USA). Methanol (Sigma-Aldrich, HPLC grade, ≥99.9%, USA), chloroform (Sigma-Aldrich, analytical grade, ≥99.8%, USA), hexane (Sigma-Aldrich, analytical grade, ≥95%), 1-vinylimidazole (Sigma-Aldrich, ≥99.8%), methacrylic acid (Acros Organics, 99.5%), trimethylolpropanetrimethacrylate (TRIM) (Sigma-Aldrich, ≥99%), 2,2'-azoisobutyl nitrile (Sigma-Aldrich, 98%), acetic acid (JTBaker, 99.9%), ethanol (JTBaker, 99.7%), acetonitrile (Sigma-Aldrich, HPLC grade, ≥99.9%), dichloromethane (Sigma-Aldrich, analytical grade, 99.5%) were used in the study. The water used to prepare the mobile phase was ultrapure from a Milli Q (Millipore) system and filtered through a 0.45 µm nylon membrane daily. The water and solvents used in mobile phase were also degassed using an ultrasonic Bath model USC 1400 (Marconi®, Piracicaba, Brazil).

The chromatographic determinations were performed on a liquid chromatograph model LC-20AD/T LPGE kit, Shimadzu, operating isocratically. The chromatographic separation of tebuthiuron was carried out on a CLC-ODS column (250 mm × 4.6 mm id, 5 mm in particle size) containing a guard column Phenomenex (4.0 mm × 3.0 mm i.d., 5 mm in particle size). The flow rate of the mobile phase (MeOH : water, 65 : 35, v/v) was



0.7 mL min⁻¹ and the injection volume was 20 µL. For multi-residue analysis, the separation of herbicides was carried out on a Luna 5 µm C8(2) column (250 mm × 4.6 mm id, 5 mm in particle size) and a guard column Phenomenex (4.0 mm × 3.0 mm i.d., 5 mm in particle size) using acetonitrile : water (35 : 65, v/v) as mobile phase at 1.0 mL min⁻¹ flow rate. The temperature of chromatographic separation (25 °C) was controlled using a column oven. The peaks' purity was determined on a diode-array detector (DAD) and monitored at λ_{max} 254 nm. A manifold system (Bio-Rad) with a capacity for 12 cartridges, coupled to a vacuum pump (Marconi MA 2057) was used in the SPE procedure.

Synthesis of polymers and SPE procedure

The syntheses of poly(methacrylic acid-TRIM) and poly(vinylimidazole-TRIM) have been reported by our research group.³⁵ The SPE procedure was based on preconcentration of 50.0 mL of multiresidues solution at pH 6.0 through 200 mg of polymers packed into empty SPE cartridges and capped with fritted polyethylene disks at the top and bottom. The cartridge was placed in a manifold system coupled to a vacuum pump and operated under flow rate of 2.0 mL min⁻¹. Before analysis, the cartridges were conditioned with 6.0 mL of ultrapure water. The elution was performed with 3.0 mL of methanol and analyzed by HPLC-DAD. It is worth mentioning that the adsorption pH (pH 6) was obtained from batch experiments as already reported in literature.³⁵

Breakthrough curve

In order to obtain the maximum adsorption capacity of polymers towards herbicides under dynamic conditions, a breakthrough curve was obtained, choosing tebuthiuron as target analyte. The experiments were performed by percolating aliquots of 5.0 mL of 100.0 mg L⁻¹ solution of tebuthiuron through a SPE cartridge packed with 200 mg of polymers, previously conditioned with ultrapure water, until saturation was reached. Each aliquot was collected and analyzed by HPLC-UV, and the amount of tebuthiuron adsorbed on the polymers for each aliquot was determined according to eqn (1):

$$Q \text{ (mg g}^{-1}\text{)} = \frac{(C_0 - C_f)V}{m} \quad (1)$$

where C_0 is the initial tebuthiuron concentration (mg L⁻¹), C_f is the concentration of tebuthiuron in the column effluent (mg L⁻¹), V is the solution volume (mL) of each aliquot and m is the polymer mass (g).

Results and discussion

Optimization of SPE procedure

Influence of type of elution solvent. In order to evaluate the efficiency of elution solvent, 200 mg of the polymers PV-TRIM or PMA-TRIM were packed into SPE cartridges and capped with fritted polyethylene disks at the top and bottom. The SPE cartridges were coupled to a manifold. After conditioning the solid phase with 5.0 mL of ultrapure water, 6.0 mL of herbicide

tebuthiuron solution at 20 mg L⁻¹ concentration was percolated through the cartridges at a flow rate of 2.0 mL min⁻¹. Different elution solvents with different polarities were evaluated; dichloromethane, acetone, ethanol, chloroform, acetonitrile and methanol were chosen. Elution was performed using aliquots of 2.0 mL (×3). The eluate was then collected and dried at 40 °C, and the residues were redissolved in the mobile phase and analyzed by HPLC-UV at 254 nm. The outcomes are depicted in Fig. 1.

As can be seen, the polar and protic solvents were capable to disrupt the binding between the polymers and tebuthiuron. Higher elution percentage was also obtained using acetonitrile, which can be justified by high solubility of tebuthiuron, while a much lower desorption was observed for chloroform most likely due to its apolar properties, thus making it very difficult to disrupt the binding between the polymers and tebuthiuron. Therefore, methanol as the elution solvent was adopted in SPE procedure.

Influence of volume of elution solvent. After adopting methanol as the elution solvent, the influence of volume was evaluated. For this task, 100.0 mL of tebuthiuron solution at very low concentration (5.0 µg L⁻¹) was percolated through SPE cartridges at a flow rate of 2.0 mL min⁻¹. Different aliquots 6.0, 3.0 and 2.0 mL of methanol were tested. Table 1 shows the obtained outcomes represented by the preconcentration factor (PF), which was determined by preconcentration volume (100.0 mL)/elution volume ratio.

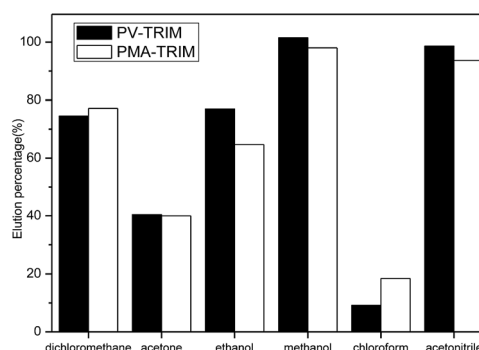


Fig. 1 Elution percentage (%) of tebuthiuron by using different elution solvents.

Table 1 Preconcentration factors obtained by using different volumes of elution solvents

Sorbent material	Elution (mL)	PF _{theoretical} ^a	PF _{experimental} ^a
PV-TRIM	6.00	16.66	17.06
	3.00	33.33	32.57
	2.00	50.00	40.74
PMA-TRIM	6.00	16.66	16.86
	3.00	33.33	33.65
	2.00	50.00	43.16

^a PF – preconcentration factor.



According to data presented in Table 1, 3.0 mL of methanol was sufficient to provide quantitative elution of tebuthiuron from both polymers, since the theoretical PF were very similar to the ones obtained experimentally. These findings reveal that SPE procedure may greatly improve the detectability of herbicides.

Breakthrough curve

The breakthrough curve is shown in Fig. 2. It was observed, under experimental procedure previously mentioned, that the breakthrough volume for PV-TRIM was found to be 60.0 mL, which corresponds to the amount of tebuthiuron adsorbed on the polymer of 29.15 mg g⁻¹. The column saturation was achieved by loading 220.0 mL of 100.0 mg L⁻¹ tebuthiuron solution, yielding a maximum adsorption capacity (MAC) of 55.18 mg g⁻¹. For the PMA-TRIM, a breakthrough volume of 35.0 mL was observed, corresponding to the amount of tebuthiuron adsorbed on the polymer of 12.45 mg g⁻¹, while the column saturation was achieved by loading 265.0 mL of tebuthiuron solution, with a maximum adsorption capacity (MAC) of 62.48 mg g⁻¹.

From the analytical point of view, the values of breakthrough volume play an important role on the preconcentration method. Therefore, the quantitative adsorption of tebuthiuron for PV-TRIM and PMA-TRIM was found to be 5.83 mg and 2.49 mg, respectively. Such outcomes show that larger sample volume of tebuthiuron solution at very low concentration can be loaded in the cartridges packed with polymers, without loss of adsorption capacity, consequently yielding higher preconcentration factors. For instance, if a tebuthiuron solution of 100 µg L⁻¹ concentration is used, 58.3 and 24.9 liters can be preconcentrated on the PV-TRIM and PMA-TRIM, respectively. One should note still that PV-TRIM shows higher adsorption towards tebuthiuron, most likely due to its higher porosity.³⁵

Analytical features of SPE for tebuthiuron determination by HPLC-DAD

Fig. 3 shows the analytical curves for herbicide tebuthiuron after preconcentration (50.0 mL) on PV-TRIM, PMA-TRIM, and

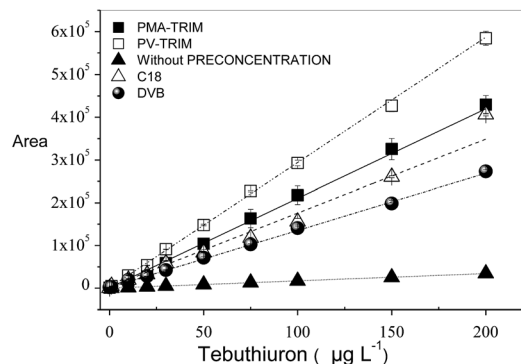


Fig. 3 Calibration curves obtained for tebuthiuron after preconcentration step on PMA-TRIM, PV-TRIM, C18, DVB and without preconcentration.

commercial sorbents octadecyl-C18-silica (C18) and Amberlite® XAD4 poly(styrene-divinylbenzene) (DVB) as well as the analytical curve without preconcentration step. The obtained linear correlation coefficients were found to be 0.998, 0.995, 0.990 and 0.998 for PV-TRIM, PMA-TRIM, C18 and DVB, respectively. The improvement on the sensitivity could be clearly observed by implementing the preconcentration step, mainly when PV-TRIM was used as sorbent. The preconcentration factor was determined as the ratio of slope of the calibration curve with and without preconcentration. Therefore, under optimized conditions, the preconcentration factor was found to be 17.1, 12.2, 8.6 and 7.8 for PV-TRIM, PMA-TRIM, C18 and DVB, respectively. The limits of detection (LOD) and quantification (LOQ) were determined as $3 \times \text{Sb}$ (standard deviation of ten blank measurements) m⁻¹ and $10 \times \text{Sb}$ m⁻¹, respectively, according to IUPAC recommendation, where m is the slope of analytical curve.³⁶ The obtained values of LOD were found to be 0.07 µg L⁻¹, 0.12 µg L⁻¹, 0.16 µg L⁻¹ and 0.57 µg L⁻¹ and LOQ values were 0.25 µg L⁻¹, 0.39 µg L⁻¹, 0.53 µg L⁻¹ and 1.91 µg L⁻¹ for PV-TRIM, PMA-TRIM, C18 and DVB respectively. The precision of method for tebuthiuron determination was evaluated in terms of repeatability ($n = 10$) by preconcentrating solutions of 10.0 µg L⁻¹ and 100.0 µg L⁻¹, yielding relative standard deviation (RSD) of 1.7% and 1.4% for the polymer PV-TRIM and 4.6% and 1.9% for the polymer PMA-TRIM.

Evaluation of PV-TRIM and PMA-TRIM for adsorption of other herbicides

In order to evaluate the potential of polymers for multiresidue adsorption, particularly those used in sugarcane crops, adsorption studies with diuron, hexazinone and ametryn were carried out. First, a competitive adsorption experiment in batch mode of tebuthiuron in the presence of diuron was performed. For this task, a binary solution of tebuthiuron and diuron at 20.0 mg L⁻¹ and 10.0 mg L⁻¹ was stirred with 50 mg of each polymer for 20 min. Then, the supernatant was analyzed by HPLC. From the obtained results, the distribution coefficient (K_d) was calculated according to eqn (2)

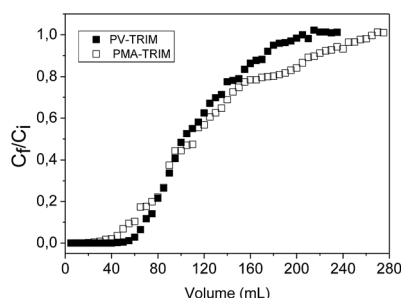


Fig. 2 Breakthrough curves of the polymers. The experiments were performed by percolating aliquots of 5.0 mL of 100.0 mg L⁻¹ solution of tebuthiuron through a SPE cartridge packed with 200 mg of polymers PV-TRIM or PMA-TRIM at a flow rate 1.0 mL min⁻¹. C_e = tebuthiuron concentration in the column effluent and C_i = initial tebuthiuron concentration.



$$K_d = \left[\frac{(C_i - C_f)}{C_f} \right] \times \frac{V \text{ (mL)}}{m \text{ (g)}} \quad (2)$$

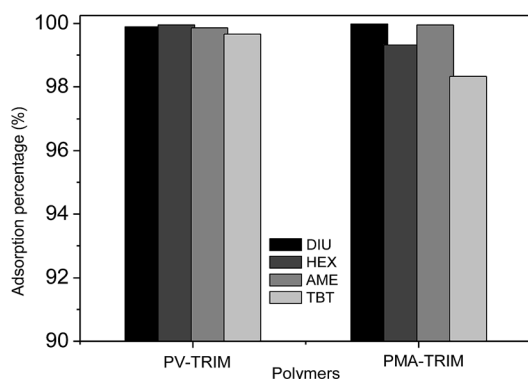
where C_i and C_f are the initial and final concentrations of tebuthiuron or diuron; V (mL) is the sample volume; m (g) is the PV-TRIM or PMA-TRIM mass. From K_d , the obtained the selectivity coefficients (k) were determined according to eqn (3) and (4).

$$k_{\text{PV-TRIM}} = \frac{K_d \text{ tebuthiuron}}{K_d \text{ diuron}} \quad (3)$$

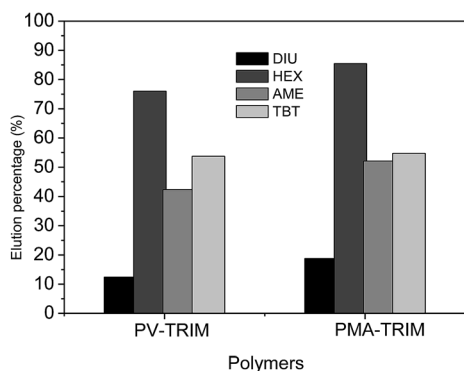
$$k_{\text{PMA-TRIM}} = \frac{K_d \text{ tebuthiuron}}{K_d \text{ diuron}} \quad (4)$$

Table 2 Results of distribution coefficients (K_d) and selectivity coefficients (k) obtained for tebuthiuron and diuron using PV-TRIM and PMA-TRIM

Sorbent	Initial concentration (mg L ⁻¹)		K_d (mLg ⁻¹)		k
	Tebuthiuron	Diuron	Tebuthiuron	Diuron	
PV-TRIM	20	10	1577.78	15 184.62	0.10
PMA-TRIM			2163.79	11 812.01	0.18



(a)

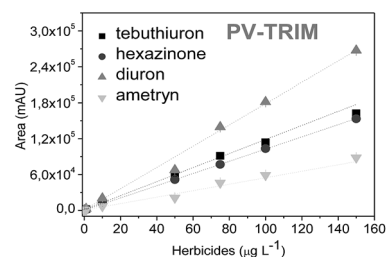


(b)

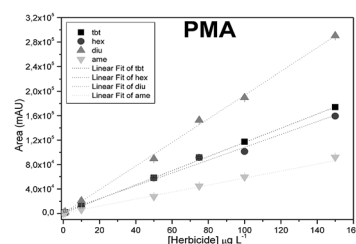
Fig. 4 Adsorption percentage (%) of herbicides by PV-TRIM and PMA-TRIM (a) and elution percentage (%) of herbicides from PV-TRIM and PMA-TRIM using 3.0 mL of methanol as eluent (b).

Table 2 shows comparison of K_d and k values. As observed, the K_d values of diuron were considerably higher compared to those of tebuthiuron for both polymers, thus showing a better affinity for diuron, which can be explained due to smaller size of the molecule.

Upon achieving outstanding adsorption of diuron in the presence of tebuthiuron, the potential of polymers for multi-residues adsorption was evaluated. In this case, adsorption experiments on column were carried out by loading 6.0 mL of quaternary mixture (tebuthiuron, hexazinone, diuron and ametryn) at 10.0 mg L⁻¹ concentration of each herbicide through 200 mg of packed polymers under pH 6.0 and flow rate of 2.0 mL min⁻¹. After loading, the elution was carried out with 3.0 mL of methanol. As shown in Fig. 4a, the obtained outcomes for adsorption of ametryn, diuron, tebuthiuron and hexazinone indicate the high potential of polymers for



(a)



(b)

Fig. 5 Analytical curves of quaternary solution of herbicides obtained after preconcentration on PV-TRIM (a) and PMA-TRIM (b).

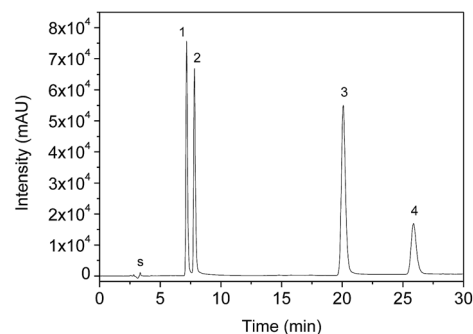


Fig. 6 Chromatogram of quaternary solution (1 – tebuthiuron, 2 – hexazinone, 3 – diuron, 4 – ametryn and s – solvent). Mobile phase, ACN : H₂O (35 : 65, v/v), isocratic, flow rate of 1.0 mL min⁻¹, column Gemini C8 Phenomenex, λ = 254 nm.



multiresidues adsorption considering the great adsorption rate above 97%.

Although the experimental condition optimized for tebuthiuron adsorption has been satisfactory for adsorption of hexazinone, ametryn and diuron, the elution with 3.0 mL of methanol was not satisfactory (Fig. 4b). Such outcome can be attributed to high concentration of herbicides (10.0 mg L^{-1}) and, as a consequence, 3.0 mL of methanol were not sufficient to strip off the herbicides quantitatively. It is important to point out that even though quantitative elution had not been achieved, the applicability of method was possible as will be further demonstrated, since in real samples, the concentrations of herbicides are much lower than 10.0 mg L^{-1} .

Multiresidue analysis of herbicides

Taking into account the potential of polymers for multiresidues adsorption of urea, triazine and triazione classes, analytical curves in the range $1\text{--}150.0 \text{ } \mu\text{g L}^{-1}$ under optimized conditions were built after preconcentration of 50.0 mL and elution with 3.0 mL of methanol (Fig. 5). The chromatographic profile for the separation of herbicides is shown in Fig. 6.

Tables 3 and 4 show the linear regression and the LOD and LOQ for herbicides achieved using the polymers. The values of LOD and LOQ for hexazinone, ametryn and diuron were similar, as found by comparing the polymers. However, lower LOD and LOQ for tebuthiuron were observed when the PV-TRIM was used as the sorbent. Moreover, the detectability for tebuthiuron in the quaternary mixture was lower than the one achieved in a single solution, thus indicating competitive adsorption of herbicides towards binding sites of polymers.

The analytical precision of multiresidues analysis using the polymers is shown in Table 5. The outcomes show that the method is precise owing to the low relative standard deviations. Furthermore, the reusability of sorbents was exceptional since

adsorption/desorption cycles were performed repeatedly (161 recycles) without any significant loss in the initial binding affinity.

The applicability of method in real water samples (well and river water) by using PV-TRIM as sorbent is shown in Table 6.

Water was collected from rivers and wells situated near sugarcane crops in the São Paulo and Paraná States – Brazil. Sample collection was carried out in amber flasks, and the samples were acidified with $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and the pH was adjusted to 6.0. From the data, the herbicides were not found in the samples and after spiking sample with known amount of herbicides, satisfactory recovery in the range 96–101% was obtained, indicating that the polymers were prone to sorb the herbicides free of interferences from natural water. Although herbicides were not determined naturally in the analyzed water samples, the detectability of method may be considerably improved by increasing the sample volume, according to breakthrough curve.

Table 5 Values obtained for the analytical precision ($n = 10$) of multiresidue analysis of herbicides for PV-TRIM and PMA-TRIM polymers

Herbicides	PV-TRIM							
	$10 \text{ } \mu\text{g L}^{-1}$				$100 \text{ } \mu\text{g L}^{-1}$			
	TBT	HEX	DIU	AME	TBT	HEX	DIU	AME
Mean (\bar{x})	10.0	10.5	10.2	10.1	100.4	100.3	100.8	101.5
R.S.D (%)	1.2	1.9	1.8	1.9	1.1	1.3	1.0	1.8
Herbicide	PMA-TRIM							
	$10 \text{ } \mu\text{g L}^{-1}$				$100 \text{ } \mu\text{g L}^{-1}$			
	TBT	HEX	DIU	AME	TBT	HEX	DIU	AME
Mean (\bar{x})	10.1	9.7	9.84	9.8	99.3	102.1	101.2	103.2
R.S.D (%)	3.0	3.3	2.1	3.2	2.0	1.4	2.4	2.9

Table 3 Linear regression equation, determination coefficients and limits of detection and quantification obtained by quaternary solution of herbicides in column of PMA-TRIM

Herbicide	Linear regression	R^2	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)
TBT	Area = $522.71\text{--}1158.03[\text{TBT } (\mu\text{g L}^{-1})]$	0.999	0.40	1.35
HEX	Area = $3147.08\text{--}1051.60[\text{HEX } (\mu\text{g L}^{-1})]$	0.997	0.31	1.04
DIU	Area = $422.87\text{--}1931.33[\text{DIU } (\mu\text{g L}^{-1})]$	0.999	0.12	0.40
AME	Area = $522.96\text{--}573.70[\text{AME } (\mu\text{g L}^{-1})]$	0.997	0.34	1.14

Table 4 Linear regression equation, determination coefficients and limits of detection and quantification obtained by quaternary solution of herbicides in column of PV-TRIM

Herbicide	Linear regression	R^2	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)
TBT	Area = $1008.32\text{--}1176.31[\text{TBT } (\mu\text{g L}^{-1})]$	0.998	0.14	0.47
HEX	Area = $346.115\text{--}1022.45[\text{HEX } (\mu\text{g L}^{-1})]$	0.999	0.44	1.49
DIU	Area = $661.70\text{--}1779.20[\text{DIU } (\mu\text{g L}^{-1})]$	0.999	0.17	0.58
AME	Area = $425.02\text{--}541.84[\text{AME } (\mu\text{g L}^{-1})]$	0.986	0.39	1.32



Table 6 Recovery of herbicides in different waters samples using SPE procedure^a

Water samples	Herbicides					
	Tebuthiuron			Hexazinone		
	Added ($\mu\text{g L}^{-1}$)	Concentration found ^b ($\mu\text{g L}^{-1}$)	Rec. (%)	Added ($\mu\text{g L}^{-1}$)	Concentration found ^b ($\mu\text{g L}^{-1}$)	Rec. (%)
Well	0	ND	—	0	ND	—
	8	8.0 ± 0.1	100	8	8.1 ± 0.1	101
	16	16.1 ± 0.1	100	16	16.2 ± 0.1	101
River 1	0	ND	—	0	ND	—
	8	8.0 ± 0.1	100	8	8.1 ± 0.1	100
	16	16.0 ± 0.1	100	16	16.1 ± 0.7	100
River 2	0	ND	—	0	ND	—
	8	8.0 ± 0.1	100	8	7.9 ± 0.1	99
	16	16.1 ± 0.1	100	16	15.9 ± 0.1	99
River 3	0	ND	—	0	ND	—
	8	7.9 ± 0.1	99	8	7.9 ± 0.1	99
	16	15.7 ± 0.3	98	16	15.8 ± 0.2	98
River 4	0	ND	—	0	ND	—
	8	8.0 ± 0.2	100	8	7.7 ± 0.2	96
	16	16.0 ± 0.2	100	16	15.5 ± 0.3	97

Sample	Herbicides					
	Diuron			Ametryn		
	Added ($\mu\text{g L}^{-1}$)	Concentration found ^b ($\mu\text{g L}^{-1}$)	Rec. (%)	Added ($\mu\text{g L}^{-1}$)	Concentration found ^b ($\mu\text{g L}^{-1}$)	Rec. (%)
Well	0	ND	—	0	ND	—
	8	8.0 ± 0.1	100	8	7.9 ± 0.1	98
	16	16.0 ± 0.1	100	16	15.9 ± 0.1	99
River 1	0	ND	—	0	ND	—
	8	7.9 ± 0.1	99	8	8.1 ± 0.1	101
	16	15.9 ± 0.1	99	16	15.9 ± 0.1	99
River 2	0	ND	—	0	ND	—
	8	7.9 ± 0.1	98	8	7.9 ± 0.1	98
	16	16.0 ± 0.1	100	16	16.0 ± 0.1	100
River 3	0	ND	—	0	ND	—
	8	7.9 ± 0.3	99	8	8.0 ± 0.3	100
	16	15.5 ± 0.4	96	16	16.2 ± 0.3	101
River 4	0	ND	—	0	ND	—
	8	7.8 ± 0.4	98	8	7.8 ± 0.2	98
	16	15.6 ± 0.3	98	16	15.7 ± 0.4	98

^a ND (not detected) = below the limit of detection. ^b The results are expressed as mean value \pm S.D. based on two replicates ($n = 3$) determinations.

Conclusions

A solid-phase extraction method for simultaneous preconcentration of tebuthiuron, diuron, hexazinone and ametryn using PVI-TRIM and PMA-TRIM as sorbents was developed. The suitability of PVI-TRIM for interference-free multiresidues analysis in natural waters was demonstrated by high recovery values and good precision. In general, PV-TRIM adsorbs higher amounts of tebuthiuron either in single or quaternary solutions compared to other herbicides. However, bearing in mind the analytical performance of SPE procedure using PMA-TRIM as sorbent, most likely this material can also be successfully applied in real samples. The polymers were advantageous relative to the commercial sorbents C18 and DVB, due to

exceptional reusability (161-recycles) and a better detectability by loading larger volumes of samples (>50.0 mL). For final remarks and from the results, it can be concluded that new applications of cross-linked polymers synthesized with different functional monomers deserve to be expanded to other analytes aiming at developing of new analytical methods for multi-residue analysis.

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References

- 1 S. S. Caldas, F. F. Gonçalves, E. G. Primel, O. D. Prestes, M. L. Martins and R. Zanella, *Quim. Nova*, 2011, **9**, 1604–1617.
- 2 C. S. Machado, R. I. S. Alves, B. M. Fregonesi, K. A. A. Tonani, B. S. Martinis, J. Sierra, M. Nadal, J. L. Domingo and S. Segura-Muñoz, *Procedia Eng.*, 2016, **162**, 230–237.
- 3 J. Vymazal and T. Brezinová, *Environ. Int.*, 2015, **75**, 11–20.
- 4 FAOSTAT – Food and Agriculture Organization of the United Nations, Statistics Division, Word crop production, http://faostat3.fao.org/browse/Q/*E, 2016, accessed April, 11, 2017.
- 5 IBGE – Brazilian Institute of Geography and Statistics, Statistics of agricultural production, [ftp://ftp.ibge.gov.br/Producao_Agricola/Producao_Agricola_Municipal_\[anual\]/2013/pam2013.pdf](ftp://ftp.ibge.gov.br/Producao_Agricola/Producao_Agricola_Municipal_[anual]/2013/pam2013.pdf), 2013, accessed April, 11, 2017.
- 6 S. H. G. Brondi and F. M. Lanças, *J. Braz. Chem. Soc.*, 2005, **16**, 650–653.
- 7 S. C. N. Queiroz, V. L. Ferracini, M. A. F. Gomes and M. A. Rosa, *Quim. Nova*, 2009, **32**, 378–381.
- 8 P. Y. Caux, R. A. Kent, V. Bergeron, J. E. Warner and J. Busharda, *Environ. Toxicol.*, 1997, **12**, 61–65.
- 9 A. Saleh, N. S. Fumani and S. Molaei, *J. Chromatogr., A*, 2014, **1356**, 32–37.
- 10 S. Giacomazzi and N. Cochet, *Chemosphere*, 2004, **56**, 1021–1032.
- 11 T. Santos, G. Cancian, D. N. R. Neodini, D. R. S. Mano, C. Capucho, F. S. Predes, R. Barbieri, C. A. Oliveira, A. A. Pigoso, H. Dolder and G. D. C. Severi-Aguiar, *Exp. Toxicol. Pathol.*, 2015, **67**, 525–550.
- 12 World Health Organization (WHO), Guidelines for drinking-water quality, Third edition incorporating the first and second addenda, volume 1, 2008, http://www.who.int/water_sanitation_health/dwq/fulltext.pdf, accessed April, 11 2017.
- 13 European Commission, “Priority substances under the water framework directive”, http://ec.europa.eu/environment/water/waterframework/priority_substances.html, accessed April, 11 2017.
- 14 A. Wong, M. R. V. Lanza and M. D. P. T. Sotomayor, *J. Electroanal. Chem.*, 2013, **690**, 83–88.
- 15 Brazilian Ministry of Health; Act No. 2.914 of December 12, http://bvsms.saude.gov.br/bvs/saudelegis/gm/2011/prt2914_12_12_2011.html, 2011, accessed April 11, 2017.
- 16 D. J. Hamilton, Á. Ambrus, R. M. Dieterlie, A. S. Felsot, C. A. Harris, P. T. Holland, A. Katayama, Kurihara, N. J. Linders, J. Unsworth and S. S. Wong, *Pure Appl. Chem.*, 2003, **75**, 1123–1155.
- 17 S. H. G. Brondi and F. M. Lanças, *J. Liq. Chromatogr. Relat. Technol.*, 2004, **27**, 171–179.
- 18 S. Saha, R. Mistri and B. C. Ray, *J. Chromatogr. A*, 2010, **1217**, 307–3011.
- 19 S. Saha, R. Mistri and B. B. C. Ray, *Anal. Bioanal. Chem.*, 2013, **405**, 9265–9272.
- 20 W. T. Ma, K. K. Fu, Z. Cai and G. B. Jiang, *Chemosphere*, 2003, **52**, 1627–1632.
- 21 J. Wang, F. Wu and Q. Zhao, *Chin. J. Chromatogr.*, 2015, **33**, 849–855.
- 22 G. L. Sheel and C. R. T. Tarley, *Microchem. J.*, 2017, **133**, 650–657.
- 23 C. Wang, S. Ju, Q. Wu and Z. Wang, *J. Chromatogr. Sci.*, 2011, **49**, 689–694.
- 24 J. Wang, Y. Cui, W. Liu, M. Yang and J. Chen, *Chin. J. Chromatogr.*, 2007, **25**, 853–856.
- 25 M. Saraji and B. Farajmand, *J. Chromatogr., A*, 2008, **1178**, 17–23.
- 26 J. Ma, L. Jiang, G. Wu, Y. Xia, W. Lu, J. Li and L. Chen, *J. Chromatogr., A*, 2016, **1466**, 12–20.
- 27 A. R. Koophaei, S. J. Shahtaheri, M. R. Ganjali, A. R. Forushani and F. Golbabaie, *J. Hazard. Mater.*, 2009, **170**, 1247–1255.
- 28 E. I. P. Rezende, P. G. Peralta-Zamora, W. F. Jardim, C. Vidal and G. Abate, *Anal. Lett.*, 2013, **46**, 439–451.
- 29 J. M. Pozzebon, S. C. N. Queiroz and I. C. S. F. Jardim, *J. Liq. Chromatogr. Relat. Technol.*, 2003, **26**, 78–790.
- 30 X. L. Wu, L. Meng, Y. Wu, Y.-Y. Luk, Y. Ma and Y. Du, *J. Braz. Chem. Soc.*, 2015, **26**, 131–139.
- 31 S. C. Queiroz, L. F. Melo and I. C. Jardim, *J. Chromatogr. A*, 2002, **948**, 171–176.
- 32 X. Liu, C. Wang, Q. Wu and Z. Wang, *Anal. Chim. Acta*, 2015, **22**, 870.
- 33 G. Mendas, V. Drevenkar and L. Zupancic-Kralj, *J. Chromatogr.*, 2001, **918**, 351–359.
- 34 V. Pichon, *J. Chromatogr. A*, 2000, **885**, 195–215.
- 35 R. J. Fonseca, M. G. Segatelli, K. C. Borges and C. R. T. Tarley, *React. Funct. Polym.*, 2015, **93**, 1–9.
- 36 G. L. Long and J. D. Winefordner, *Anal. Chem.*, 1983, **55**, 712–722.

