

NEW CHEMICALLY MODIFIED POLYMERIC RESIN FOR SOLID-PHASE EXTRACTION OF PESTICIDES AND PHENOLIC COMPOUNDS FROM WATER

ABSTRACT

A new chemically modified polymeric resin, with an *o*-carboxybenzoyl moiety, is developed to be used in the on-line solid-phase extraction (SPE) of some pesticides and phenolic compounds from aqueous samples, in order to obtain better breakthrough volumes than other commercial sorbents. The chemical introduction of this moiety improves the efficiency of SPE by providing better surface contact with aqueous samples. This synthesized sorbent enables higher volumes of sample to be concentrated for determining polar compounds. When analyzing real samples, tap and river waters, different quantities of sulphite were added to decrease the initial band due to fulvic and humic acids. The matrix peaks decreased and there were no losses in the studied compounds observed when 500 μl and 1000 μl of 10% Na_2SO_3 solution for every 100 ml of sample were added to tap and river water, respectively.

Keywords: Solid-phase extraction; Chemically modified polymeric resin; Water analysis; Pesticides; Phenols.

INTRODUCTION

Pesticides and phenolic compounds are organic pollutants of great environmental interest. Their determination has been increasing in recent years because of their toxicity, even at low concentrations. A preconcentration step is usually necessary to detect these low levels. Solid-phase extraction (SPE) is the most important technique for sample enrichment, because it overcomes many of the disadvantages of liquid-liquid extraction (LLE) [1,2].

The SPE of these analytes is most commonly used with chemically bonded silica, usually with a C₁₈ or C₈ organic group [3-6], or with some styrene-divinylbenzene copolymers such as PLRP-S [5-12] and Envi-Chrom P [11-14]. Recoveries for the polar compounds are higher when styrene-divinylbenzene copolymers are used [6,11,12], because in chemically bonded silica, while silica itself is hydrophilic, the hydrocarbon chains make the surface hydrophobic and so there is little poor surface contact with aqueous solutions; on the other hand, although the styrene-divinylbenzene copolymers also have a hydrophobic surface they contain a relatively large number of active aromatic sites which allow $\pi-\pi$ interactions with these aromatic analytes. Other authors have used graphitized carbon blacks (GCBs) to preconcentrate these organic pollutants [15-18] and have shown that GCB is more efficient than a C₁₈ for extracting very polar pesticides from aqueous samples [15]. However, different results are shown in literature when GCB is compared with polymeric sorbents [16-18] depending on the kind of GCB used. It should also be pointed out that higher recoveries are obtained with GCB when the adsorbates are recovered by back-flushing elution because of the higher retention capacity of the carbon [17,18].

When solid-phase extraction is on-line coupled to liquid chromatography, peak broadening appears if the sorbent in the precolumn retains the analytes stronger than the sorbent in the analytical columns and this fact limits the use of sorbents in the precolumn with high capacity. Since the solvent of the mobile phase is not strong enough to elute the compounds trapped in the precolumn, peak broadening

appears, although this may be solved by eluting the compounds retained in the precolumn using only the organic solvent of the mobile phase [11,19].

In recent years, new highly cross-linked packing materials have been developed as highly crosslinked porous ethylvinylbenzene-divinylbenzene copolymers such as LiChrolut EN and hypercrosslinked polystyrene-type sorbents such as Styrosorb and Macronet Hypersol.

LiChrolut EN has been used to determine several pollutants in water [14,20,21]. For instance, Puig and Barceló [20] explain that the breakthrough volumes of phenolic compounds increase when this sorbent is used instead of PLRP-S, because of its open structure which increases the specific surface area available and allows more $\pi-\pi$ interactions. This sorbent is also used by Junker-Buchheit and Witzenbacher [21] to preconcentrate pesticides in the low ppb range and they can be efficiently concentrated from large water samples.

Styrosorb and Macronet Hypersol are used by Tsyurupa et al. [22] in the SPE of phenols from water, and they are shown to be superior to other polymeric sorbents. They have large transport macropores in addition to a highly developed microporous structure and display adsorption and desorption performance allowing rapid treatment of large volumes.

Recently, chemically modified resins have also been used [23-28]. Different functional groups (such as acetyl and hydroxymethyl) have been chemically introduced into polymeric resins [23,24,26]. These modified resins have excellent hydrophilicity, and they also give higher recoveries than their unmodified analogues. This has been attributed to an increase in surface polarity which enables the aqueous sample to make better contact with the resin surface. Lightly sulphonated resins have also been used [24,25]. If a polymeric resin is sulphonated, it changes into a cation exchanger and, a hydrogen bonding between the amine groups of

some analytes and the sulphonic acid group on the resin is also possible. Some authors [28] have studied SPE for organic pollutants in water with a binary cartridge, made up of a chemically modified resin and anion exchange phase as an alternative to the LLE.

In previous papers [26,27] polystyrene-divinylbenzene resin was chemically modified by two chemical groups, acetyl and benzoyl, and retained more polar compounds than the unmodified resin. This paper tests another chemical modification to increase the polarity of the sorbent. A new chemically modified polystyrene-divinylbenzene resin with an *o*-carboxybenzoyl moiety was synthesized and tested in the SPE of some pesticides and phenolic compounds in environmental waters. The aim of this paper is to compare the new sorbent synthesized with other commercial sorbents for the SPE of these pollutants.

EXPERIMENTAL

Equipment

The chromatographic experiments were performed with two Shimadzu (Tokyo, Japan) LC-10AD pumps with a Shimadzu SPD-10A UV spectrophotometric detector. The temperature of the column was controlled by a Shimadzu CTO-10A oven and the chromatographic data were collected and recorded using an HP-3365 Series II Chemstation which was controlled by Windows 3.1 (Microsoft). The

analytical column was a 250x4.6 mm I.D. stainless-steel column packed with Spherisorb ODS 2, 5 μm (Teknokroma, Barcelona, Spain).

To check the response of the instrument, standard solutions were injected through a Rheodyne (Cotati, CA, USA) valve with a 20- μl loop, and an automatic Must column-switching device (Spark Holland, Emmen, Netherlands) was used for the on-line solid-phase extraction. The on-line trace enrichment process was carried out using steel 10x3 mm I.D. precolumns, purchased from the Free University (Amsterdam, The Netherlands) which were laboratory-packed with the new sorbent synthesized. A Waters (Milford, MA, USA) M45 pump was used to deliver the sample.

Reagents and Standards

The compounds studied were phenolic compounds, such as phenol (Ph), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP) and 2-chlorophenol (2-CP), and pesticides such as simazine and atrazine (triazines), methomyl and oxamyl (carbamates), MCPA (chlorophenoxy acid) and bentazone (diazine). The phenolic compounds were obtained from Aldrich-Chemie (Steinheim, Germany), and the pesticides, except bentazone which was obtained from Dr. Ehrenstorfer (Augsburg, Germany), were from Riedel-de Haën (Seelze, Germany).

Standard solutions of 2000 mg l^{-1} of each compound were prepared in methanol. An additional step for triazine solution was included prior to the preparation of diluted standards, that consisted in using an ultrasonic bath. A mixture of 100 mg l^{-1} of all the compounds used was prepared weekly by diluting the standard solutions with Milli-Q water (Millipore, Bedford, MA, USA), and more diluted working solutions were prepared daily by diluting this mixture with Milli-Q, tap or river water. All solutions were stored at 4 $^{\circ}\text{C}$ in the refrigerator.

HPLC-gradient-grade methanol (Scharlau, Barcelona, Spain) and Milli-Q quality water were used to prepare the mobile phase. Sulphuric acid (Probus, Badalona, Spain) was used to adjust the pH of the mobile phase to 3. Hydrochloric acid (Probus, Badalona, Spain) and sodium sulphite (Panreac, Barcelona, Spain) were used in the sample preparation.

The reagents used in the synthesis procedure were: nitrobenzene from Probus (Badalona, Spain), and aluminium chloride and phthalic anhydride, both obtained from Fluka (Buchs, Switzerland).

Synthetic Procedure

The chemically modified resin was obtained from porous crosslinked PS-DVB beads. Amberchrom GC-161m (Tosohaas, Montgomeryville, PA, USA) is a spherical resin with an average particle size of 50-100 μm and an average pore size of 110-175 \AA .

The *o*-carboxybenzoyl derivative was prepared as follows: 2.5 g of divinylbenzene-crosslinked-polystyrene was stirred in 70 ml of nitrobenzene at room temperature for 8 h. Then, 4.5 g of aluminium chloride was added slowly under mechanical stirring. Subsequently, 5.2 g of phthalic acid anhydride was added. The reaction mixture was stirred for 15 h at room temperature. The reaction was quenched by adding acetone with 1% hydrochloric acid. The filtered polymer was washed twice with methanol and dried under vacuum at 60°C. The polymer was characterized by IR spectroscopy. The extent of the modification (11%) was established from elemental analysis (C 88% and H 8%.)

Chromatographic Conditions

The gradient elution was carried out with Milli-Q water adjusted to pH 3 with sulphuric acid (solvent A) and methanol as organic modifier (solvent B). The flow-rate was 1 ml min^{-1} and the temperature of the column oven was set at 65°C . The solvent program was as follows: initially 20% B, 50%B after 25 min, 100% at 32 min, isocratic for 2 min, and the mobile phase returned to initial conditions in 2 min for a subsequent analysis run.

The detection was performed at 280 nm for phenolic compounds and at 240 nm for pesticides, except for MCPA which was quantified at 230 nm. The wavelength program used, which allows each compound to be detected at its maximum absorbance, was: first at 240 nm, then at 280 nm after 8 min, at 240 nm after 15.7 min, then 230 nm after 24 min and finally 240 nm after 26.5 min.

Sample Pretreatment

Water samples from tap and Ebro river were filtered through $0.45 \mu\text{m}$ nylon membranes (Supelco INC, Bellefonte, PA, USA) before the preconcentration step to eliminate particulate matter. Water samples were acidified with hydrochloric acid at pH 2.5 in order to prevent the analytes from occurring in ionic form.

Five hundred or $1000 \mu\text{l}$ of 10% sodium sulphite solution was added for every 100 ml of sample prior to the extraction process in order to reduce the influence of the matrix in river and tap water.

On-line Trace Enrichment

A 10 x 3 mm I.D. stainless steel precolumn, laboratory-packed with the synthesized sorbent, was used to perform the solid-phase extraction process.

During the SPE process the Must automatic column-switching device was used which enabled the program in Table 1 to preconcentrate the sample. The M45 Waters pump was used to deliver the sample and the conditioning solutions.

After the sample had been preconcentrated, analytes were desorbed in the backflush mode only by the organic solvent (methanol) of the mobile phase so as to prevent the peaks from broadening because of the different nature of the sorbent on the precolumn and the analytical column. The set-up used is shown in Fig. 1.

Table 1

Sample preconcentration program in the on-line SPE process

Step	Time (min)	Flow rate (ml min ⁻¹)	Event
1	0	2	Washing tubes with methanol
2	5	2	Conditioning precolumn with methanol
3	6	2	Washing tubes with Milli-Q water at pH 2.5
4	11	2	Activating precolumn with Milli-Q water at pH 2.5
5	12	2	Washing tubes with sample
6	17	4	Sample preconcentration

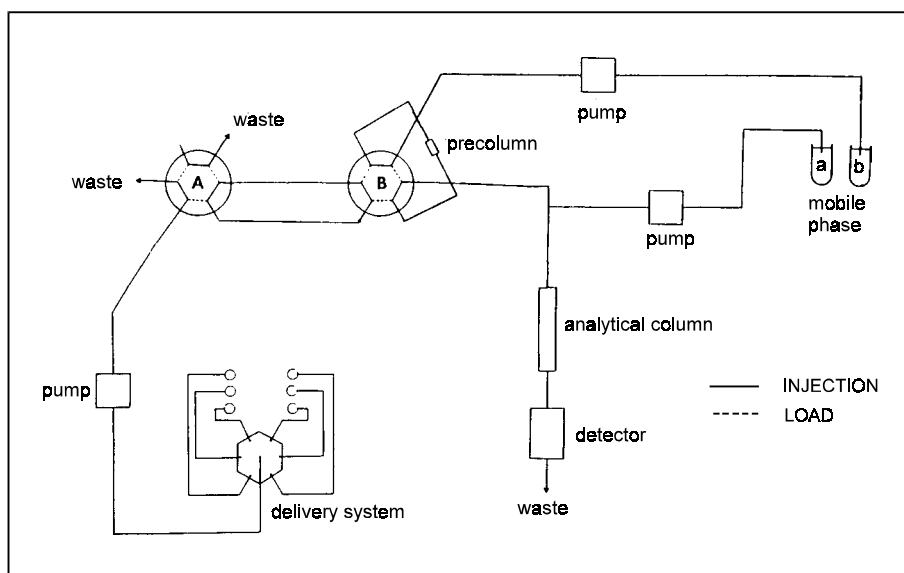


Fig. 1. Set-up used

RESULTS AND DISCUSSION

Derivatizing polymeric resins with a hydrophilic functional group increases their capacity for retaining polar compounds. These sorbents have been used by several authors [23-28] to preconcentrate polar compounds, such as phenols, pesticides and aromatic compounds, and the recoveries have been higher than when the same underivatized resins were used.

In this study a new chemical modification of the polystyrene-divinylbenzene resin (PS-DVB) is presented to be used as sorbent in the solid-phase extraction of the analytes mentioned above. The PS-DVB beads were chemically modified by aromatic electrophilic substitution with phthalic acid anhydride, using nitrobenzene as the solvent and aluminium chloride as the catalyst. In order to prevent the beads from degrading, suitable stirring conditions were established. The polymer was characterized by IR spectroscopy. The salient features of the infrared spectrum of the resin show a broad H-bonded νOH at ca. 3500 cm^{-1} , $\nu\text{C=O}$ of the ketonic carbonyl at 1670 cm^{-1} and COOH absorption at ca. 1700 cm^{-1} .

Two reaction temperatures (room temperature and 40°C) were tested in order to study the extent of the reaction, and similar degrees of substitution (11% from elemental analysis) were obtained, so the conclusion was that the reaction temperature does not influence the modification degree. The low degree of substitution may be due to the restricted accessibility of reactive sites. The reaction was carried out five times with similar results.

After the sorbent had been synthesised and characterised, the breakthrough curve for phenol, which is a polar compound with a low breakthrough volume for most commercial sorbents [6,26,27], was recorded in order to establish the suitability of this sorbent for on-line SPE. This curve was obtained by introducing a standard solution of 10 mg l^{-1} of phenol in Milli-Q water at pH 2.5 (with HCl) directly into the

UV detector at 280 nm bypassing the Rheodyne with the precolumn; when a stable response was obtained, the Rheodyne valve was moved so that the sample was passed through the precolumn at 1 ml min⁻¹. If the breakthrough volume is the volume at which the detector reaches 10% of its 100% value, the breakthrough volume of phenol obtained with this sorbent was 14 ml. In previous works [26,27], breakthrough volumes for phenol, obtained under the same conditions, with commercial sorbents have been determined. These breakthrough volumes were 5 ml for PLRP-S, 7 ml for Envi-Chrom P and 8 ml for Amberchrom CG-161 m. Therefore, the capacity of this sorbent for phenol is higher than other sorbents used.

To determine the linearity of the response of the chromatographic method by direct injection, 20 µl of standard solutions of the analytes studied was injected. Good linearity was found between 0.25 or 0.1 and 40 mg l⁻¹ for all compounds, with good regression coefficients (r^2) between 0.9995 for atrazine and MCPA to 0.9998 for oxamyl. Detection limits were calculated by the statistical criteria [29] with k value equal to 6 and the values found were between 2.5 and 25 µg l⁻¹ for oxamyl and MCPA, respectively, except for 2-CP and phenol which were 40 and 100 µg l⁻¹, respectively.

Different sample volumes (10, 25, 50, 100 ml) of Milli-Q water at pH 2.5 spiked with the analytes studied in a concentration between 20 µg l⁻¹ for 10 ml and 2 µg l⁻¹ for 100 ml were on-line preconcentrated in the new sorbent.

Table 2

Recovery values (%) and relative standard deviation ($n=5$) obtained with the new sorbent using different volumes of Milli-Q water sample

Compound	Volume (ml)
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	10		25		50		100	
	R%	RSD %	R%	RSD %	R%	RSD %	R%	RSD %
Oxamyl	79	1	79	3	81	3	74	1
Methomyl	73	2	79	3	77	2	71	1
Ph	70	2	72	2	72	5	41	3
4-NP	79	1	80	2	83	1	81	1
2,4-DNP	74	1	79	1	83	1	81	1
2-CP	79	1	83	2	86	1	85	1
Bentazone	79	2	80	1	85	3	83	1
Simazine	86	3	83	2	79	3	84	2
MCPA	72	2	75	3	78	1	79	1
Atrazine	76	2	81	1	87	2	86	1

For all conditions see text.

Table 2 shows the recoveries of these compounds which, in some cases, were higher than those of other chemically modified polymeric resins. Good recoveries were obtained when 100 ml of $2 \mu\text{g l}^{-1}$ was preconcentrated, and for all compounds the recovery values were higher than 70%, except for phenol for which it was nearly 40%. When 50 ml of $4 \mu\text{g l}^{-1}$ was preconcentrated all the recoveries were higher than 72% (phenol included). For this reason, 50 ml of sample was selected for further analysis. These recoveries were higher than the obtained in previous works with PLRP-S and Envi-Chrom P, and mainly, for the most polar compounds, such as oxamyl, methomyl and phenol [26,27]. In the preconcentration of 25 ml of sample, the recoveries for these three analytes were 75, 68 and 33%, respectively, with PLRP-S, and 65, 64, and 47% with Envi-Chrom P, whereas with the new chemically modified resin, they were higher than 72% for the three compounds. From the results obtained, the new sorbent seems to be more suitable for the

determination of polar compounds in water than other commercially available sorbents.

The performance of the method was tested on tap and Ebro river water. As a first step, 50 ml of tap water at pH 2.5 spiked with $4 \mu\text{g l}^{-1}$ was preconcentrated, but some peaks, such as phenol, 2-CP and bentazone did not appear (Fig. 2d). So, 300 μl of 10% Na_2SO_3 solution was added for every 100 ml of tap water to eliminate free chlorine, and then all the peaks of the analytes appeared; moreover, the initial peak corresponding to fulvic and humic acids decreased (Fig. 2c). For this reason, 500 μl of 10% Na_2SO_3 solution was added to the sample, and the initial peak became even smaller than in the previous analysis (Fig. 2b). The recovery values attained by adding 500 μl of sulphite solution to this matrix were as good as those with Milli-Q water. Fig. 2a shows the chromatogram obtained from analysing 50 ml of tap water with an addition of 500 μl of sulphite solution for every 100 ml of sample but without standard addition. None of the polar analytes were found in these samples, however a peak with the same retention time as atrazine appears in the chromatogram but in further studies it was not positively identified by GC-MS.

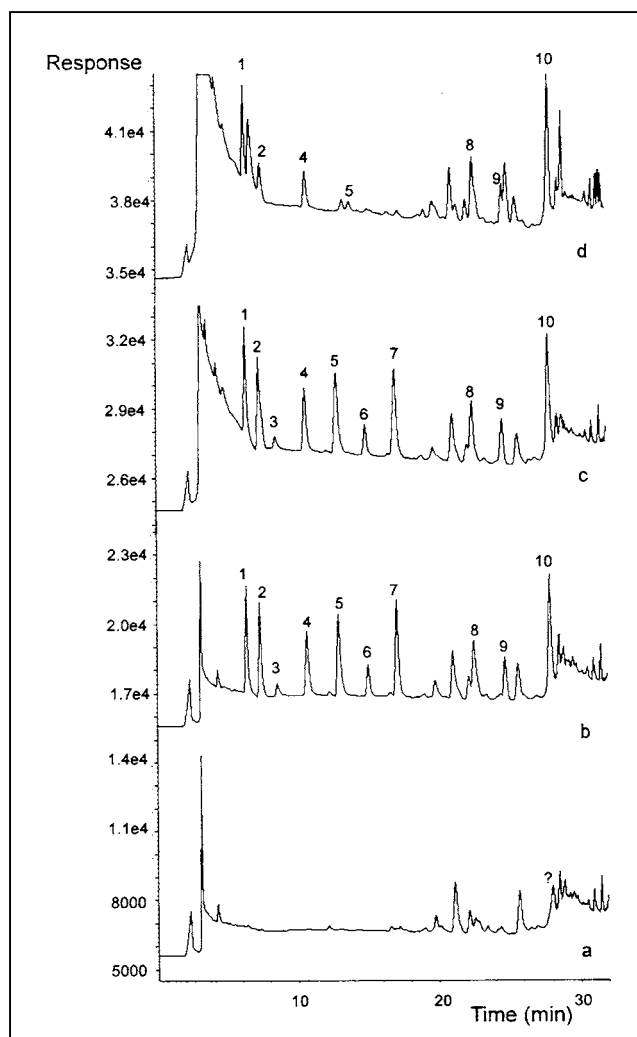


Fig. 2. Chromatograms obtained by on-line trace enrichment of 50 ml of tap water with and without the addition of different volumes of 10% Na_2SO_3 solution for every 100 ml of sample: (a) blank with the addition of 500 μl of sulphite; (b) spiked with 4 $\mu\text{g l}^{-1}$ of the analytes and 500 μl of sulphite; (c) spiked with 4 $\mu\text{g l}^{-1}$ of the analytes and 300 μl of sulphite; and (d) spiked with 4 $\mu\text{g l}^{-1}$ of the analytes without sulphite. Peak designation: (1) oxamyl, (2) methomyl, (3) phenol, (4) 4-NP, (5) 2,4-DNP, (6) 2-CP, (7) bentazone, (8) simazine, (9) MCPA, (10) atrazine.

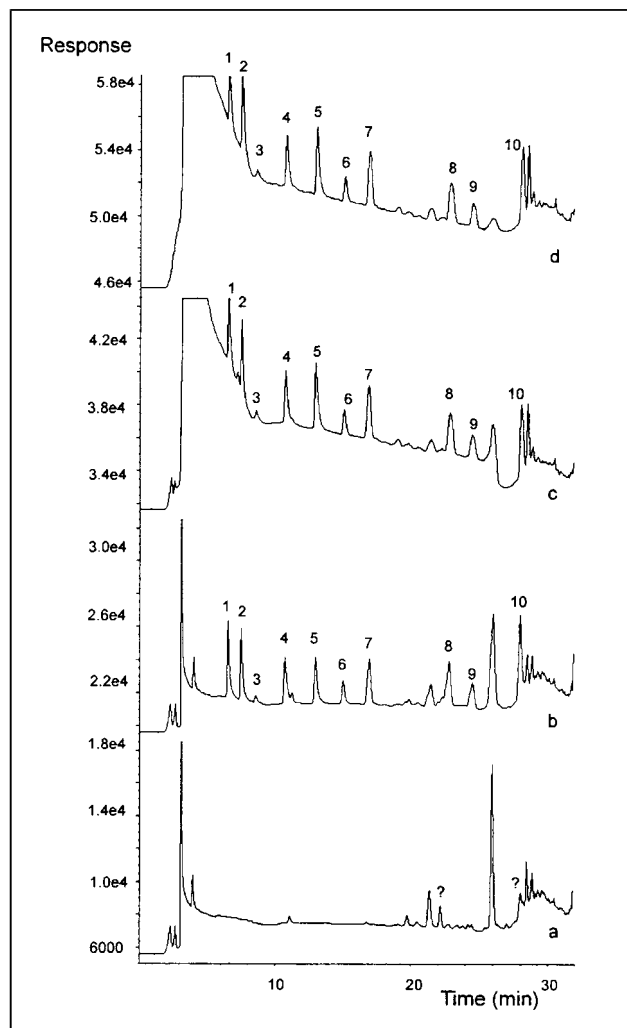


Fig. 3. Chromatograms obtained by on-line trace enrichment of 50 ml of Ebro river water with and without the addition of different volumes of 10% Na_2SO_3 solution for every 100 ml of sample: (a) blank with the addition of 1000 μl of sulphite; (b) spiked with $4 \mu\text{g l}^{-1}$ of the analytes and 1000 μl of sulphite; (c) spiked with $4 \mu\text{g l}^{-1}$ of the analytes and 500 μl of sulphite; and (d) spiked with $4 \mu\text{g l}^{-1}$ of the analytes without sulphite. For peak designation see Fig.2.

The same study was carried out with Ebro river water. Different volumes of 10% Na₂SO₃ solution were added to 50 ml of Ebro river water at pH 2.5 and spiked with 4 µg l⁻¹ of the pesticide and phenolic compound mixture in order to reduce the influence of the matrix. The volumes tested were 500 µl and 1000 µl for every 100 ml of sample, and when 500 µl was added the initial peak of humic and fulvic acids was similar to the peak without sulphite, but when 1000 µl was added the effect of the matrix decreased, and the initial peak was narrower than in the other two analyses. Results are depicted in Fig. 3, where Fig. 3a shows the chromatogram obtained for the analysis of 50 ml of Ebro river water to which 1000 µl of sulphite solution (in 100 ml of sample) has been added, and Fig. 3b-d show the chromatograms obtained for the analysis of this sample with a standard addition of 4 µg l⁻¹ of each compound without (Fig. 3d) and with 500 µl (Fig. 3c) and 1000 µl of sulphite solution (in 100 ml of sample).

Table 3

Recoveries (R%) and relative standard deviation ($n=5$) obtained with 50 ml of Ebro river water at pH 2.5 spiked with 4 µg l⁻¹ of analytes and an addition of 1000 µl of 10% Na₂SO₃ for every 100 ml of sample

Compound	R%	R.S.D.%
Oxamyl	76	2
Methomyl	71	5
Ph	41	6
4-NP	74	3
2,4-DNP	55	6
2-CP	84	5
Bentazone	72	6
Simazine	84	5
MCPA	74	1
Atrazine	83	3

The recoveries obtained by preconcentrating 50 ml of river water with the addition of 1000 µl of sulphite for every 100 ml of sample are shown in Table 3. These are

slightly lower than the ones obtained with Milli-Q water, except for Ph and 2,4-DNP, whose recoveries were about 41 and 55%, respectively.

The linearity of the response for the total analytical system, including the preconcentration step, with Ebro river water was checked for a sample volume of 50 ml spiked with different concentrations of each compound and with the addition of 1000 μl of sulphite for every 100 ml of sample. The results obtained for the linear range and the detection limits [29] (with $k=6$) are included in Table 4.

Table 4

Linear ranges, r^2 and detection limits with on-line trace enrichment of 50 ml of Ebro river water at pH 2.5 and with 1000 μl of Na_2SO_3 added (for every 100 ml of sample)

Compound	Linear range ($\mu\text{g l}^{-1}$)	r^2	Detection limit ($\mu\text{g l}^{-1}$)
Oxamyl	1-50	0.9999	0.3
Methomyl	1.2-50	0.9999	0.4
Ph	2-50	0.9991	0.6
4-NP	1.2-50	0.9998	0.4
2,4-DNP	1.2-50	0.9999	0.4
2-CP	1.5-50	0.9999	0.5
Bentazone	1-50	0.9997	0.3
Simazine	1.8-50	0.9995	0.6
MCPA	3-50	0.9998	0.9
Atrazine	4-50	0.9999	1.4

In Fig. 3a, two peaks with the same retention time as simazine and atrazine appear in the chromatogram, whereas peaks corresponding to the rest of the analytes cannot be observed. To confirm the presence of these compounds, 500 ml of the sample was off-line concentrated with a Lichrolut EN cartridge using a procedure described by Aguilar et al. [30], and simazine was identified by full scan (90%) and

quantified by SIM. The concentration of this compound in the sample is $1.2 \mu\text{g l}^{-1}$ by GC-MS and $1.5 \mu\text{g l}^{-1}$ by the HPLC method discussed in this paper.

CONCLUSIONS

This study demonstrates that the introduction of a hydrophilic *o*-carboxybenzoyl moiety into polystyrene-divinylbenzene resin increases surface polarity and allows better contact with the resin surface and aqueous samples. For this reason, with this synthesized sorbent, the breakthrough volume for phenol and the recoveries for the phenolic compounds and pesticides studied are higher than when other commercially available sorbents are used.

The addition of a sulphite solution to real samples has a great effect on the initial humic and fulvic acids band. When sulphite was added this interference decreased. Better results were obtained when 500 and 1000 μl of 10% Na_2SO_3 solution, for every 100 ml of sample, were added to tap and river water, respectively, and in these cases the initial band decreases significantly.

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