# HYDROPHILIC HYPERCROSSLINKED POLYMERIC SORBENTS FOR THE SOLID-PHASE EXTRACTION OF POLAR CONTAMINANTS FROM WATER

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**Abstract**

Three new hypercrosslinked polymers with hydrophilic character arising from hydroxyl moieties in their skeletons have been prepared in microsphere format and applied to the off-line solid-phase extraction (SPE) of polar compounds from water samples. For sample volumes of 1000 ml, the recoveries of various polar pesticides, such as oxamyl, methomyl, selected phenolic compounds, as well as some pharmaceuticals, were close to 90%. The HXLPP-polar polymer with the best performance characteristics was applied to real samples. Its performance was also compared to commercially available sorbents, such as LiChrolut EN (hydrophobic, hypercrosslinked), Oasis HLB (hydrophilic, macroporous) and Isolute ENV+ (hydrophilic, hypercrosslinked); the new sorbent out-performed the commercially available sorbents. The polymer was applied successfully in off-line SPE of river water samples followed by liquid chromatography and ultraviolet detection, providing a good linear range and detection limits of 0.2 μg $l^{-1}$ for the majority of the compounds, with the exception of oxamyl, methomyl, guaiacol and salicylic acid where the detection limit was 0.5 μg $l^{-1}$.

## 1. Introduction

In recent years, solid-phase extraction (SPE) has become the preferred extraction technique to enrich pollutants from aqueous samples. An important consideration in SPE is the rational selection of the sorbent depending on the characteristics of the analytes to be extracted and also on the complexity of the sample matrix. For this reason, over the last few years several sorbents with a broad range of properties have been developed and commercialised. Traditionally, sorbents have been divided into silica-based, carbon-based and polymer-based sorbents, with polymeric sorbents being particularly attractive in light of their chemical stability and easily tailored physico-chemical characteristics [1-3]. A very important feature of polymeric sorbents is their porous character, which provides the surface area necessary for sorption of the compounds, therefore porous character is directly related to the efficacy of the sorbent in the SPE process [4].

Conventional, commercially available polymeric sorbents are normally based on styrene-divinylbenzene copolymers with macroporous structure and hydrophobic characteristics. Therefore, they are more effective in the retention of non-polar compounds than the retention of polar compounds [5,6]. In order to improve the retention of polar compounds on SPE sorbents, several sorbents that increase both the specific surface area (expressed in $m^2\ g^{-1}$) and the hydrophilicity have been developed [3].

Regarding the enhancement of the specific surface area, hypercrosslinked polymers belong to a new generation of permanently porous polymeric resins. They have high specific surface areas (up to ~2000 $m^2\ g^{-1}$), and their high micropore content makes them particularly well-suited for sorption processes [7].

The hydrophilicity of a sorbent can be increased by introducing a polar comonomer into the polymerisation [8-11] or by post-polymerisation chemical modification to introduce polar functional groups into the polymer structure [12-14]. Commercially available hydrophilic sorbents include, for instance, Oasis HLB (from Waters), which is a macroporous poly(N-vinylpyrrolidone-co-divinylbenzene) copolymer with a specific surface area of ~ 800 $m^2 g^{-1}$ or Strata-X (from Phenomenex) which is poly(styrene-co-divinylbenzene) modified chemically with pyrrolidone groups, with a specific surface area of ~ 800 $m^2 g^{-1}$.

Previous studies [8,14-19], which include the SPE of various families of analytes from several aqueous matrices, have demonstrated that the retention properties of sorbents for polar analytes are enhanced as the specific surface area and the degree of hydrophilicity of the sorbent is increased. This relationship was exemplified in a previous study [16] in which a hypercrosslinked sorbent with a styrenic skeleton and pendent hydroxyl groups performed better than the hydrophobic analogues. Moreover, in a recent study with hydrophobic sorbents [15] it was demonstrated clearly that the lower the particle size of the sorbent the better the SPE performance. Considering these facts, an ideal hypercrosslinked sorbent for the efficient capture of polar analytes ought to combine the features of hydrophilicity and low particle size.

The aim of this study was therefore to synthesise new hypercrosslinked polymers in the form of small particles with hydroxyl moieties in place in the skeleton to confer hydrophilic behaviour, and then to evaluate the polymers as novel sorbents for the retention of polar pollutants using SPE.

## 2. Experimental

### 2.1 Reagents and standards

The polar pollutants selected to evaluate the performance of the sorbents included: pesticides such as oxamyl, methomyl and (4-chloro-2-methylphenoxy) acetic acid (MCPA) obtained from Riedel-de-Haen (Seelze, Germany); phenolic compounds such as phenol, 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), guaiacol; pharmaceuticals such as antipyrine, salicylic acid and ibuprofen obtained from Sigma-Aldrich (Steinheim, Germany). Their chemical structures are shown in Fig. 1S.

Standard solutions for each compound were prepared at a concentration of 2000 mg $l^{-1}$ in methanol. A mixture of all the compounds was prepared by diluting the standard solutions with Milli-Q water (Millipore, Bedford, MA, USA).

HPLC grade acetonitrile and methanol were from SDS (Peypin, France). Hydrochloric acid, used to adjust the pH of the mobile phases and the samples prior to SPE, was from Probus (Barcelona, Spain).

The reagents for the polymer syntheses were divinylbenzene (DVB) (80% grade) and 2-hydroxyethyl methacrylate (HEMA) (98% grade) supplied by Aldrich, *para*-vinylbenzylchloride (VBC) (95% grade) supplied by Fluka (Steinheim, Germany). The monomers were purified by passing them through short neutral alumina columns. The 2,2'-azobisisobutyronitrile (AIBN) used as initiator was supplied by BDH (Poole, UK) and was purified by recrystallisation from acetone. Ferric chloride ($FeCl_3$) and anhydrous 1,2-dichloroethane (DCE), from Aldrich, were used in the hypercrosslinking reactions.

**2.2 Resin preparation**

The complete synthetic procedure is outlined in Fig. 1. In more detail, micrometer-sized, spherical precursor particles (PP-polar) were obtained by an

optimised precipitation polymerisation (PP) method [20]. The crosslinking monomer (DVB) and AIBN (2 mol% relative to the total number of polymerisable double bonds present in all three comonomers) were added to acetonitrile (200 ml) in a polypropylene bottle (250 ml). The monomer solution was de-oxygenated with $N_2$ at 0 $^oC$ and the bottle then placed on a low-profile roller (Stovall, Essex, UK) in a temperature-controllable incubator (Stuart Scientific, Surrey, UK). The temperature was ramped from ambient to 60 $^oC$ over a period of ~ 2 hours and the polymerisation allowed to proceed at 60 $^oC$ for 6 hours, at which point the reaction mixture started to get milky. The reaction mixture was cooled to room temperature and the remaining monomers (HEMA and VBC) then added to the milky suspension (N.B. the total monomer concentration was 2 % w/v relative to solvent). This mixture was de-oxygenated with $N_2$ at 0 $^oC$ and the bottle placed back into the low-profile roller in the temperature-controllable incubator at 60 $^oC$ for a further 48 hours. The resulting particles were filtered on a 0.2 μm nylon membrane filter and washed successively with MeOH, toluene and acetone, before overnight drying *in vacuo* at 40 $^oC$.

The mole ratio of comonomer in the feed was varied systematically, with the hydrophilic comonomer (HEMA) being fed at three different levels (25, 20 and 10 mol %). Table 1 details the monomer feed ratios for each polymerisation, as well as information on the characterisation of the products.

The hypercrosslinking of the PP-polar particles was carried out using a procedure described previously [20] (see also detailed information in the Supporting Information Section). The hypercrosslinked resins (HXLPP-polar) were characterised by measuring their specific surface areas using a BET treatment of $N_2$ sorption isotherm data generated on a Micromeritics ASAP

2000 porosimeter. The chlorine and nitrogen contents for the resins were obtained with elemental microanalysis using a Carlo-Erba EA 1106 instrument. The ATR mode FTIR spectra were recorded using Perkin-Elmer Spectrum One Spectrometer. Microsphere diameters and homogeneity in size were determined using ImageJ software analysis of 100 individual particles in scanning electron microscopy (SEM) images, which were acquired using a JEOL 6400 Instrument [20]. Fig. 1 also shows the SEM image for HXLPP-polar microspheres. The characterisation data obtained for all the resins produced is detailed in Table 1.

**2.3 Chromatographic equipment and conditions**

The chromatographic experiments were performed with an HP 1090 Liquid Chromatograph and UV-Detector (Hewlett-Packard, Waldbronn, Germany) equipped with an injection valve with a 20 µl loop. The analytical column was a 250 mm × 4.6 mm i.d. stainless-steel column packed with Kromasil 100 $C_{18}$, 5 µm (Teknokroma, Barcelona, Spain).

The mobile phase was: Milli-Q water adjusted to pH 2.8 with HCl and acetonitrile (ACN). The flow rate was 1 ml $min^{-1}$ and the temperature of the column oven was set at 65 ˚C. The gradient profile was 20% of ACN initially, held for 8 minutes, then to 25% ACN in 7 min, to 80 % ACN in 5 min, to 100% ACN in 2 min, held for 4 min, after which time the mobile phase was returned to the initial conditions (20% ACN) in 2 min. The total run time was 28 min.

The wavelengths used to detect the compounds were 240 nm (oxamyl and methomyl), 210 nm (antipyrine, phenol, guaiacol, 4-NP, salicylic acid and 2,4-DNP), and 220 nm (MCPA and ibuprofen).

## 2.4 Solid-phase extraction

200 mg of the synthesised sorbents (HXLPP-polarA, HXLPP-polarB, HXLPP-polarC) in the form of 4-6 μm particles were packed in 6 ml polypropylene syringes with the sorbents being retained by two frits (a metal frit of 2 μm pore size on the bottom and a polyethylene frit with 20 μm pore size on the top). The retention capabilities of the sorbents were compared to the commercial cartridges LiChrolut EN (200 mg, 6 ml) from Merck (Darmstadt, Germany), Oasis HLB (200 mg, 6 ml) from Waters (Milford, MA, USA) and Isolute ENV+ (200 mg, 6 ml) from International Sorbent Technology (Cambridge, UK). A vacuum manifold (Teknokroma, Barcelona, Spain) was used to manipulate the cartridges in the off-line SPE procedure.

Prior to the extractions, all samples were adjusted to pH 2.5 with HCl. The SPE procedure for all cartridges was the same: the cartridge was activated with 10 ml of MeOH followed by 5 ml of Milli-Q water adjusted to pH 2.5 with HCl, then the sample was loaded at a flow rate 10 ml $min^{-1}$ using the vacuum manifold connected to the cartridge. Finally, the compounds were eluted from the cartridge using 7 ml of MeOH.

Before injection onto the LC system, the eluate was evaporated to 1 ml and 1 ml of Milli-Q water added to obtain a MeOH:$H_2O$ mixture (1:1) suitable for injection onto the HPLC.

Real samples from the Ebre river and tap water were filtered through 0.22 μm nylon membranes (Supelco, Bellefont, PA, USA) prior to the pre-concentration step to eliminate the particulate matter present in real samples.

## 3. Results and discussions

### 3.1. Synthesis of the hypercrosslinked resins

Three hydrophilic, hypercrosslinked polymer resins (HXLPP-polarA, HXLPP-polarB and HXLPP-polarC) were synthesised. The resin characterisation data is detailed in Table 1. The polymer precursors used in the hypercrosslinking reactions were three swellable, gel-type resins (PP-polarA, PP-polarB and PP-polarC) prepared by precipitation polymerisation (PP).

PP is a simple and straightforward polymer synthesis method used to obtain, in a single step, micrometer-sized, spherical particles which, as has been demonstrated previously [15], show advantages in SPE. PP has been studied widely for polyDVB production [for examples, see 21,22], but also for some copolymerisations which include poly(VBC-co-DVB) [23] and poly(HEMA-co-DVB) [24]. However, there are few studies reporting terpolymer production by PP, possibly because of the difficulty in establishing suitable polymerisation conditions. The aim of the present paper was to synthesise the terpolymer poly(HEMA-co-VBC-co-DVB) and thereby a resin which combines hydrophilicity (through HEMA) in a hypercrosslinked polymer (hypercrosslinking reaction through VBC) with control of shape and form of the particles (through DVB). Various attempts to establish suitable conditions for the terpolymerisation failed to deliver the desired products when all three comonomers were present at the outset of the polymerisations (data not shown). As detailed in the Experimental section, an alternative synthesis strategy was attempted which turned out to be successful. This strategy involved the delayed addition of the HEMA and VBC comonomers to a DVB polymerisation; HEMA and VBC were added once the nucleation phase of the reaction was complete. Figure 1 outlines the synthetic

procedure. As shown in Table 1, using this strategy we obtained a set of PP-polar precursor resins with variable chlorine and oxygen contents, which indicates that all three monomers were incorporated into the final resins. The incorporation of the HEMA and VBC monomers was confirmed by the FTIR spectra of PP-polar particles: absorption bands for HEMA: at ~ 3400 cm $^{-1}$, indicative of the OH group, ~ 1730 cm $^{-1}$, indicative of the C=O group and at ~ 1200 cm $^{-1}$, indicative of the C - O group; and, for VBC: by the sharp band at ~ 1265 cm $^{-1}$, which is characteristic of the $CH_2Cl$ group.

The pendent chloromethyl groups from VBC in the PP-polar resins were subsequently consumed in hypercrosslinking reactions to generate the hypercrosslinked resins, such that we produced a series of HXLPP-polar resins with variable specific surface areas and degrees of hydrophilicity, properties that were dependent upon the initial monomer contents in the polymerisation feeds. The FTIR spectra for the HXLPP derivatives also confirms the disappearance of the of the $CH_2Cl$ band; meanwhile, the bands characteristic for HEMA remain relatively unchanged. It should be highlighted that, to the best of our knowledge, this is the first time that a hydrophilic hypercrosslinked polymer has been synthesised. In a previous study [16] a hypercrosslinked resin with residual -OH groups was synthesised starting from a hydrophilic monomer. However, the -OH content was difficult to control since the -OH groups arose from hydrolysis of VBC during polymer synthesis.

Regarding particle size, all three resins had average diameters in the range 3.9 - 5.7 μm (see Table1), thus are well-suited for SPE purposes. However, none of the particles was monodisperse (coefficient of variation was > 33%, in all cases) which can be attributed to the presence of three different

comonomers in the PP and the conditions under which the polymerisations were performed. As an example, Fig. 1 also depicts the SEM image for HXLPP-polarB, to show the spherical shape of the particles produced, as well as their relatively narrow particle size distribution

### 3.2 Evaluation of the sorbents

Before exploiting the new sorbents in SPE, the LC separation was optimised. The linear range of the method was determined by directly injecting 20 µl of the standard solutions (0.1 - 10 mg $l^{-1}$ of analytes) onto the LC column. The regression coefficients ($r^2$) were good and ranged from 0.9989 for ibuprofen to 0.9998 for phenol and 2,4-DNP.

In the SPE process, we firstly optimised the nature and volume of the elution solvent; in this regard, several volumes of acetonitrile and methanol were tested. The recovery values obtained for 100 ml of standard solution with 10 ml acetonitrile in the elution step were not satisfactory, especially for 2,4-DNP and MCPA (35% and 28%, respectively). Thus, we decided to use methanol as the elution solvent. The recovery values obtained with 10 ml of methanol were noticeably higher in the case of 2,4-DNP and MCPA than those obtained with acetonitrile as the elution solvent. Then, we reduced the volume of methanol to below 10 ml and noticed that 5 ml of methanol was insufficient to complete elute all the studied analytes. Finally, 7 ml was found to be a sufficient volume of methanol to obtain excellent recoveries (greater than 90% for all compounds). Therefore, we chose 7 ml of methanol since it provided the quantitative elution of all compounds.

To test the performance of the resins we needed to select the SPE conditions in order to increase the retention of the compounds. We evaluated

the behaviour of the resins under acidic (pH=2.5) and neutral pH (pH=7) conditions; better results were obtained under acidic conditions where ionisation of the analytes is prevented; therefore, the pH was set at 2.5 in subsequent experiments.

The next step was to identify the highest sample volume which could be loaded onto the SPE cartridges without significant breakthrough. To do this, volumes from 100 to 1000 ml of Milli-Q water at pH 2.5 (with HCl) were spiked with the analytes in concentrations from 5 - 50 μg $l^{-1}$, depending on the volume, and then extracted.

Table 2 compares the recoveries of analytes obtained with the three hypercrosslinked materials for the higher sample volumes percolated (i.e, 500 and 1000 ml). From the results shown, it can be seen that the recoveries of all analytes, even the most polar ones such as oxamyl, methomyl and phenol, have values close to 90% or higher, even for a sample volume of 1000 ml. Only for one of the sorbents (HXLPP-polarA) did phenol show a lower recovery (73%), and this was when a 1000 ml sample was extracted. This result can be explained by the lower specific surface area of HXLPP-polarA compared with the other two resins, and is in keeping with expectations [3,9].

In view of these preliminary evaluation results we selected the HXLPP-polarB sorbent to evaluate further the application of this type of novel sorbent to real samples. The selection of HXLPP-polarB was based mainly on the recoveries for phenol, but also because this resin offers a balance of specific surface area (850 $m^2 g^{-1}$) and hydrophilicity (7.5% O) over all the resins tested.

To broaden the scope of application of these sorbents, three additional pharmaceutical compounds which are problematic in SPE processes with

conventional sorbents were tested with the HXLPP-polarB sorbent. These compounds, which were selected in order to check the recovery of analytes with a wide range of polarity, were the two polar pharmaceuticals antipyrine and salicylic acid, and the less polar ibuprofen; antipyrine and salicylic acid are known to be particularly difficult to handle in SPE [25-27]. The recoveries (Table 3) for the SPE of 1000 ml of Milli-Q water spiked with 50 $\mu g\ l^{-1}$ of each compound were 91%, 89% and 93% (with %RSD (n=3) < 6) for antipyrine, salicylic acid and ibuprofen, respectively.

In view of the highly satisfactory results obtained for the HXLPP-polar resins (Table 2), we tested and compared one of these resins to the commercially available sorbents LiChrolut EN, Oasis HLB and Isolute ENV+ (Table 3). LiChrolut EN (1200 $m^2\ g^{-1}$) is a hydrophobic hypercrosslinked ethylvinylbenzene-divinylbenzene copolymer, Oasis HLB (~800 $m^2\ g^{-1}$) is a macroporous copolymer derived from two monomers, the lipophilic divinylbenzene and the hydrophilic N-vinylpyrrolidone (these monomers create a hydrophilic-lipophilic balance), and Isolute ENV+ (~1000 $m^2\ g^{-1}$) which is a hypercrosslinked hydroxylated poly(styrene-co-divinylbenzene) copolymer.

From the recovery values listed in Table 3, one can see that the hypercrosslinked sorbent HXLPP-polarB gave better recovery values for the most polar compounds than commercially available LiChrolut EN and Oasis HLB, and similar recovery values to Isolute ENV+. For instance, when 1000 ml of sample was percolated the recovery of methomyl was 91%, 86%, 66% and 95% for HXLPP-polarB, LiChrolut EN, Oasis HLB and Isolute ENV+, respectively. The recovery of oxamyl on all HXLPP-polar resins (see Table 2) at the same sample volume was around 95%. The observed variation in the

recovery values with the HXLPP-polarB, LiChrolut EN, Oasis HLB and Isolute ENV+ sorbents is more significant with antipyrine, since for the same sample volume (1000 ml) the antipyrine recoveries were 91%, 83%, 84 and 68%, respectively; again; the best results were for the new HXLPP-polarB material.

Thus, in view of the detailed SPE comparison which has been carried out for all these sorbents, and bearing in mind their wide range of chemical and physical characteristics which includes variations in the type of network (macroporous or hypercrosslinked), specific surface area and hydrophilicity, the clearly beneficial features of the HXLPP-polar resins would appear to be derived from the combination of both high specific surface area, hydrophilicity, and their homogeneity in shape, relatively small particle size and relatively low particle size distribution. In particular, the impressive extraction performance of the HXLPP-polar sorbents may be ascribed to the efficiency and ease with which they can be packed reproducibly into the columns and the high chromatographic efficiency when applied in column format [15].

### 3.3 Application to real samples

The performance of the HXLPP-polarB sorbent when applied to real samples was investigated for three environmental water samples: mineral water, tap water and Ebre river water.

In this set of experiments, after the SPE process the eluate was evaporated to improve the overall sensitivity of the method and thereby to allow quantification of the analytes at those concentration levels typically encountered when handling real water samples. However, the eluate was not evaporated to dryness; instead, the volume was nearly reduced to 1 ml, since the recovery of

volatile phenols (e.g., phenol and guaiacol) was observed to fall when the eluate was evaporated under a nitrogen stream to dryness [28-29].

Table 4 shows the SPE results for the different water samples. As can be seen, the data for mineral and river water is excellent, with recovery values close to 90% and very similar to the values obtained for extractions from Milli-Q water, demonstrating yet again the impressive ability of these sorbents to retain the most polar compounds even when in the presence of matrix interferences. Moreover, the real water SPE results for HXLPP-polarB are superior to those reported [30] for Oasis HLB and Isolute ENV+; in this study, the results obtained with commercial sorbents after percolating 350 ml of river water were 60% and 70% (Oasis HLB) and 29% and 52% (Isolute ENV+) for oxamyl and methomyl, respectively. By comparison, in the present study the recovery results with HXLPP-polarB for 1000 ml of river water sample were 93% and 91% for the same analytes, respectively. With respect to tap water, the results obtained with the HXLPP-polarB sorbent were excellent for the majority of the compounds, except for the first three compounds eluted. For oxamyl, the recovery was 29%, whereas methomyl and antipyrine were not recovered. Generally speaking, for the rest of compounds the recoveries were rather good, especially when taking into account the fact that 1000 ml of sample was being extracted. The analogous results from the same previous study [30], supports these low recoveries; for example the recoveries obtained for oxamyl were 59% (Oasis HLB) and 50% (Isolute ENV+). This effect may be due to the presence of chlorine in the sample; we did try to reduce the chlorine content prior to SPE, but were not successful in increasing the recoveries for these problematic analytes.

Since the SPE results for river water were highly satisfactory, we proceeded to validation of the method using the same type of samples. First, we aimed to reduce the initial band which appears at the beginning of the chromatogram. Figure 2 shows the chromatograms of 1000 ml of Ebre river sample (b) and the same sample spiked with a standard solution at 2 μg $l^{-1}$ for each compound (a). The initial band is due to the presence of humic and fulvic acids in the sample; previous studies reported [31] that this band decreases when $Na_2SO_3$ is added to the sample. We investigated a similar approach by adding 10 ml and 2 ml of 10% (*w/v*) $Na_2SO_3$ aqueous solution per 1000 ml of sample. Unfortunately, although the band decreased slightly the salt precipitated during the SPE loading step and partially blocked the cartridge. Therefore, in spite of the good results reported in a previous paper where this strategy was applied successfully, ,we discarded this as a viable option.

Several samples of river water were analysed. Subsequent analyses of water samples taken from different locations on the Ebre river revealed that in one of the samples three peaks appeared at the retention time corresponding to methomyl, phenol and 2,4-DNP (see the Ebre river blank chromatogram Fig. 2b), but this observation needs to be confirmed in an independent study using a more powerful detector, such as a mass spectrometer.

In the validation studies using 1000 ml of river water, all the analytes exhibited good linearity from 0.5 - 20 μg $l^{-1}$, with the exception of oxamyl and methomyl (1 - 20 μg $l^{-1}$), with regression coefficients ($r^2$) higher than 0.9995. The detection limits (LODs), calculated using a signal to noise ratio of ≥ 3, were 0.2 μg $l^{-1}$ for most of compounds, with the exception of oxamyl, methomyl, guaiacol and salicylic acid (0.5 μg $l^{-1}$). The repeatability and reproducibility of

the method, expressed as the relative standard deviation (RSD) of 3 analyses of 1000 ml of Ebre river water spiked at 1 μg $l^{-1}$ were lower than 15% for all compounds. Although the limits of detection are not as low as those reported elsewhere for these kind of samples, they could be lowered significantly by use of a more sensitive detection method such as mass spectrometer, or even tandem mass spectrometry. In any case, the excellent performance of the HXLPP-polarB sorbent has been demonstrated unequivocally.

## Conclusions

Three hydrophilic, hypercrosslinked sorbents in the form of micrometer-sized polymer microspheres were synthesised successfully from poly(HEMA-co-VBC-co-DVB) precursors of varying chemical composition. The hypercrosslinked sorbents varied in terms of their hydrophilicity and had tuneable specific surface areas. The three sorbents were evaluated in off-line SPE studies for the extraction of polar analytes from water samples, and were found to perform well. The sorbent with optimal performance characteristics (HXLPP-polarB) was selected for further evaluation.

In comparative SPE studies with the commercial sorbents LiChrolut EN, Oasis HLB and Isolute ENV+, the HXLPP-polarB sorbent significantly out-performed the commercial materials.

When real samples were extracted, recoveries of analytes from 1000 ml of mineral or river water were high, even for the most polar compounds, such as oxamyl, methomyl, phenol and salicylic acid.

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**Table 1.** Monomer feed and analytical data for PP-polar precursor particles and their hypercrosslinked derivatives (HXLPP-polar)

| Resin | HEMA/VBC/DVB (mole ratio) | D[a] (μm) | Coef. Var.(%) | Yield (%) | %C[b] | %H[b] | %Cl[b] | %O[c] | O[c] (mmol $g^{-1}$) | S.A.[d] ($m^2g^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| PP-polarA | 25/25/50 | n.d. | n.d. | 54 | 77.6 | 7.6 | 5.3 | 9.5 | 1.98 | ~5 |
| PP-polarB | 20/40/40 | n.d. | n.d. | 44 | 76.6 | 7.3 | 8.6 | 7.5 | 1.56 | ~5 |
| PP-polarC | 10/50/40 | n.d. | n.d. | 48 | 78.5 | 7.1 | 10.1 | 4.3 | 0.90 | ~5 |
| HXLPP-polarA | 25/25/50 | 5.7 ± 2.4 | 42.4 | 90[e] | 80.2 | 7.5 | 3.8 | 9.5 | 1.89 | 670 |
| HXLPP-polarB | 20/40/40 | 5.5 ± 1.8 | 33.4 | 90[e] | 81.2 | 6.6 | 4.9 | 7.5 | 1.56 | 850 |
| HXLPP-polarC | 10/50/40 | 3.9 ± 1.3 | 33.8 | 88[e] | 84.1 | 6.4 | 3.9 | 4.3 | 0.90 | 925 |

n.d. no data

[a] average particle diameter ± standard deviation (S.D.) calculated from the image analysis of 100 individual particles in SEM micrographs (using ImageJ software); [b] Obtained experimentally with elemental microanalysis; [c] Obtained by subtraction with the rest of elements based on monomer feed; [d] Specific surface area computed from $N_2$ sorption isotherms and BET analysis; [e] Relative to the mass of the corresponding (non-hypercrosslinked) precursor particles.

**Table 2**. % Recoveries of the analytes obtained with different sorbents in off-line SPE for different sample volumes spiked with the analyte mixture at 50 µg $l^{-1}$ in Milli-Q water.

| | Recovery (%) | | | | | |
|---|---|---|---|---|---|---|
| Analyte | HXLPP-polarA (670 $m^2$ $g^{-1}$) | | HXLPP-polarB (850 $m^2$ $g^{-1}$) | | HXLPP-polarC (925 $m^2$ $g^{-1}$) | |
| Sample volume | 500 ml | 1000 ml | 500 ml | 1000 ml | 500 ml | 1000 ml |
| Oxamyl | 98 | 95 | 95 | 90 | 96 | 96 |
| Methomyl | 98 | 93 | 99 | 97 | 99 | 99 |
| Phenol | 83 | 73 | 86 | 85 | 84 | 83 |
| Guaiacol | 87 | 84 | 88 | 89 | 84 | 84 |
| 4-NP | 98 | 95 | 95 | 90 | 92 | 93 |
| 2,4-DNP | 91 | 88 | 94 | 91 | 91 | 92 |
| MCPA | 84 | 85 | 89 | 90 | 90 | 87 |

% relative standard deviations (RSD) (n=3) were lower than 7.

**Table 3.** Recoveries of analytes on the HXLPP-polarB sorbent, LiChrolut EN, Oasis HLB and Isolute ENV+ in off-line SPE for 1000 ml of standard solution spiked with 50 µg $l^{-1}$ of each compound in Milli-Q water

| Analyte | Recovery (%) | | | |
|---|---|---|---|---|
| | HXLPP-polarB 850 $m^2$ $g^{-1}$ | LiChrolut EN 1200 $m^2$ $g^{-1}$ | Oasis HLB 800 $m^2$ $g^{-1}$ | Isolute ENV+ 1000 $m^2$ $g^{-1}$ |
| Oxamyl | 91 | 84 | 74 | 95 |
| Methomyl | 91 | 86 | 66 | 95 |
| Antipyrine | 91 | 83 | 84 | 68 |
| Phenol | 86 | 79 | 78 | 92 |
| Guaiacol | 91 | 85 | 82 | 97 |
| 4-NP | 91 | 85 | 86 | 95 |
| Salicylic Acid | 89 | 88 | 85 | 94 |
| 2,4-DNP | 88 | 84 | 86 | 80 |
| MCPA | 90 | 84 | 84 | 93 |
| Ibuprofen | 93 | 86 | 86 | 99 |

% RSD (n=3) were lower than 6.

**Table 4**. % Recoveries of the analytes on the HXLPP-polarB sorbent in off-line SPE for 1000 ml of standard solution spiked at 2 µg $l^{-1}$ with each compound in mineral, tap and Ebre river water.

| | Recovery (%) | | |
|---|---|---|---|
| Analyte | Mineral water | Tap water | River water |
| Oxamyl | 93 | 29 | 93 |
| Methomyl | 89 | - | 91 |
| Antipyrine | 93 | - | 93 |
| Phenol | 78 | 76 | 84 |
| Guaiacol | 90 | 81 | 92 |
| 4-NP | 97 | 93 | 97 |
| Salicylic Acid | 97 | 90 | 100 |
| 2,4-DNP | 96 | 92 | 98 |
| MCPA | 97 | 137 | 97 |
| Ibuprofen | 98 | 96 | 96 |

% RSD (n=3) were lower than 8; - not recovered.

## Figure captions

**Figure 1.** Schematic representation of the synthetic procedure used in the production of HXLPP-polar resins and SEM images of HXLPP-polarB resin (the applied acceleration voltage of the incident electron beam was 20 kV).

**Figure 2.** Chromatograms obtained by off-line trace enrichment of 1000 ml of Ebre river water samples with (a) and without (b) the addition of 2 μg $l^{-1}$ level of analytes. Peak designation: (A) Oxamyl, (B) methomyl, (C) antipyrine, (D) phenol, (E) guaiacol, (F) 4-NP, (G) salicylic acid, (H) 2,4-DNP, (I) MCPA, (J) ibuprofen. * Peaks at the same retention time as the studied analytes.

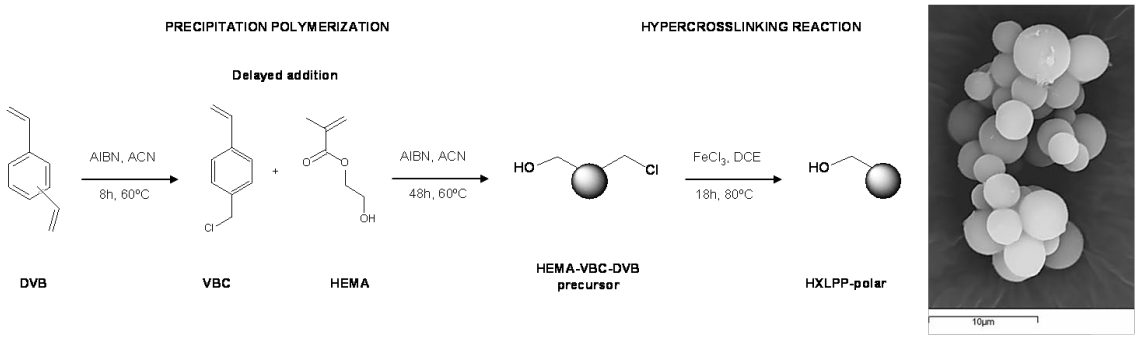
PRECIPITATION POLYMERIZATION
HYPERCROSSLINKING REACTION
Delayed addition
AIBN, ACN
8h, 60ºC
AIBN, ACN
48h, 60ºC
FeCl3, DCE
18h, 80ºC
HO
Cl
HO
Cl
OH
DVB
VBC
HEMA
HEMA-VBC-DVB precursor
HXLPP-polar
10µm

**Figure 1**

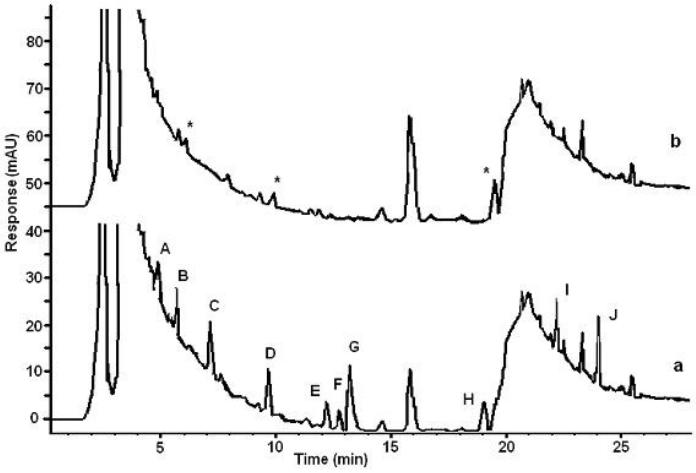


**Figure 2**