

β -Cyclodextrin-bonded silica particles as the solid-phase extraction medium for the determination of phenol compounds in water samples followed by gas chromatography with flame ionization and mass spectrometry detection

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Abstract

A new absorbent for solid-phase extraction (SPE) was prepared by a β -cyclodextrin bonded silica stationary phase (CDS) has been applied to determine the concentrations of phenol compounds in water samples. SPE of selected phenolic compounds from aqueous samples were performed using 250 mg CDS. The determination was subsequently carried out by gas chromatography–flame ionization detection (GC–FID) and gas chromatography–mass spectrometry (GC–MS). Compared with available SPE, the CDS showed high sensitivity and fast velocity of mass transfer for phenolic compound because of its porous structure of β -cyclodextrin. The relative standard deviation (RSD) for river water sample spiked with phenolic compounds at sub-ppb level was lower than 10% and limit of detection (LOD) for these compounds were between 10 and 100 ng l⁻¹.

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1. Introduction

Phenolic compounds are important water pollutions which are subject to legislation because of their toxicity, even at low concentration. A European Community (EC) directive specifies a legal tolerance level of 0.1 $\mu\text{g l}^{-1}$ for each phenolic compounds and 0.5 $\mu\text{g l}^{-1}$ for the sum of all compounds in water intended for human consumption [1,2].

Phenolic compounds are usually determined by many analytical approaches have been used for the trace-level analysis of phenols, mainly using high-performance liquid chromatography (HPLC) [3–5] or capillary gas chromatography (GC). Although HPLC methods are frequently applied for analysis of phenols, GC is often preferred, offering unrivalled high resolution and easy coupling with sensitive and selective detectors. Actually, HPLC detection was reported to be

prone to interferences from matrix compounds such as humic substances naturally occurring in environmental samples [6].

In general, phenols are amenable to GC without derivatization [7–9]. But at lower concentration, peak tailing and discrimination in the injector of capillary column might occur [9,10], especially when environmental samples are analyzed. To overcome these problems, phenols have to be derivatized with a suitable derivatizing reagent [11–14]. Among the wide variety of derivatizing reagents used for this purpose, acetylating agents have been employed to the greatest extent [7,15–17].

Because of the low concentrations of micro organic pollutants in water samples, it is necessary to apply a preconcentration step prior to the chromatographic analysis. Nowadays, solid-phase extraction (SPE) is the most common technique for sample enrichment, because of its advantages over liquid–liquid extraction [18]. A large number of procedures for the determination of phenolic compounds in water using SPE have been tested [3,4,17–19]. Various types of solid-phase sorbents have been used, including

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C₁₈ [20,21], polystyrene–divinylbenzene-based polymers [21,22], and various forms of carbon [17,19]. A number of these sorbents show relatively low recovery for some phenolic compounds [3,4,7,23,24].

β -Cyclodextrin is a cyclic oligosaccharide with seven glucose units, with its cavity structure, and can form an inclusion complex with certain molecules through a host-guest interaction. Thus, it has found wide application as HPLC stationary phases for the separation of various compounds [25–27]. Feng et al. have utilized β -cyclodextrin bonded silica as a selective sorbent for on-line solid-phase extraction of 4-nitrophenol [28]. Also, Li et al. have applied β -cyclodextrin bonded silica as a coating material for solid phase microextraction of some phenolic compounds [29].

In this study, a β -cyclodextrin bonded silica stationary phase as SPE was investigated by the extraction of phenolic compounds from an aqueous matrix.

2. Experimental

2.1. Reagents

β -Cyclodextrin and irregular silica gel were purchased from Merck (Darmstadt, Germany). 3-Glycidypropyltrimethoxysilane (KH-560) and high-temperature epoxy resin of type 5203 were obtained from Huili company (Jiangsu, China). Phenol (PN), 2,4-dimethylphenol (2,4-DMP), 4-nitrophenol (4-NP), 3-chlorophenol (3-CP) and 4-methylphenol (4-MP) were obtained from Merck (Darmstadt, Germany). Standard solutions (2000 mg l⁻¹) from each individual compounds were prepared in methanol. A mixture of these phenolic compounds applied to different detection systems, was prepared weekly by diluting the standard solution with methanol, and more diluted working solutions were prepared daily by diluting these solutions with triple distilled water or river water. The concentration of mixture to be analyzed by gas chromatography–flame ionization detection (GC–FID) was made at a range of 100–200 mg l⁻¹. The commercial cartridges used were LiChrolut EN (200 mg) from Merck, Oasis HLB (60 mg) from Waters (Milford, MA, USA) and C₁₈ (200 mg) from IST (Cambridge, UK).

2.2. Apparatus

A Perkin-Elmer liquid chromatograph model 601 equipped with two reservoirs was modified for preconcentration and elution of the SPE precolumn. SPE was carried out on a 70 mm × 3 mm I.D., stainless steel precolumn packed with 120 mg β -cyclodextrin bonded silica stationary phase (CDS). A gas chromatograph model shimadzu 17A equipped with a flame ionization detector and a split/splitless injector was used. Separations of phenols were carried out using a capillary column CBP 10 low bleed MS (25 m × 0.22 mm I.D.) with 0.25 μ m film thickness. The injector and detector temperatures were set at 250 and 280 °C, respectively. The

separation of phenolic compounds on (GC–FID) was performed by a temperature program as follows: 60 °C during 5 min, at 10 °C min⁻¹ to 230 °C, 5 min hold at 230 °C. An aliquot of 1–2 μ l from each sample was introduced into the chromatographic columns using splitless mode injection.

A Hewlett-Packard (HP, Palo Alto, USA) HP 6890 series gas chromatograph equipped with a split/splitless injector and a HP 5973 mass-selective detector was also used. The analytical column was a HP-5 MS 0.25 μ m of 30 m × 250 μ m I.D. The column temperature was programmed as follow: 80 °C for 3 min then was heated at 20 °C min⁻¹ to 260 °C and 30 °C min⁻¹ to 290 °C. The mass spectrometry was operated at electron energy of 70 eV. The injection and GC–MS interface temperature were set at 220 and 250 °C, respectively. The ion source temperature was set at 200 °C, and quadrupole temperature was set at 150 °C. The mass control system was programmed for a selected-ion monitor (SIM); the monitored ions were *m/z* at 96 for PN, *m/z* at 125 for 2, 4-DMP, *m/z* at 137 for 4-NP, *m/z* at 130 for 3-CP and *m/z* at 110 for 4-MP.

Chromatographic data were recorded using an HP Chemstation, which was controlled by Windows NT (Microsoft) and equipped with Wiley mass spectral library. Helium and nitrogen (99.999%) were used as carrier and make-up gas, respectively. The flow rate of carrier gas was adjusted at 1 ml min⁻¹.

A JSM-6330F scanning electron micro analyzer (Japan Electronic Company) was used to investigate the CDS surface.

2.3. Preparation of a β -cyclodextrin bonded silica stationary phase

CDS was prepared according to a procedure reported elsewhere with some modification [25,29]. The synthetic scheme is depicted in Fig. 1 briefly, 1.145 g of β -cyclodextrin was dissolved in 25 ml of dry dimethyl formamide (DMF), to which 0.1 g of metal sodium was added. The reaction was allowed to occur with stirring at room temperature for about 30 min. After filtration, 0.45 ml of KH-560 was added to the filtration which was allowed to react at 90 °C for 5 h. Then, 5.0 g of silica gel was added, and the mixture was allowed to react for 10 h at 80–100 °C. The CDS was filtered, and washed with DMF, methanol, doubly distilled water and acetone in sequence. Subsequently, the CDS was dried at 120 °C for 3 h, and kept in a desiccator before use.

2.4. Sample preparation and derivatization

Prior to the preconcentration step, the pH of sample was adjusted to 1.5 with sulfuric acid. A known volume of distilled or river water was spiked with phenolic compounds standards and was subsequently passed through a preconditioned SPE column at a flow-rate of 2–6 ml min⁻¹. When the sample had passed through, the cartridge was eluted with 2 ml of methanol at the flow-rate of 0.2 ml min⁻¹. The cartridge was preconditioned by washing with 5 ml of methanol

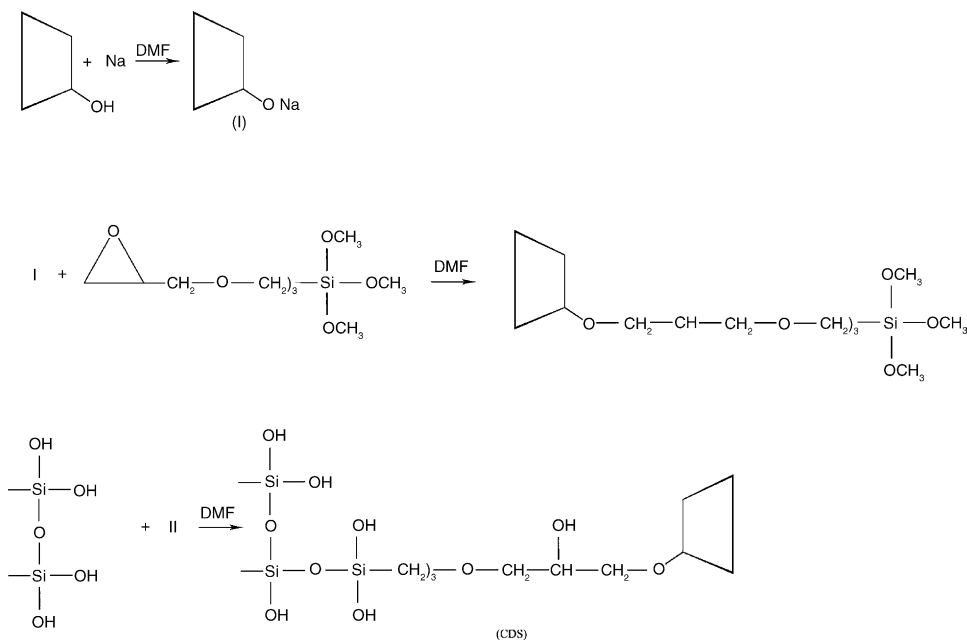


Fig. 1. Synthetic scheme of the CDS.

and activated with 5 ml of distilled water at pH 1.5. For those experiments where the pH effects were studied, citrate buffer (pH 1.5–5) was used for the adjustment. The derivatization procedure used was based on previous report by Rodríguez et al. [30]. A volume of 2 ml of a methanol solution containing phenolic compounds was mixed with 1 ml of 5% K_2CO_3 and 2 ml of *n*-hexane containing 200 μ l of acetic anhydride and internal standard. The mixture was shaken for 1 min and the organic phase was allowed to be separate. The aqueous phase was then extracted with a further 1 ml of *n*-hexane containing only internal standard. The two *n*-hexane portions were collected, mixed and dried over anhydrous sodium sulfate and injected into the GC system. To access lower detection limits in the sample solution at sub-ppb concentrations, the final extract was concentrated to 0.5 ml under a gentle stream of nitrogen.

3. Results and discussion

Fig. 2 shows an electron micrograph of the CDS surface. As can be seen from the graph, the CDS possesses a porous structure. Such a porous structure should significantly increase the available surface area of it, and therefore, increase the extraction capacity.

3.1. Evaluation of sorbent

To evaluate the ability of the CDS for the extraction of phenolic compounds from water samples, a mixture of five phenolic compounds including PN, 2, 4-DMP, 4-NP, 3-CP and 4-MP were used as model compounds. In general, phenols are amenable to GC without derivatization [17,7–9]. But

at lower concentration, peak tailing and discrimination in the injector of capillary column might occur [9,10], especially when environmental samples are analyzed. To overcome these problems, phenols could be derivatized with a suitable derivatizing reagent [11–14]. Among the wide variety of derivatizing reagents used for this purpose, acetylating agents have been employed to the greatest extent [15–17].

Effects of different parameters such as the sample pH, the sample volume, the volume of eluting solvent, the capacity of sorbent and the linearity of recovery were evaluated using this sorbent.

The sample pH is an important factor, which may affect on the recovery of phenols from water. To increase the extraction recovery of phenolic compounds by sorbents, it is necessary to acidify the sample [7]. At low pH, the acid–base equilibrium for the phenolic compounds shifts significantly toward

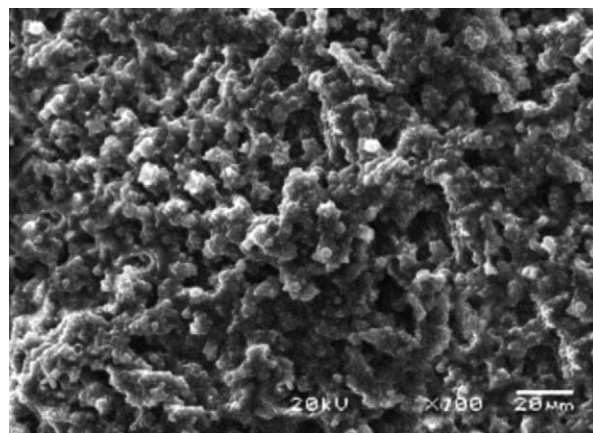


Fig. 2. Scanning electron micrograph of the CDS.

Table 1
The extraction recoveries obtained for the studied phenols at different sample pH

Compound	Recovery (%)		
	pH		
	1.5	3	5
PN	92.4 (5.2) ^a	91.5 (6.4)	87.4 (5.9)
3-CP	95.4 (5.8)	92.7 (6.9)	84.8 (7.4)
2,4-DMP	93.5 (4.5)	90.3 (5.9)	78.6 (7.3)
4-NP	90.3 (5.9)	87.9 (7.1)	75.4 (6.8)
4-MP	97.8 (6.1)	95.1 (7.2)	87.3 (8.7)

^a The relative standard deviations (RSD) of recoveries ($n = 4$).

the neutral forms, which have greater affinities toward the sorbent, and the extraction efficiencies are, therefore, increased. To study the effect of sample pH on the recovery of phenols from water samples, 120 ml samples with same concentration in the 200–300 $\mu\text{g l}^{-1}$ levels at different pH values (1.5, 3, and 5) were preconcentrated using CDS as a sorbent. Table 1 shows the recovery obtained at each pH and clearly, the maximum recovery is obtained at pH 1.5. Higher recovery results at low pH could indicate that the ion exchange interactions have little contribution in retaining mechanisms. The pronounced recovery decrease for phenolic compounds in comparison with phenol at higher pH, justifies the non-ion-exchange interactions.

In order to determine the volume of the sample that can be concentrated with acceptable recoveries for all the compounds studied, it was necessary to obtain the breakthrough volumes. Different volumes (200, 300, 500, and 1000 ml) of distilled water, at pH 1.5, were spiked with a solution containing five phenolic compounds at the 200–300 $\mu\text{g l}^{-1}$ levels. Following the preconcentration step, the trapped analytes on the percolumn were eluted with 2 ml of methanol. After derivatization and extraction with a total of 3 ml of *n*-hexane, an aliquot of 2 μl was injected into the GC system. The recovery of phenolic compounds and the repeatability for the different volumes are given in Table 2. Good recoveries were obtained for all compounds studied using 250 ml sample volumes. Of course, when samples of 500 ml were preconcentrated, the recoveries were, still, acceptable, except for phenol. Further experiments revealed that, for less polar compounds, i.e. 2,4-DMP, 3-CP

breakthrough volumes higher than 600 ml was obtainable. It was also found that flow rates up to 7 ml min^{-1} for water samples loading on the percolumn had no effect on the recovery percentage.

To find the required volume of methanol to elute all phenols from the cartridge, elution volumes up to 4 ml were examined. It was found that a volume of 1 ml was sufficient to desorb the trapped pollutants from the SPE per column; of course includes the volume of solvent to saturate the packed cartridge. This relatively low volume of methanol eluted all compounds from the cartridge easily and other solvents were, therefore, excluded from any further examination. The low consumption of desorbing solvent is a clear advantage of this sorbent, which would be far more useful in on-line applications.

In order to study the capacity of the sorbent and the linearity of recovery, each compound was determined using a river water sample spiked at much higher levels, i.e. 2–3 $\mu\text{g l}^{-1}$, by GC-MS. No significant differences were obtained, indicating that its capacity is sufficiently high. It also demonstrates that even the preconcentration of water samples spiked with such levels of concentrations has no negative influence on the recovery results.

3.2. Comparison studies

In comparison with other reports, it appears that, these recoveries, at least for some, are better than those which obtained using some commercial sorbents such as C₁₈ [4,7,23,24], cyclohexyl [24] and monofunctional C₁₈ (C₁₈/OH) [4]. In a report [23], 250 mg Amberchrom CG-161 was used for the preconcentration of 100 ml of water and recoveries lower than 75% for these phenolic compounds were obtained. Also, in another work [7] SPE of 250 ml of water sample by 250 mg C₁₈, led to low recoveries, specially for 2-CP and pentachlorophenol (5-CP) that were 40 and 48%, respectively. At the same time, another group [21] used cartridges of 500 mg of C₁₈, cyclohexyl and PLRP-S, a styrene-divinyl benzene-based copolymer, for the preconcentration of phenols. Acceptable recoveries were obtained with these sorbents using different volumes of solution with and/or without use of ion-pair reagent for extraction of all compounds studied except 3-CP and 5-CP which had recoveries lower than 70% for all conditions

Table 2
The extraction recoveries obtained for the studied phenolic compounds at different volume of sample solution ($n = 4$)

Compound	Volume (ml)							
	200		300		500		1000	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
PN	71.3	5.4	44.2	5.4	23.4	6.2	n.d.	–
3-CP	97.8	4.2	89.8	3.5	72.2	5.3	55.4	8.5
2, 4-DMP	93.4	3.7	90.7	4.8	85.9	4.7	78.3	7.7
4-NP	90.1	6.7	84.3	4.2	75.3	5.1	55.8	7.2
4-MP	101.7	8.6	99.1	9.2	98.1	8.2	79.7	6.8

n.d., not detection.

Table 3

The extraction recoveries obtained for the studied phenols at 200 ml volume of sample solution spiked in the range between 2 and 3 $\mu\text{g l}^{-1}$ using CDS^a, LiChrolut EN^b, Oasis HLB^c and C₁₈^d

Compound	CDS		LiChrolut EN		Oasis HLB		C ₁₈	
	Recovery (%)	LOD (%)	Recovery (%)	LOD (%)	Recovery (%)	LOD (%)	Recovery (%)	LOD (%)
PN	99.4	10	92.3	35	83.4	51	10.4	144
3-CP	94.9	60	95.4	56	89.2	85	20.2	158
2, 4-DMP	98.3	50	92.1	74	92.8	74	38.3	128
4-NP	99.2	62	88.7	98	95.1	69	30.7	153
4-MP	98.7	100	97.6	106	93.1	131	35.9	191

The relative standard deviations (RSD) for a, b, c and d are between 4.2–9.3%, 3.4–10.4%, 3.3–9.8% and 4.1–11.7%, respectively ($n = 4$).

applied. While some authors [4] have demonstrated that PLRP-S provides the best recoveries even for 3-CP and 5-CP as compared to other sorbents, in the previously described work [24] recoveries were reported to be lower than 70% for 3-CP and 5-CP. Generally, styrene–divinylbenzene-based polymers especially LiChrolut EN [33,34] because of its high surface area of $1200\text{ m}^2\text{ g}^{-1}$, has shown satisfactory results.

Other sorbents, such as divinylbenzene-*n*-vinylpyrrolidone (Oasis HLB) [35], polypyrrol (PPy) [36], polyaniline [31], poly-*N*-methylalanine (PNMA) and polydiphenylamine [32] have been used for the SPE of a variety of organic pollutants including chlorophenolic compounds. Although Oasis HLB was demonstrated to be an effective and universal sorbent, preconcentration based on polyaniline led to improved recovery results for those chlorophenols having higher numbers of chlorine atoms.

Other sorbents such as Carboxen B and ENVI Chrom P were used by Pocurull et al. [3] for extraction of phenols from water sample with and without ion-pair reagent (tetra-butylammonium bromide). Recoveries higher than 90% were obtained for all compounds except pentachlorophenol which had a recovery value of about 75%. Comparing these related results using some common sorbents with the present work demonstrates that CDS has an enhanced performance for the extraction of phenolic compounds, especially 3-CP and 4-MP.

To have a better overview on the efficiency of the CDS, a comparison study was carried out using C₁₈, Oasis HLB and LiChrolut EN. C₁₈ is a well-known and widely used commercial sorbent and the other two polymers are relatively new and more efficient sorbents. Spiked distilled water samples with phenols were passed through the cartridges. After elution and derivatization, an aliquot of 2 μl was injected onto the GC. As Table 3 demonstrates, the recoveries of all compounds are less than 40% using 250 ml of water samples when C₁₈ was used. As Table 3 demonstrates, CDS shows a clear advantage, over C₁₈, on the recoveries of phenols under similar circumstances. Moreover, Oasis HLB and LiChrolut EN showed excellent recoveries for all compounds, which are listed in the Table. The results obtained from CDS are comparable with those listed in the Table. From the results obtained, the CDS seems to be suitable for determining phenolic compounds.

3.3. Real sample

In order to study the effects of sample matrix on the performance of the sorbent, the recovery results were examined using real-life sample spiked with the phenolic compounds at two different concentration levels. A water sample from Jaj-rood river (Tehran, Iran) was spiked with the selected phenols at 2–3 $\mu\text{g l}^{-1}$ levels. After the SPE and

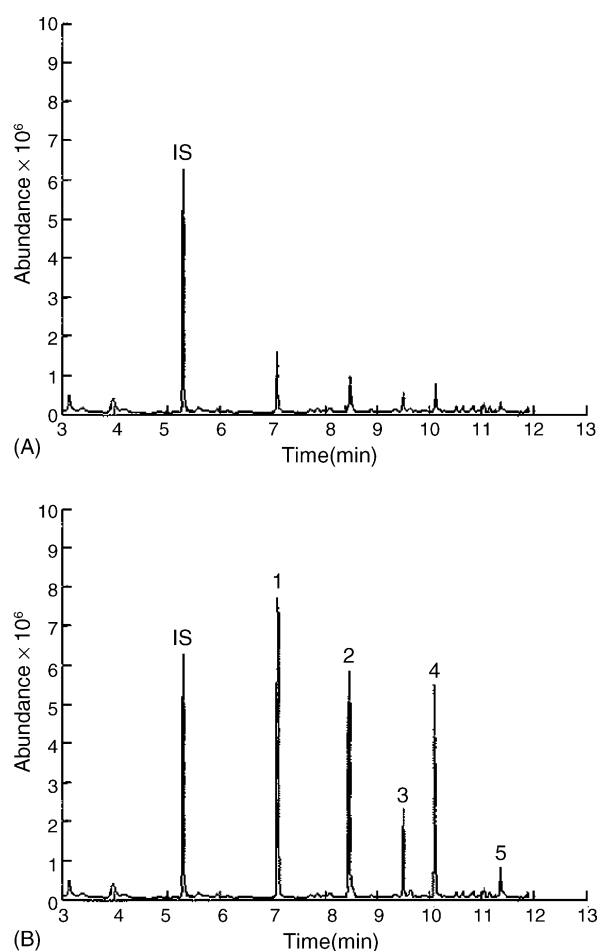


Fig. 3. Gas chromatograms obtained after SPE of (A) 200 ml Jaj rood river water and (B) 200 ml Jaj rood river water spiked with 2–3 $\mu\text{g l}^{-1}$ of phenolic compounds. Internal standard (I.S.), (1) PN, (2) 4-NP, (3) 2,4-DMP, (4) 4-MP, and (5) 3-CP.

derivatization step, an aliquot of final extraction was injected into the GC–MS system. The TIC traces obtained from SPE of 200 ml of river water spiked with a standard solution of phenols when CDS was used revealed that, in this case, the clean up process was more efficient. The capacity of CDS for retaining phenolic compounds were 50–125 mg g⁻¹, while for phenol was 30 mg g⁻¹. Fig. 3 shows the gas chromatograms of the Jaj rood river water sample and the same sample spiked with a standard solution of phenolic compounds. The limits of detection using 200 ml of water were calculated based on a signal-to-noise ratio of 3 and were in the range of 15–120 ng l⁻¹, using TIC mode (Table 3).

4. Conclusions

A synthesized sorbent, has been introduced and evaluated for extraction of organic pollutants from water samples. The capability of this sorbent to extract phenols has been compared with the results obtained for commercial sorbents and this laboratory-made with a relatively small specific surface area, showed comparable breakthrough volumes for the studied compounds. Using CDS as a SPE sorbent, led to quantitative results for preconcentration of phenolic compounds from 1 l water sample. The CDS as a SPE sorbent, can used for preconcentration of phenolic compounds in aqueous samples, and acceptable results were obtained. The low consumption of desorbing solvent, more efficient clean-up and the stability against pH are clear advantages of this sorbent in comparison with Oasis HLB C₁₈ and highly cross-linked commercial LiChrolut EN, which would be far more beneficial for on-line sample enrichment. Our observations indicate that this laboratory-made can be used frequently even after being dried out. Clearly, enlarging the specific surface area by changing the synthesis conditions could lead to much more efficient sorbents.

A CDS sorbent was prepared and investigated with five phenolic compounds. It could be used more than 150 times. It exhibited fast equilibrium in the extraction for the porous structure of silica particles.

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