

β -Cyclodextrin-Bonded Silica Particles as Novel Sorbent for Stir Bar Sorptive Extraction of Phenolic Compounds

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Abstract

A stir bar coated with β -cyclodextrin-bonded-silica (CDS) as novel sorbent has been developed and used to analyze seven phenolic compounds in aqueous samples, followed by thermal desorption and gas chromatography-mass spectrometric detection. Significant parameters affecting sorption process such as the time and temperature of sorption and desorption, ionic strength, pH and stirring rate have been optimized and discussed. The coating has a high thermal stability up to 300°C and long application lifetime (80 times). The porous structure of CDS coating provides high surface area and allows high extraction efficiency. Under the selected conditions, linearity range of 0.1–400 $\mu\text{g/L}$, limit of quantifications of 0.08–3.3 $\mu\text{g/L}$ and method detection limits of 0.02–1.00 $\mu\text{g/L}$ have been obtained. A satisfactory repeatability ($\text{RSD} \leq 6.5\%$, $n = 7$) with good linearity ($0.9975 \leq r^2 \leq 0.9996$) of results illustrated a good performance of the present method. The recovery of different natural water samples was higher than 81.5%.

Introduction

Stir bar sorptive extraction (SBSE) has been reported by Baltussen et al. (1) based on solid phase microextraction (SPME), which provides many advantages over conventional sample preparation methods by integration of the extraction, concentration and clean up in one step. In this technique a magnetic rod encapsulated in glass jacket and coated with a stationary sorbent phase. SBSE has been successfully applied in the analysis of environmental samples (2,3), essential oils (4), food (5,6), polar phenols (7), and utilized to measure organic compounds in biological matrixes (8,9). These applications have been accomplished using only commercial stir bar under the name of Twister (Gerstel GmbH), and its sorbent polydimethylsiloxane (PDMS), which is apolar and less accordant for the polar compounds. Bicchi et al. (10) have reported a dual-phase stir bar which consisted of a short PDMS tube closed at both ends with two magnets, and packed with different carbons. It has been employed for the extraction of polar compounds. Sol-gel technology in stir bar has also been used for selective extraction of

poly aromatic hydrocarbons (PAHs), organophosphorous pesticides (OPPs), bisphenol A and organic sulfur compounds (11–13). A novel approach that applied molecular imprinted polymers (MIP) to the coating material for stir bar has also been recently reported by Zhu and coworkers (14). Huang et al. (15) have reported the potential of a stir bar coated with monolithic material to extract PAHs. Alkyl-diol-silica restricted access material (RAM) as the coating layer has been applied by Lambert et al. (16). Also, a novel multi residue method for screening organic compounds by multi-stir bar sorptive extraction has been presented (17,18).

β -Cyclodextrin is a cyclic oligosaccharide with seven glucose units, with a cavity structure, and can create an inclusion complex with certain molecules through a host-guest interaction. Thus, it has been used as HPLC stationary phase for the separation of various compounds (19,20). β -Cyclodextrin bonded silica as a stationary sorbent for solid phase extraction of phenol compounds has been expanded (21,22). Also, the application of β -cyclodextrin in SPME (23,24) and membrane (25) has enhanced enrichment factor. In this study, the stir bar coated with β -cyclodextrin bonded silica stationary phase (CDS) has been developed and used for selective adsorption and separation of phenolic compounds in water samples, followed by thermal desorption and gas chromatography-mass spectrometry detection (GC-MS), with improved efficiency.

Experimental

Reagents

β -Cyclodextrin and irregular silica gel were obtained from Merck (Darmstadt, Germany). 3-Glycidoxy-propyltrimethoxysilane (KH-560) and high-temperature epoxy resin of type 5203 were acquired from Huili Company (Jiangsu, China). Phenol (PN), 2,4-dimethylphenol (24DMP), 2,4-dinitrophenol (24DNP), 4-nitrophenol (4NP), 2-methyl 4,6-dinitrophenol (2M46DNP), 3-chlorophenol (3CP) and 4-methylphenol (4MP) were obtained from Merck (Darmstadt, Germany). Standard solutions (2000 mg/L) for each individual compounds were prepared in methanol. A mixture of these phenolic compounds was prepared weekly by diluting the standard solution with methanol, and

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more diluted working solutions were prepared daily by diluting these solutions with Milli-Q water or sample water to give the corresponding solutions for calibration, limits of detection and linearity test.

Well water was collected from a well in our university, river water was obtained from Jajrood River (northeast of Tehran, Iran), and drinking mineral water sample available at the super-market packed in polymeric containers. The river, well and mineral water samples were collected in glass bottles. The river and well water sample were filtered before the analysis by a 0.45 μm membrane filter (MSI, Westboro, MA). The water samples were stored in refrigerator at 4 °C.

Method validation

Method detection limits (MDL) and limit of quantifications (LOQ) for each analyte were determined by the accepted procedure of the U.S. Environmental Protection Agency (26). A series of eight replicate samples at 10 $\mu\text{g/L}$ were analyzed. Precision was assessed by determination of repeatability, which expresses the precision of the method under the same operating conditions over a short interval of time. It is also identified intraday precision and is explained as %RSD. For repeatability, seven samples of same concentration (15 $\mu\text{g/L}$) were analyzed by the CDS-coated stir bar to examine variation arising, expressed as %RSD. The accuracy of the analytical procedure was appraised using the recovery test. The recoveries were examined in fortified water samples at two levels of mixed standard solutions. The recovery (R%) was expressed as observed concentration \times 100 / theoretical concentration.

Apparatus

A Hewlett-Packard (HP, Palo Alto, CA) HP 6890 series gas chromatograph equipped with a split/split less injector and a HP 5973 mass-selective detector was also used. The analytical column was a HP-5 MS 0.25 μm of 30 m \times 250 μm i.d. The column temperature was programmed as follows: 80 °C for 3 min then was heated with a rate of 20 °C/min up to 260 °C and then with a rate of 30 °C/min up to 290 °C. The mass spectrometry was run at electron energy of 70 eV. The injection and GC-MS interface temperatures were set at 260 °C and 280 °C, respectively. The ion source temperature was set at 250 °C, and quadrupole temperature was set at 200 °C. The mass range scanned was 40–250 amu, quantitative assessment of phenolic compounds were carried out in the selected ion monitoring mode (SIM) in order to enhance the limit of detection. Helium and nitrogen (99.999%) were utilized as carrier and make-up gases, respectively. PDMS-coated stir bars (10 mm length, 0.5 mm film thickness, Twister, Gerstel GmbH and Mulheim, Germany) were preconditioned for 1 h at 250 °C under a stream of high-purity N_2 . A home-made thermal desorption system was assembled according to a procedure reported by Liu et al. (11). A JSM-6330F scanning electron micro analyzer (Japan Electronic Company) was used to measure the CDS surface.

Preparation of CDS sorptive bars

The CDS was prepared according to previous study reported elsewhere with some modification (22). 1.718 g of β -cyclodextrin was dissolved in 37.5 mL of dry dimethylformamide (DMF), to which 0.15 g of metal sodium was added. It was stirred at room

temperature, for ~ 30 min to cause a reaction. After filtration, to remove no reacted sodium hydride 0.68 mL of 3-glycidioxypropyltriethoxysilane was added to the filtrate, which was allowed to react at 90 °C for 5 h under a nitrogen atmosphere. Then, 7.5 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, distilled water and acetone in sequence. Subsequently, the CDS was dried at 120 °C for 3 h, and kept in a desiccator before use.

The glass tubes (15 mm \times 1 mm O.D.) with magnetic bar were sealed by the alcohol flame and sequentially cleaned by water and acetone, followed by 1 mol/L NaOH and 1 mol/L HCl for 3 h, respectively. After washing by distilled water, the bars were kept at room temperature inside desiccator. The CDS was then fixed on the glass bars utilizing a high temperature epoxy resin. After that the bars were dried at room temperature for 4 h, and then they were heated at 280 °C under nitrogen protection for 2 h. Finally, they were allowed to cool to room temperature inside desiccator. The procedure was repeated three times.

Procedure

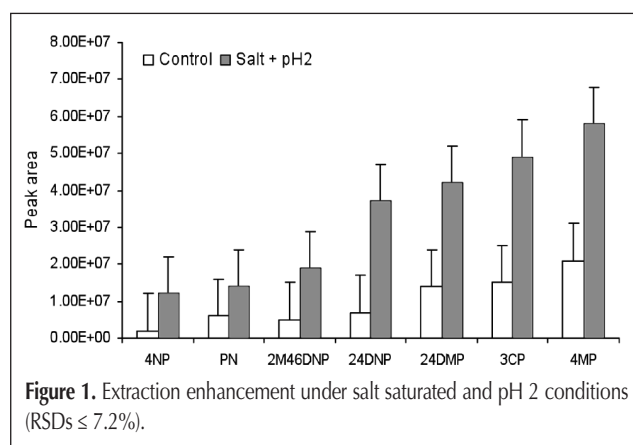
The spiking standard was added to a 10 mL sample of pH 2 buffer solution, which had been saturated with sodium chloride. The stir bar was immersed in the vial and it was stirred in the sample for 50 min at 50 °C with 800 rpm. Then, the stir bar was removed from the vial and the water remaining on the surface was desiccated with lint-free tissue, placed in glass thermal desorption tube and thermally desorbed in the laboratory-made desorption unit for 5 min at 250 °C.

Results and Discussion

Sorptive enrichment in aqueous media is an equilibrium process; therefore, extraction efficiency is significantly influenced by different parameters such as sample pH, ionic strength, stirring rate, sample solution temperature and extraction time, and have been studied.

Optimized SBSE conditions

The addition of acid and salt, singularly and in combination, was studied as a means of enhancing the amount extracted by



the sorbent. Figure 1 shows the amounts of different phenolic compounds extracted from the pH 2 buffer-saturated salt solution and the control sample at neutral pH and with no salt added. Generally, in order to increase the extraction efficiencies of the phenolic compounds in aqueous solution, the solution is acidified to preclude them from dissociating during extraction (27). At low pH the acid-base equilibrium for the phenolic compounds transfers significantly towards the neutral forms, which have greater affinities for the sorbent, and the extraction efficiencies are, therefore, enhanced. The effect of neutral molecules becoming insoluble as the water molecules prefer to solvate the salt ions is prevalently demonstrated as "salting out" (28). The presence of the salt prevents their solubility in the water and forces more of these analytes into the sorbent. The positive effects of both acid and salt can be conceived when they are utilized in combination. With pH 2 and saturated salt circumstances, the amount extracted for every analyte in the mixture was higher than the control sample at pH 7 and with no salt added. Under these conditions, all phenolic compounds are in their neutral form and are salted out of solution into the sorbent.

Stirring intensity is one of the important parameter that increases the extraction efficiency and lowers extraction time. The agitation can renovate a new sample solution surface, therefore accelerating the mass transfer from the aqueous phase to the sorbent phase. The optimum stirring rate was evaluated by testing different stirring rates between 400 and 1000 rpm. The results demonstrated that the equilibrium was attained at 800 rpm and no significant enhancement after that was observed. Hence, 800 rpm was applied in the following experiments.

Temperature greatly influences the kinetics of extraction. By increasing the temperature of the sample solution, molecules of the analytes become more active; therefore, this process expedites the mass transfer of the analyte from the sample solution to sorbent phase. The effect of temperature on the extraction efficiency was also studied for 10 mL of a saturated salt solution at pH 2 containing 10.0 $\mu\text{g/L}$ of each phenolic compound in the range of 20–70°C by the CDS stir bar. The stirred solution (800 rpm) was kept for 50 min. Figure 2 shows that the extraction efficiencies of the analytes were first increased slowly with increasing extraction temperature from 25°C to 50°C, but after that they were declined. However, because the adsorption process was exothermic, the stir bar coating/sample partition coefficient (K) reduced with increased temperature, and affinity of the

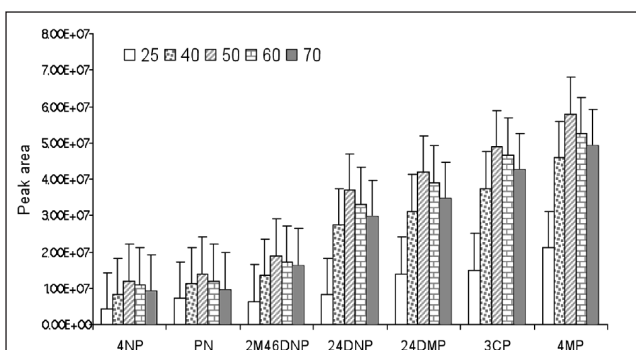


Figure 2. The effect of temperature on the extraction efficiency of CDS-coated stir bar (RSDs \leq 6.5%).

analytes for the stir bar coating decreased at high temperature, which resulted in lower equilibrium amounts of analytes that the coating was able to extract (29). Thus, 50°C was selected as optimum temperature.

The SBSE process depends on equilibrium. Therefore, the equilibration time was determined by exposing the stir bar to sample matrix containing the studied analytes for a variety of times, from 10 to 70 min, until the amounts extracted remained constant. The experimental results illustrated that the equilibrium of phenolic compounds was reached within 50 min.

The amounts of analytes desorbed from the loaded stir bar will modify detection sensitivity. These quantities depended on desorption temperature and the time, while the stir bar was in the thermal desorption unit. The optimum desorption conditions were also examined and on the basis of the results obtained, it was desorbed at 250°C for 5 min in all experiments.

Characterization of CDS stir bar

To investigate the thermal stability of the CDS-coated stir bar it was conditioned at 230, 250, 270, 290, and 300°C for 1 h under the protection of a nitrogen atmosphere. After thermal conditioning at each temperature it was utilized to extract 10 mL an aqueous sample containing 10.0 $\mu\text{g/L}^{-1}$ of each analyte under optimum conditions. It is clear from Figure 3 that the extraction capacity of sorbent was not significantly affected by the temperature applied for thermal condition.

The use of capillary glass bars as the carrier of coating can extend the amount of sorbent on the bar. Figure 4 shows the scanning electron micrograph of the CDS-coated stir bar. It is clear

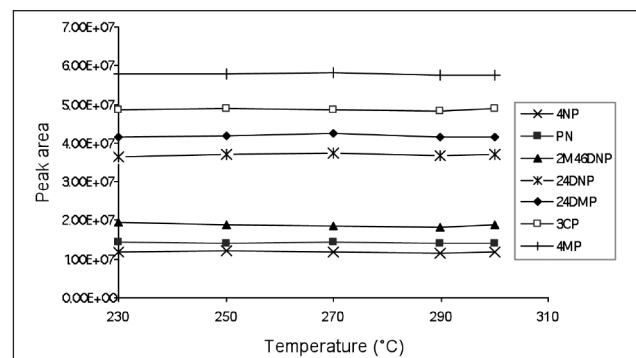


Figure 3. Thermal stability profile of the CDS-coated stir bar (RSDs \leq 6.2%).

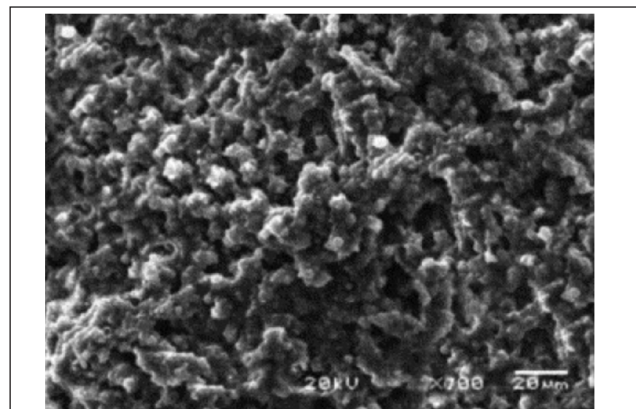


Figure 4. Scanning electron micrograph of the CDS-coated stir bar.

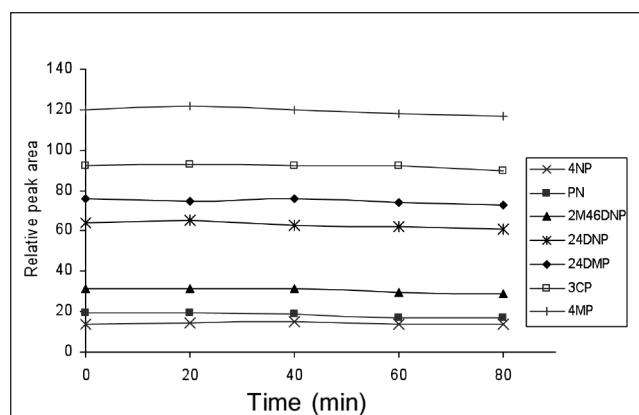


Figure 5. Lifetime profile of the CDS-coated stir bar for different times of their use (RSDs \leq 5.7%).

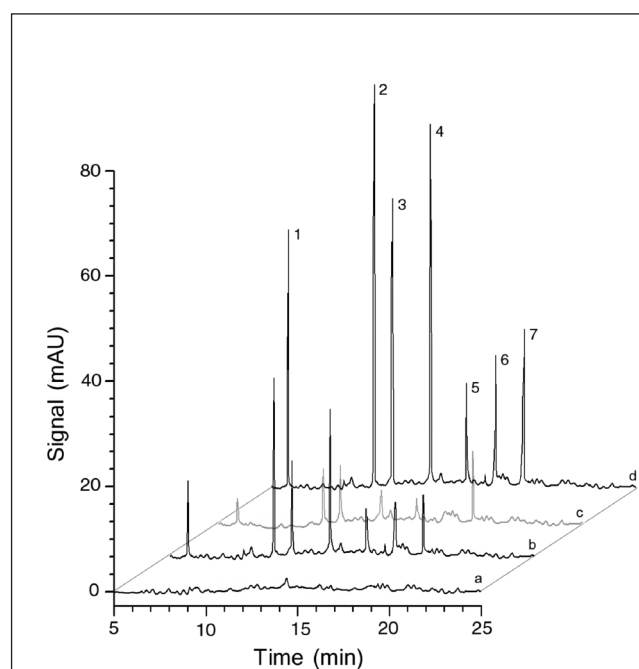


Figure 6. SBSE-GC-MS chromatograms of mineral water sample: (A) unspiked, (B) spiked at 10.0 $\mu\text{g/L}$ and (D) spiked at 25.0 $\mu\text{g/L}$ of phenolic compounds utilizing CDS coating, and (C) spiked at 25.0 $\mu\text{g/L}$ of analytes using PDMS-coated stir bar. (1) PN, (2) 4MP, (3) 24DMP, (4) 3CP, (5) 24DNP, (6) 4NP, and (7) 2M46DNP.

Table 1. Figures of Merit of the Proposed Method for SBSE of Phenolic Compounds

Analytes	MDL ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)	r^2	LR ($\mu\text{g/L}$)	Reproducibility (RSD %)		Repeatability (RSD %, $n = 7$)
					Bar-to-bar [†]	Batch-to-batch [‡]	
24DNP	1.0	3.3	0.9975	5–400	10.2	11.3	6.5
4NP	1.0	3.3	0.9981	5–400	9.8	10.1	5.8
2M46DNP	1.0	3.3	0.9978	5–400	8.3	12.3	5.7
PN	0.5	1.5	0.9989	2–200	7.5	10.3	6.1
24DMP	0.5	1.5	0.9996	2–200	8.3	9.6	4.8
3CP	0.04	0.09	0.9993	0.1–100	9.8	9.8	5.2
4MP	0.02	0.08	0.9991	0.1–100	6.9	8.5	3.1

* MDL = Method detection limit. LOQ = Limit of quantification. LR = Linearity range.

[†] ($n = 5$). [‡] ($n = 3$).

that the CDS bar has a porous structure. Such a porous structure should significantly enhance the extraction capacity. Figure 5 shows the extraction efficiency of the CDS-coated stir bar in extracting target analytes from the aqueous solution under optimum conditions after being used for 20, 40, 60, and 80 times. To ensure the reproducibility, the data utilized for the y-axis are the comparison of the areas in the chromatogram measured using the CDS-coated stir bar (to extract 10 mL aqueous sample containing 10.0 $\mu\text{g/L}$ of each analyte under optimum conditions) with the corresponding peak areas obtained by direct injection of a solution with the same concentration. The ratios of areas achieved after the stir bars were employed for different times are convenient in order to compute the change of factors in SBSE-GC conditions. The ratios are displayed in Figure 5 and indicate that there is nearly no obvious decrease after being used for 80 times.

The chromatograms of phenolic compounds using CDS and commercial PDMS coating are shown in Figure 6D and 6C, respectively. Examination of the chromatograms reveals that the response signals of the CDS coating were significantly stronger than those of PDMS coating. The polar compounds have higher affinities for the polar coating than for the nonpolar coating; therefore, the amount of phenolic compounds extracted by polar CDS coating was more than with the nonpolar PDMS coating. This is because the surface area of the CDS coating is much higher due to the porosity of the bonded silica particles. Moreover, the unique molecular structure of β -cyclodextrin on the surface of coating performs a role in the extraction of phenolic compounds. The β -cyclodextrin molecule has the shape of a hollow truncated cone. The interior of the cavity, which contains two rings of C-H groups with a ring of glycoside oxygen in between, is relatively hydrophobic, and the external faces with hydroxyl groups are also hydrophobic (19). On account of this special structure, they can selectively embrace guest molecules into their hydrophobic cavity to create inclusion compounds with different stabilities.

Quantitative evaluation

The coefficient of determinations (r^2), linearity, reproducibility, repeatability, limit of quantifications (LOQ) and MDL were calculated and are recorded in Table I. The coefficient of determinations and linearity values for the tested phenolic compounds were in the range 0.9975–0.9996 and 0.1–400 $\mu\text{g/L}$, respectively. The bar-to-bar and batch-to-batch reproducibility of the CDS coating procedure were also studied. Five different bars were coated under the same conditions and three identically prepared bars among three different batches were examined for the extraction target analytes from aqueous solution. The relative standard deviations (RSDs) for different bars and different batches were 6.9–10.2% and 8.5–12.3%, respectively. These results show a good reproducibility for preparation of the CDS-coated stir bars. The repeatability of the CDS-coated stir bar attained at 15.0 $\mu\text{g/L}$ for each studied analyte by calculating the RSDs of seven replicates were 3.1–6.5%. The obtained LOQs and MDLs were in the range of 0.08–3.3 $\mu\text{g/L}$ and 0.02–1.00 $\mu\text{g/L}$, respectively.

Table II. the Results Obtained from Analysis of Real Water Samples

Analytes	Recovery of well water (%)				Recovery of river water (%)				Recovery of mineral water (%)			
	25.0 (µg/L)	(RSD*)	10.0 (µg/L)	(RSD*)	25.0 (µg/L)	(RSD*)	10.0 (µg/L)	(RSD*)	25.0 (µg/L)	(RSD*)	10.0 (µg/L)	(RSD*)
24DNP	81.7	(7.2)	82.5	(8.6)	86.1	(8.4)	88.2	(6.2)	87.5	(9.7)	81.5	(11.4)
4NP	84.7	(6.1)	83.8	(9.3)	92.7	(6.2)	85.7	(7.5)	91.6	(7.5)	89.5	(9.2)
2M46DNP	90.3	(7.2)	88.7	(10.6)	93.1	(9.7)	93.1	(9.7)	93.2	(10.9)	82.3	(10.1)
PN	91.6	(9.5)	94.3	(7.6)	89.5	(6.8)	90.6	(11.3)	95.8	(6.2)	90.6	(6.8)
24DMP	89.8	(5.1)	86.1	(6.4)	97.4	(7.1)	91.8	(4.7)	94.1	(8.7)	86.4	(7.5)
3CP	96.2	(4.8)	95.7	(10.2)	95.9	(5.8)	94.9	(8.7)	96.8	(9.3)	95.7	(10.5)
4MP	98.5	(5.5)	99.3	(9.3)	100.4	(7.7)	98.4	(6.5)	101.7	(6.7)	99.1	(9.4)

* n = 3

Application to real samples

Finally, the applicability of the extraction method was evaluated by analysis of the real samples including well water, river water, and mineral water. The results indicated that analyzed samples had not been contaminated by phenolic compounds. All the real water samples were spiked at two different concentration levels (10.0 and 25 µg/L) to assess the matrix effect. The relative recovery defined as the peak area ratio of a natural water sample and ultrapure water sample spiked with analytes at the same level, was applied (30). The relative recoveries of the analytes are given in Table II which varies from 81.5% to 101.7%, it shows that the influence of matrix is not significant on the extraction recoveries. The chromatograms obtained by GC-MS of unspiked mineral water and that spiked at two concentrations of each analyte after the developed method at optimum conditions is shown in Figure 6.

Conclusion

A novel CDS-coated stir bar is developed and has been investigated with seven phenolic compounds. The porous structure provided large adsorption capacity, high adsorption rate and strong analyte interaction. The developed stir bar indicated good thermal stability and can be reused for at least 80 times. It also demonstrates better selectivity to polar compounds compared to the PDMS coated bars. The stir bar is employed for the determination of studied analytes in aqueous samples, with good and acceptable results.

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