



Micro-solid phase extraction of benzene, toluene, ethylbenzene and xylenes from aqueous solutions using water-insoluble β -cyclodextrin polymer as sorbent



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ABSTRACT

Water-insoluble β -cyclodextrin polymer was synthesized by chemical cross-linking using epichlorohydrin (EPI) as a cross-linker agent. The produced water-insoluble polymer was used as a sorbent for the micro-solid phase extraction (μ -SPE) of benzene, toluene, ethylbenzene and xylenes (BTEX) from water samples. The μ -SPE device consisted of a sealed tea bag envelope containing 15 mg of sorbent. For the evaluation of the extraction efficiency, parameters such as extraction and desorption time, desorption solvent and salt concentration were investigated. At an extraction time of 30 min in the course of the extraction process, analytes were extracted from a 10 mL aqueous sample solution. The analytes were desorbed by ultrasonication in 200 μ L of acetonitrile for 20 min. Analysis of the analytes was done by a gas chromatography-flame ionization detector (GC-FID) system. The enrichment factor (EF) was found to be in the range 23.0–45.4 ($EF_{max} = 50.0$). The method provided linearity ranges of between 0.5 and 500.0 ng/mL (depending on the analytes), with good coefficients of determination (r^2) ranging between 0.997 and 0.999 under optimized conditions. Detection limits for BTEX were in the range of between 0.15 and 0.60 ng/mL, while corresponding recoveries were in the range of 46.0–90.0%. The relative standard deviation of the method for the analytes at 100.0 ng/mL concentration level ranged from 5.5 to 11.2% ($n = 5$). The proposed method was concluded to be a cost effective and environmentally-friendly extraction technique with ease of operation and minimal usage of organic solvent.

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1. Introduction

Despite substantial technological advances in the field of analytical chemistry, most instruments are still not capable of directly handling relatively complex samples. Therefore, sample preparation step is critical to obtain reliable and accurate final results. New trends in sample preparation are exemplified by miniaturization of the extraction apparatus, reduction of pretreatment steps and time, and improvement of selectivity to reduce matrix effects. In the past 20 years, many efforts have been devoted to develop these ideas. The latter approach includes solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) [1,2]. SPME is a fast, simple, and green sample preparation technique that combines preconcentration and cleanup steps into a single step; however, it has some disadvantages as well. The main drawbacks of SPME include (i) high analysis cost per sample because of

using dedicated and expensive apparatus, (ii) degradation of fibers through increased usage, and (iii) carryover between extractions [3]. Basheer et al. reported a novel extraction and preconcentration technique, termed micro-solid-phase extraction (μ -SPE), based on the packing of sorbent material in a sealed porous polypropylene membrane envelope to overcome, at least partially, these disadvantages [4]. It was demonstrated to be a fast, accurate, and effective pretreatment technique. This method was subsequently applied for the determination of various target compounds in a variety of matrices [4–6].

Basheer et al. reported a μ -SPE method in which multi-walled carbon nanotubes (MWCNTs) were used to extract organophosphorus pesticides (OPPs) from environmental samples [7]. Later in 2007, they used a μ -SPE device, where C18 was used as sorbent, for analyzing acidic drugs in wastewater [8]. Many other researchers evaluated various materials as sorbent in this process. In an advanced study, molecularly imprinted polymer with 2,4,6-trichlorophenol (2,4,6-TCP), as the template molecule, was prepared and used in molecularly imprinted micro-solid phase extraction (MIMSPE) procedure to selectively preconcentrate phe-

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nolic compounds from environmental water samples [9]. In a recent investigation in this field, Naing et al. used cross-linked chitosan microspheres as a sorbent for μ -SPE of benzene, toluene, ethylbenzene, xylenes and styrene (BTEX-S) from water [10].

Cyclodextrins (CDs) are extensively used in separation processes, due to their unique property in terms of forming inclusion compounds with other smaller hydrophobic molecules [11]. These are torus-shaped cyclic oligosaccharides with hydrophobic cavities whose size depends on the number of glycosidic units [12]. Besides those, which are known as native or natural CDs, many of their derivatives are also of interest for various reasons such as separation and purification purposes using chromatographic techniques [13]. Chemical cross-linking the hydroxyl groups of β -CDs using epichlorohydrin (EPI) as a cross-linker agent is the most straightforward method among all the reactions proposed to produce a stable cross-linked network of β -CD molecules, a new type of adsorbent which is useful for the removal of organic pollutants and heavy metals from water. Because of its cross-linked network structure, the β -CDP is stable and insoluble in water [14,15]. The inclusion interaction within CD cavity is one of the driving forces to be considered in the extraction of analytes by β -CDP. Albeit the solutes can also interact with the cross-linking network [16,17], the increasing number of publications on pollutant removal using CD-based materials shows that there is a growing interest in the development of new materials used in wastewater treatment. Although their higher cost compared to that of activated carbon is a drawback, the usefulness of β -CDP in water and wastewater treatment applications arises from several advantages including easy synthesis, easy regeneration, possibility of being tailored for special applications, and high sorption capacity for and selectivity toward targeted pollutants. For sorption-oriented processes, β -CDP materials could represent an interesting alternative [15].

Moon et al. were the first to propose SPE technique based on the formation of an inclusion complex with β -CDP polymer [18]. After that, β -CDP had been applied as a SPE material to separate/preconcentrate trace metal elements [19]. However, to the best of our knowledge, a report on the use of this polymer as μ -SPE sorbent for the separation of analytes from environmental samples is yet to be released.

As mentioned before, other researchers worked based on the packing of sorbent material in a sealed porous polypropylene membrane envelope [2,4,5,8,9]. But the polypropylene membrane suffers from too long extraction time due to the small pore size of the membrane and low extraction rate because of low wettability of the hydrophobic polypropylene membrane [20]. Pelden et al. examined the possibility of replacing the polypropylene membrane with a cellulosic tea bag filter paper [20]. Their study showed that, the tea bag filter paper provides a highly durable and protective layer for any solid adsorbent with a high porosity and high tensile strength.

Aromatic hydrocarbons, such as benzene, toluene, and ethylbenzene (commonly referred to as BTEX) are usually considered as carcinogens that are harmful to the human body. Handling and disposal of the water containing such contaminations is one of the greatest environmental challenges encountered by natural gas and oil exploration and production activities [21,22]. Therefore, the research on adsorbing aromatic hydrocarbons with adsorbents (e.g., β -CD) is of extreme significance for environment protection and human health [23].

In this study, β -CDP was synthesized and used as a sorbent of μ -SPE to directly preconcentrate BTEX from water samples. Then, the analytes were determined by GC-FID system. Several important parameters affecting the extraction efficiency (e.g., sorbent material as well as extraction and desorption conditions) were carefully studied and optimized. Possible interactions between β -CDP and analytes were discussed. Finally, the proposed method was applied

to analyze BTEX in real water samples. This is the first study on μ -SPE where β -CDP is used as a sorbent and GC-FID is utilized for determining BTEX in aqueous samples.

2. Material and methods

2.1. Chemicals

β -CD and epichlorohydrin, the cross-linking agent, were supplied from Sigma Aldrich (Bornem, Belgium). Acetone, chlorobenzene, benzene, ethylbenzene and xylenes were purchased from Merck (Darmstadt, Germany). Obtained through Milli-Q[®] system (Millipore, Milford, MA, USA), HPLC grade water was used to prepare all solutions. HPLC grade acetonitrile and methanol were purchased from Dae-Jung (South Korea). Isopropanol and toluene were supplied by Fluka (Buchs, Switzerland) and dichloromethane was obtained from Ghatran Shimi (Tehran, Iran). The cellulose acetate sheet (tea bag filter paper) with 1 mm thickness and 0.1 μ m pore size were supplied by Ghazal Tea Company (Tehran, Iran).

2.2. Preparing the solutions

Standard stock solutions (1000 μ g/mL) were prepared individually in methanol. All standard solutions were kept in the refrigerator at 4 °C prior to analyses. Working solutions containing all of the BTEXs at different concentrations were prepared by being spiked into ultrapure water. Concentration of each analyte in the working solutions was 0.25 μ g/mL; these solutions were used for the optimization experiments.

Environmental water samples for the experiments were collected from a canal passing through an agricultural area in Karaj, Iran (agricultural water) and a well that was located in a residential region (well water). Rain water sample was collected in urban zone over a rainy night and drinking water sample was sampled from water supply system of Tehran, Iran. These samples were collected into glass bottles which were pre-rinsed with acetone. Each bottle was filled with water without leaving a headspace at the bottle neck and was wrapped in an aluminum foil and transported to the laboratory. The water samples were kept at 4 °C prior to the analyses.

2.3. Instrumentation

The separation and quantification of BTEX was performed on a Varian CP-3800 gas chromatographic-flame ionization detector (GC-FID) system equipped with a HP-5 (Agilent, USA) fused-silica capillary column (30 m \times 0.32 mm; film thickness: 0.25 μ m) and the following temperature program was used: initially, the temperature was set to 50 °C for 7 min, then it was increased to 110 °C at 5 °C/min and further increased to 300 °C at 20 °C/min, and held for 10 min. Nitrogen was used as the carrier gas at a pressure of 4.0 psi. The injector temperature was held at 270 °C with split ratio of 7 and the FID temperature was set to 300 °C. Quantitative calculations were made based on GC peak areas.

Fourier transform infrared (FT-IR) spectra of β -CD and β -CDP in solid phase were obtained by a Bruker IFS 66/S, FT-IR spectrometer (USA). 1 mg of each material was blended with IR grade KBr (100 mg) and pressed into tablet for analysis. FT-IR spectra were recorded at a resolution of 4 cm^{-1} within a scan range of 400–4000 cm^{-1} .

Differential scanning calorimetry (DSC) analysis was performed with a Mettler TA-4000 Stare apparatus equipped with a DSC 25 cell (Mettler Toledo, Switzerland). Accurately weighted samples (2–5 mg, as weighted on a Mettler M3 microbalance) were placed in sealed aluminum pans with pierced lid and scanned at a heating rate of 0.1 °C/min over the temperature range of 30–400 °C.

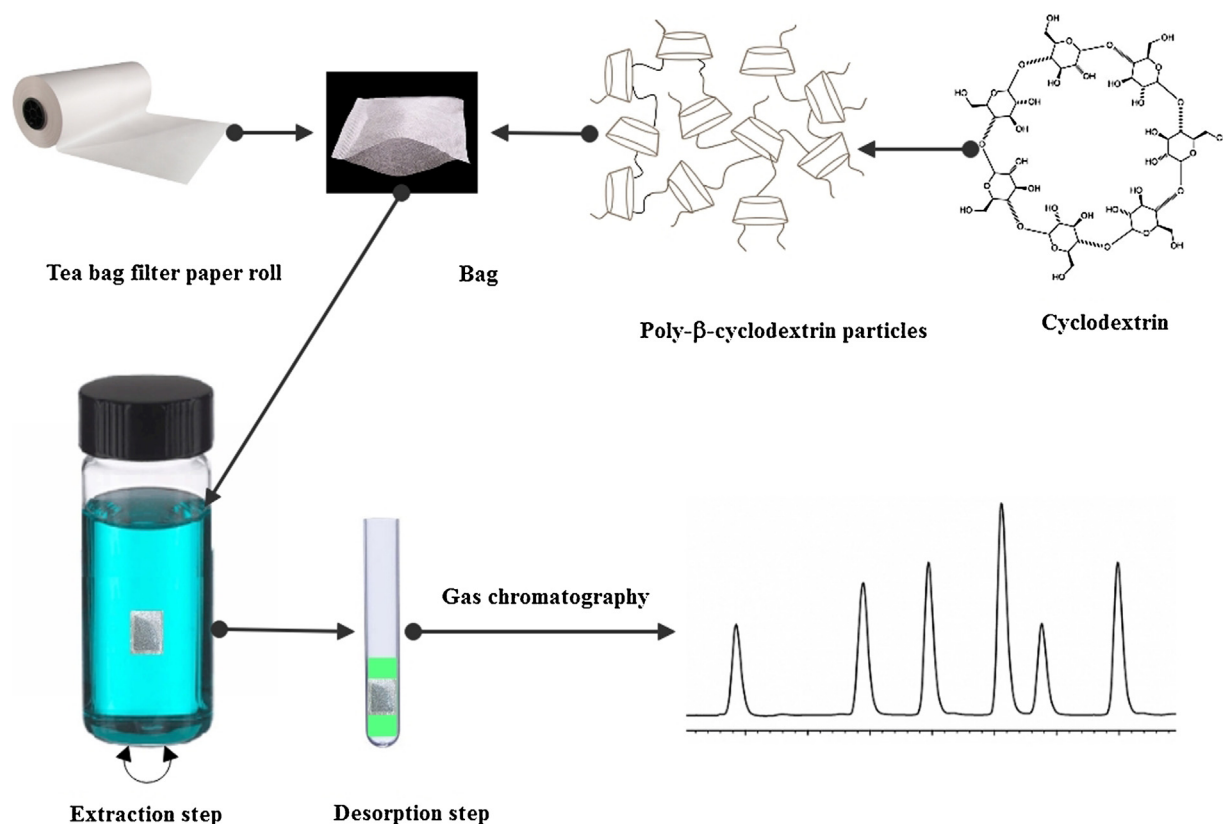


Fig 1. Scheme of preparing μ -SPE device and procedure.

Table 1
Experimental Conditions for producing β -CDP polymers.

Polymer type	Ep/ β CD ^a	T(°C)	Time (h)	NaOH(aq) ^b	solubility
A	15	60	5	50	Water insoluble
B	17	60	7	20	Water insoluble
C	30	60	2	40	Water insoluble
D	10	60	Over night	40	Water soluble

^a Molar ratio.

^b %w/v.

Thermogravimetric analysis (TGA) was carried out on a BÄHR STA 503 thermogravimetric analyzer (BÄHR-Thermoanalyse GmbH). The sample weight was 10–15 mg. The analysis was performed from room temperature up to 500 °C at a heating rate of 10 °C/min in argon atmosphere.

2.4. Preparation of water-insoluble β -CDP

A series of polymers were prepared with different molar ratios of EP/CD, temperatures, times, and aqueous sodium hydroxide solution [24,25]. The experimental conditions are summarized in Table 1. At and below the molar ratio of EP/BCD = 10, water-soluble polymer was produced.

The β -CDP polymer with high extraction efficiency (polymer A) was prepared as follows. Appropriate mass of β -CD was dissolved in a stirred aqueous solution of 50% w/v NaOH at 60 °C. Once the β -CD was dissolved, EPI was added to the solution in a dropwise fashion. The molar ratio of β -CD to the cross-linking agent was adjusted to 1:15. Throughout the reaction time, the stirring speed of the reacting bulk (300 rpm) and the temperature (60 °C) were kept constant. Meanwhile, the mixture viscosity increased gradually, so that the mixture turned, finally, into a highly viscous mass of white to pale yellow in color. The reaction time was set to 5 h. The polymer

was washed with Milli-Q water and acetone successively. Then the resulting masses were cut to pieces of appropriate size (1–3 mm in diameter) and dried in oven at 90 °C for 12 h. Different synthetic polymers were used as μ -SPE sorbent to discover their capabilities in terms of BTEX extraction from aqueous media.

2.5. Preparation of μ -SPE device

The μ -SPE device was prepared as reported by Pelden et al. [20]. Briefly, 15 mg of sorbent was enclosed inside a tea bag envelope whose final dimension was 1 cm \times 0.8 cm. The edges of the device were sealed with closing clips to secure the enclosed sorbent. Before the μ -SPE process, the tea bags were cleaned by ultrasonication in methanol and acetone for 10 min, respectively.

After the process, the μ -SPE device needed to be cleaned to get rid of overlaid residual analytes for later extractions. The washing process included ultrasonication for 15 min with 2 mL of acetonitrile and then with acetone. The carryover effect was tested with an additional extraction using 200 μ L of acetonitrile followed by GC-FID analysis of the washing product, indicating no analyte peak. Conducting a series of tests, it was shown that the extraction device was reusable for up to 15 times. Thereafter no significant changes were observed in its appearance but in most cases the used bag

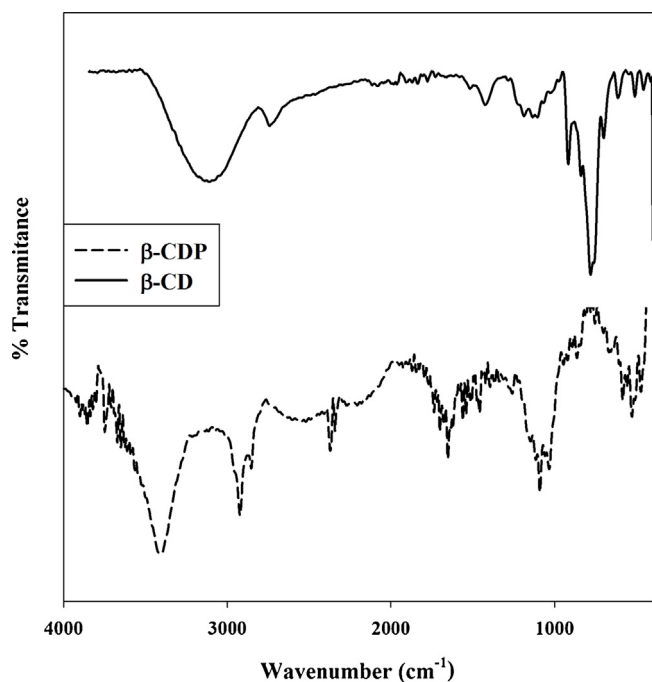


Fig. 2. IR spectrum of β -CD and β -CDP.

was torn during the extraction and the sorbent washed out. Hence one of the limitations of the continuous usage of bags was that they were torn down when we used them a lot. More importantly, after 15 times, extraction efficiency and repeatability were decreased more and more.

2.6. μ -SPE procedure

For each extraction, the μ -SPE device was placed into 10 mL of prepared sample, being stirred at 1000 rpm. The device tumbled freely within the sample during the extraction (Fig. 1). After 30 min of extraction, the device was removed with a pair of tweezers followed by drying with lint-free tissue paper. After that, the device was placed in a vial, and the analytes were desorbed by ultrasonication in 200 μ L of acetonitrile for 20 min. After desorption, internal standard (Chlorobenzene, 5 μ g/mL) was added to the collected extract and then 1.0 μ L of that was injected into GC-FID system for analysis.

3. Results and discussion

3.1. Characterization of β -CDP

The cross-linked polymer of β -CDP is a well-known material. To confirm that the material was successfully prepared, IR spectrum (KBr pellet) of the polymer was measured and compared to the spectra of β -CD and EPI, as reported in literature. The IR spectrum obtained herein (Fig. 2) did not resemble that of β -CD nor EPI. However, it matched the literature-reported spectrum of β -CDP exactly (3400 cm^{-1} , OH stretch; 3000 cm^{-1} , CH stretch; and 1040 cm^{-1} , COC stretch). Therefore, the synthesis was concluded to successfully yield β -CDP [14,25].

The corresponding TGA curves to β -CD and β -CDP are presented in Fig. 3A. Typical TGA curve with a large mass loss peak at 310 $^{\circ}\text{C}$, corresponding to the decomposition of β -CD, was seen along the spectra of pure β -CD. Meanwhile, the characteristic thermal profiles of cross-linked β -CD were distinguishable and the mass loss peaks were shifted to 350 $^{\circ}\text{C}$ for insoluble polymers. Such results

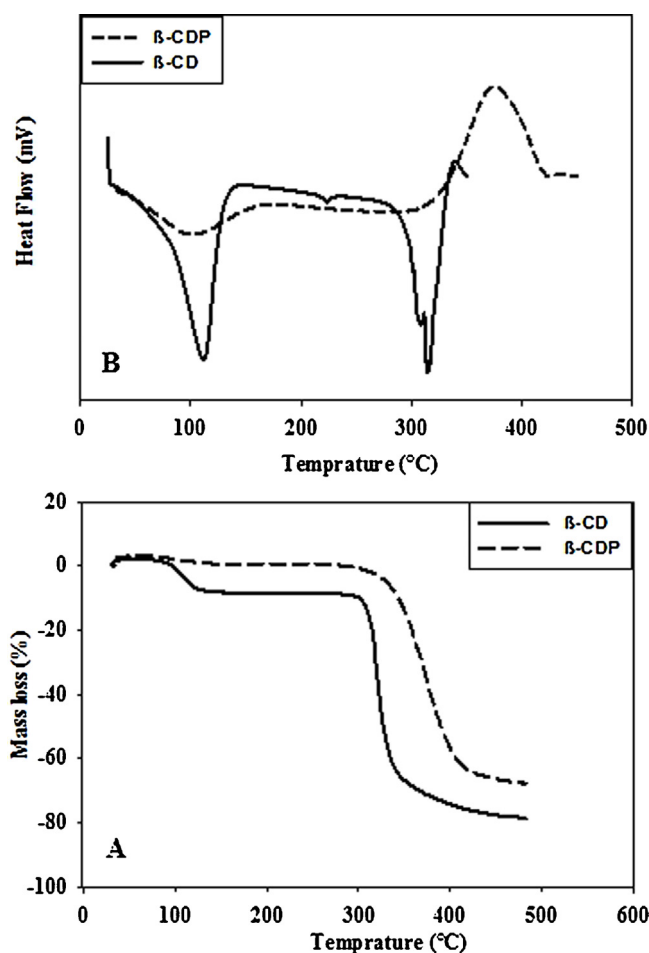


Fig. 3. A) TGA and B) DSC curves of β -CD and β -CDP.

indicated significant improvement in the stability of the insoluble polymers after polymerization. From the TG analysis, the decomposition of the β -CDP was seen at 410 $^{\circ}\text{C}$, which was indeed higher than that of β -CD (350 $^{\circ}\text{C}$) [26]. The enhanced thermal stability of β -CDP is attributed to its cross-linked nature.

In Fig. 3B, the DSC curve of β -CD exhibited a wide and strong endothermic effect in the temperature range of 80–130 $^{\circ}\text{C}$ (peak $T_{\text{max}} = 111.5$ $^{\circ}\text{C}$), which may be attributed to dehydration. Moreover, the melting peak of the CD was seen at $T_{\text{max}} = 319.66$ $^{\circ}\text{C}$ [27,28]. The DSC curve of β -CDP is shown in Fig. 3B, where no transition is observed in temperatures up to 320 $^{\circ}\text{C}$. The absence of glass transition is thought to be due to the highly cross-linked nature of the polymer. The exothermic peaks at 360 $^{\circ}\text{C}$ are attributed to the β -CDP decomposition process. These results reveal that the polymer is thermally stable at temperatures above 180 $^{\circ}\text{C}$ (melting point of neat CD) in a nitrogen atmosphere; hence it can be used under some high temperature environments [28].

3.2. Extraction optimization

In this section, parameters influencing the extraction efficiency of BTEX by β -CD epichlorohydrin polymer (e.g., adsorbent type, extraction time, desorption time, salt concentration and desorption solvent) are investigated.

3.2.1. Sorbent type

Choosing a suitable sorbent represents a significant step in μ -SPE, since it determines the selectivity towards analytes. Varying the synthesis conditions (EPI/CD molar ratio, NaOH concentration,

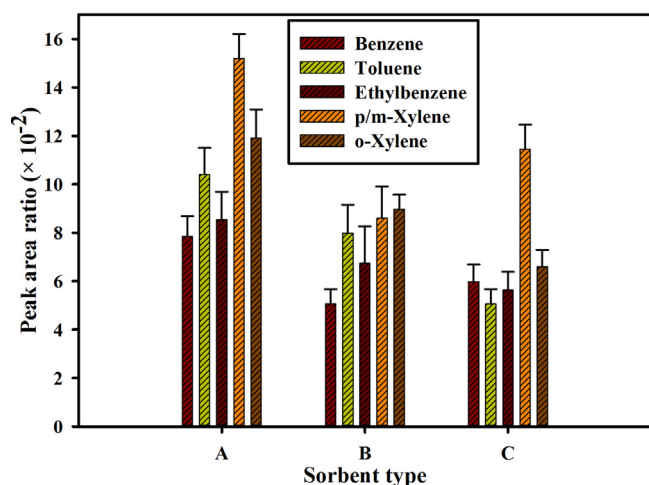


Fig. 4. Effect of different synthesized sorbents on the extraction of BTEX. Other extraction conditions: sample volume: 10 mL, extraction time: 10 min, desorption solvent: methanol, desorption time: 5 min.

reaction temperature and reaction time), different cross-linked polymers can be obtained, making it possible to induce structural modifications into polymer networks. It has been documented that, an increase in the concentration of CD monomers and a decrease in its ratio with respect to the “cross-linking agent” often results in insoluble CDPs [29].

The primary product of the reaction of β -CD with epichlorohydrin in an alkaline medium is a heterogeneous mixture of various CD glyceryl ethers: this is not a true polymer but a copolymer. [13] Therefore, the resulting β -CDP materials are a mixture containing β -CD units joined by repeating glyceryl linkers. A number of β -CD rings are interconnected and a three-dimensional (co) polymer network is formed [15]. In such a network structure, chain length is meaningless and no specific molecular weight can be measured for these polymers.

In this work, different β -CDP polymers were synthesized by varying the molar ratio of EPI/ β -CD from 10 to 30, so as to produce different insoluble polymers, and then examining their capabilities in terms of BTEX extraction from aqueous medium.

The present research was done by extracting 10 mL of 100 ng/mL aqueous solution of each analyte at 1000 rpm stirring rate for 10 min. The analytes were eluted by ultrasonication in methanol, as a desorption solvent, for 5 min. As the results in Fig. 4 shows, polymer A was found to be the most effective extraction sorbent, followed by polymers B and C. This behavior is related to the final polymer structure. At lower EPI-to- β -CD molar ratios (in this case = 10), the water-soluble polymer was synthesized which, indeed, was not suitable for aqueous media. However, when the molar ratio of the reactant (EPI) was increased, water-insoluble polymer was the final product. According to the literature, polymer-analytes interaction may follow either of three main mechanisms: (1) interactions in the β -CD cavities (i.e., the formation of inclusion compounds), (2) interactions in the internal pores of polymeric pearls, and (3) interactions on the surface (physical sorption). In general, physical sorption plays a minor role in the interaction between β -CDP and pollutants. This is because CD-based materials have a very small surface area and the results are mainly explained by the formation of inclusion complexes. Therefore in the case of highly cross-linked polymers (in this study, polymer B and C), only the surface molecules of the particles can take part in the formation of the complex. In other words, guest molecules cannot penetrate into the network and the extraction efficiency would be low for these polymers [15].

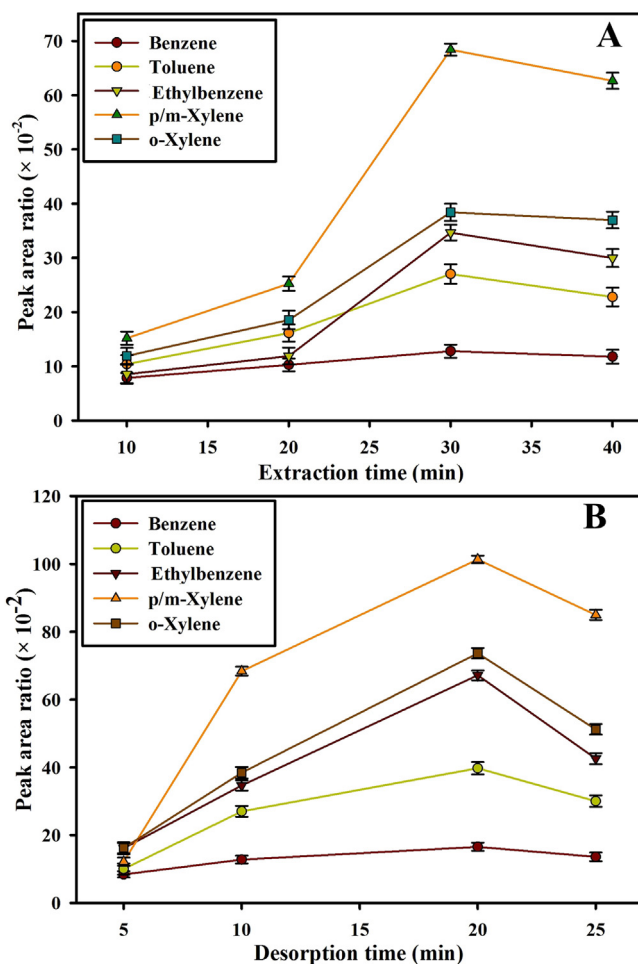


Fig. 5. Effect of A) extraction time, and B) desorption time on the extraction of BTEX. Other extraction conditions: sample volume: 10 mL, desorption solvent: methanol, desorption time: 5 min (for A), extraction time: 30 min (for B).

3.2.2. Extraction time

For μ -SPE, mass transfer of analyte from the sample to the sorbent materials is time-dependent and equilibrium-based rather than an exhaustive extraction process. Extraction time is a key factor affecting extraction efficiency [20]. In our experiments, the extraction time was set to range within 10–40 min at a constant stirring rate (1000 rpm). Our determination was done by extracting 10 mL of 100 ng/mL aqueous solution of each analyte. The analytes were eluted by ultrasonication with methanol, as a desorption solvent, for 5 min.

Generally, the analytes-to-internal standard peak area ratio increased with an extraction time up to 30 min, with no significant improvement thereafter.

As can be seen in Fig. 5A, peak area ratios of the analytes to internal standard decreased over prolonged extraction; it was due to the desorption of analytes beyond the optimum time: which is also, a common observation in microextraction studies [4]. Based on these results, an optimum extraction time of 30 min was selected for further experiments.

3.2.3. Desorption time

The effect of desorption time was explored in the range of 5–25 min. As mentioned before, experiments were done by extracting 10 mL of 100 ng/mL aqueous solution of each analyte with an elution time of 5 min with ultrasonication by methanol as a desorption solvent. Fig. 5B shows that the analytes-to-internal standard peak area ratios increased with increasing desorption time; indeed,

Table 2
Figures of merit of proposed method for determination of BTEX compounds in aqueous samples.

Parameter	Benzene	Toluene	Ethylbenzene	p/m-xylene	o-xylene
Equation	$y = 0.1396x + 0.0374$	$y = 0.2425x - 0.0978$	$y = 0.2344x - 0.0081$	$y = 0.2960x - 0.0966$	$y = 0.3154x - 0.1190$
Linearity (ng/mL)	2.0–500.0	1.0–500.0	1.0–500.0	0.5–500.0	0.5–500.0
LOQ (ng/mL)	2.0	1.0	1.0	0.5	0.5
LOD (ng/mL)	0.60	0.30	0.30	0.15	0.15
r^2	0.999	0.999	0.997	0.998	0.999
RSD (%) ^a	7.5	6.5	11.2	5.5	7.0
EF ^a	23.0	43.6	39.1	41.4	45.4
Recovery (%)	46.0	87.2	78.2	82.8	90.0

^a RSDs (n = 5) and EFs were calculated at concentration level of 100 ng/mL for each analyte.

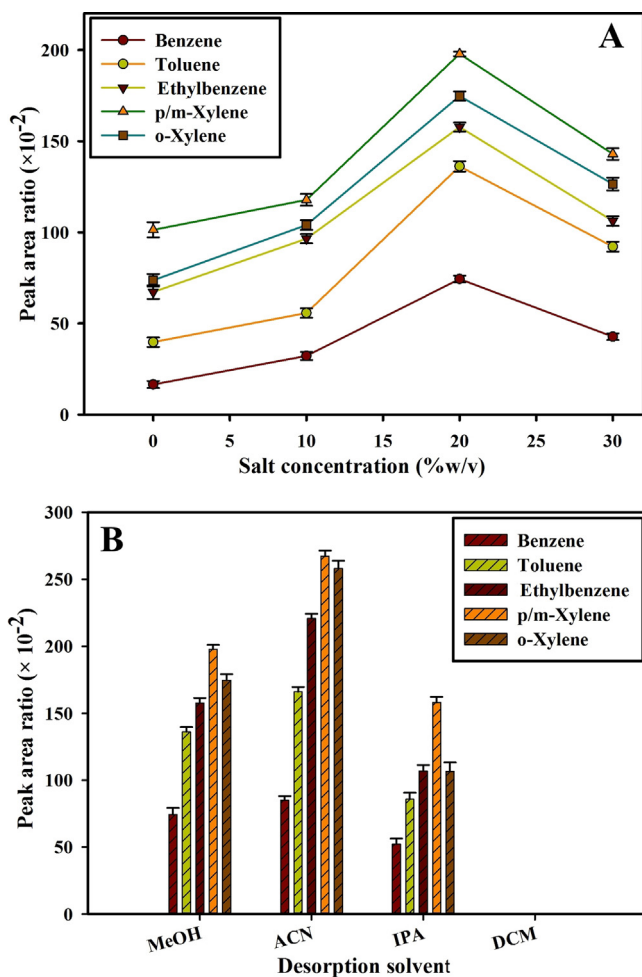


Fig. 6. Effect of A) salt concentration and B) desorption solvent on the extraction of BTEX. Other extraction conditions: sample volume: 10 mL, extraction time: 30 min, desorption solvent: methanol (for A), desorption time: 20 min.

peak areas showed an increase with desorption time from 5 to 20 min, but a decrease thereafter. Prolonged desorption time could conceivably lead to re-adsorption of the analytes. This is in agreement with other microextraction studies (e.g., Basheer et al. work on microextraction and determination of persistent organic pollutants in tissue samples [30]). Also evaporation of the analytes due to increased temperature during sonication may explain this issue. Based on this, 20 min was selected as the optimum desorption time.

3.2.4. Salt concentration

The salting out effect on the extraction efficiency of the proposed μ -SPE procedure was determined by adding NaCl salt to the aqueous solution at different percentages ranging from 10% to 30% (w/v).

Accordingly, the extraction yields of the analytes were observed to be enhanced with the salt concentration since aqueous solubility decreased with increasing the ionic strength by introducing further NaCl into the μ -SPE process. The results (Fig. 6A) showed that the extraction efficiency was maximized when NaCl concentration reached 20%. However, further increase in NaCl concentration was associated with an opposite effect, leading to reduced extraction yield. This may be due to the increase in viscosity of the aqueous sample following the addition of large amounts of sodium chloride, thereby impeding the mass-transfer process. The rate of mass transfer of analyte from aqueous phase to solid sorbent decreased, and the amount of time required to attain equilibrium increased. This is not an unusual observation for microextraction procedures [8].

3.2.5. Desorption solvent

Selection of a suitable desorption solvent was investigated based on the solubility of tea bag membrane and analytes and the polarity of the solvent. BTEX is relatively hydrophobic and has strong interactions with the sorbent, so that it may not be easily desorbed if the wrong solvent is used. Both tea bag and β -CDP are stable in many organic solvents such as methanol, isopropanol, dichloromethane, and acetonitrile. Therefore, these solvents were tested as desorption solvents. Based on the results (Fig. 6B), acetonitrile, most probably by virtue of its nonpolar characteristic, exhibited greater affinity toward the BTEX, giving better peak areas compared to other solvents. Other solvents (e.g., dichloromethane) were also investigated, but in the case of dichloromethane, it was impossible to collect the solvent desirably after ultrasonic treatment (as a result of solvent evaporation). Hence, based on the results, acetonitrile was selected as the optimal desorption solvent for further experiments.

3.3. Method validation

To evaluate the applicability of the proposed procedure for extracting BTEX, the repeatability, linearity, limits of quantification (LOQs) and limits of detection (LODs) were investigated under the optimal extraction conditions (polymer A as sorbent; extraction time of 30 min; acetonitrile as desorption solvent; desorption time of 20 min; salt addition at 20% w/v). The results are shown in Table 2. The linear ranges of between 2.0 and 500.0 ng/mL for benzene, between 1.0 and 500.0 ng/mL for toluene and ethylbenzene, and between 0.5 and 500.0 ng/mL for the other two analytes were obtained with good coefficients of determination (r^2) ranging between 0.997 and 0.999. The LODs ($S/N = 3$) were in the range of 0.15 and 0.60 ng/mL whereas the LOQs ($S/N = 10$) were in the range of 0.5 and 2.0 ng/mL. The precision of the proposed method was then evaluated; percentage relative standard deviations (RSDs) for five-replicate experiments were found to be <11.2%.

Table 3

Comparison of proposed method with other methods applied for the determination of BTEX in water samples.

Extraction Procedure	Sorbent/fiber	Linearity (ng/mL)	LOD (ng/mL)	RSD (%)	Ref.
SPE-GC-FID ^a	C ₁₈	8000–35000	104–372	2.9–3.5	[31]
SDME-GC-FID ^a	2-octanone	10–20000	0.8–7	1.81–2.47	[32]
DLLME-GC-FID ^a	CS ₂	0.2–100	0.1–0.2	0.9–6.4	[33]
HF-LPME-GC-FID ^a	1-octanol	50–20000	5–30	2–4.6	[34]
SPME-GC-FID ^a	PDMS-IL ^a	0.3–200	0.1–2	3.8–8.5	[35]
SPME-GC-FID	carbon–zirconium oxide nanocomposite	0.2–200	0.05–0.56	4.9–6.7	[36]
SPME-GC-FID	SBA–15 mesoporous silica ^a	1.5–950	0.15–0.42	6.8–10.9	[37]
HS-SPME-GC/MS ^a	PDMS	1–5000	0.3–5	2.4–6.5	[38]
HS-SPME-GC-FID	CNT/poly(o-toluidine) composite ^a	0.5–300	0.03–0.06	3.2–7.5	[39]
HS-SPME-GC/MS	PoA/GONSSs	0.1–500	0.01–0.06	4.9–7.3	[40]
MSPE-GC/MS	Chitosan	0.5–50	0.01–0.04	2–3	[11]
MSPE-GC/MS	Zeolite/iron oxide composite	1–100	0.3–3	8–11	[41]
MSPE-GC-FID	3D-HND-G	1.5–500	0.5–1	6.2	[42]
MSPE-GC-FID	Poly-β-CD	0.5–500	0.15–0.6	5.5–11.2	Current method

^a SPE: solid phase extraction, SDME: single drop microextraction, DLLME: dispersive liquid–liquid microextraction, HF-LPME: hollow fiber liquid phase microextraction, SPME: solid phase microextraction, HS: headspace; PDMS: polydimethylsiloxane; IL: ionic liquid, SBA-15: Santa Barbara Amorphous, CNT: carbon nano tube, PoA/GONSSs: poly(o-anisidine)/graphene oxide nanosheets, 3D-HND-G: high nitrogen doped graphene.

Table 4

Analysis of real samples.

Sample	Analyte	Blank concentration (ng/mL)	Spiked concentration (ng/mL)	Found (ng/mL)	RR%	RSD (%) (n = 3)
Drinking water	Benzene	n.d. ^a	20.0	13.3	66.5	7.1
	Toluene	20.1	20.0	38.6	92.5	6.6
	Ethylbenzene	13.3	10.0	21.6	83.0	11.3
	p/m-Xylene	17.9	20.0	35.2	86.5	5.7
	o-Xylene	17.2	20.0	36.1	94.5	7.3
Rain water	Benzene	19.4	20.0	32.3	64.5	7.4
	Toluene	35.3	40.0	71.5	90.5	6.5
	Ethylbenzene	38.1	40.0	75.2	92.8	11.7
	p/m-Xylene	52.8	50.0	100.2	94.8	5.7
	o-Xylene	65.6	70.0	128.9	90.4	7.1
Agricultural water	Benzene	21.6	20.0	36.8	76.0	7.5
	Toluene	30.6	30.0	61.0	101.3	7.1
	Ethylbenzene	34.1	30.0	62.3	94.0	11.8
	p/m-Xylene	58.5	60.0	118.7	100.3	5.9
	o-Xylene	71.9	70.0	138.3	94.9	7.5
Well water	Benzene	22.6	30.0	44.7	73.7	7.3
	Toluene	34.3	40.0	73.2	97.3	6.9
	Ethylbenzene	45.4	50.0	92.9	95.0	12.0
	p/m-Xylene	71.8	70.0	140.4	97.9	6.1

^a n.d.: non-detected.

The recovery (R) and enrichment factor (EF) were calculated based on the following equations:

$$R = \left(\frac{n_{\text{organic}}}{n_{\text{aqueous}}} \right) \times 100\% = \left(\frac{V_{\text{organic}}}{V_{\text{aqueous}}} \right) \times \left(\frac{C_{\text{organic}}}{C_{\text{aqueous}}} \right) \times 100 \quad (1)$$

$$EF = \left(\frac{C_{\text{organic}}}{C_{\text{aqueous}}} \right) \quad (2)$$

Where n_{organic} is the amount of analyte enriched in the organic desorption solvent while n_{aqueous} is the total amount originally present in the sample. The C_{organic} is the final analyte concentration in the organic desorption solvent and C_{aqueous} is the initial analyte concentration within the sample solution. The V_{organic} is the volume of organic desorption solvent and V_{aqueous} is the aqueous sample volume.

EFs of 23.0–45.4 ($EF_{\text{max}} = 50.0$) that corresponded to the recoveries ranging from 78.0–90.0% except for benzene (46.0%) were achieved.

The proposed method was compared with those of previous reports (Table 3) for BTEX analysis including solid phase extraction (SPE) [31], single drop microextraction (SDME) [32], dispersive

liquid–liquid microextraction (DLLME) [33], hollow fiber liquid phase microextraction (HF-LPME) [34], solid phase microextraction (SPME) [35–40], and micro-solid phase extraction (MSPE) [10,41,42] procedures. It is seen that the LODs and RSDs found in the present work are comparable with the other ones, despite the fact that some of them have used MS detection [10,38,40,41]. Also the linearity of proposed method is wider than other MSPE [10,41,42] and some SPME [35,36,39,40] procedures.

3.4. Analysis of environmental water samples

The developed method using β-CDP as μ-SPE sorbent was employed for BTEX extraction from 10 mL real samples of drinking, rain, agricultural and well water. The results are shown in Table 4. The water samples were subjected to μ-SPE without filtration. As expected, since BTEX is ubiquitous, real samples were contaminated with them. As shown by the results listed in Table 4, individual concentration of BTEX in the samples ranged between non-detectable and 71.9 ng/mL, as detected with RSDs (n = 3) in the range of 5.7–12.0%. Their presence was confirmed by spiking BTEX standards into real samples at the same concentration as that in

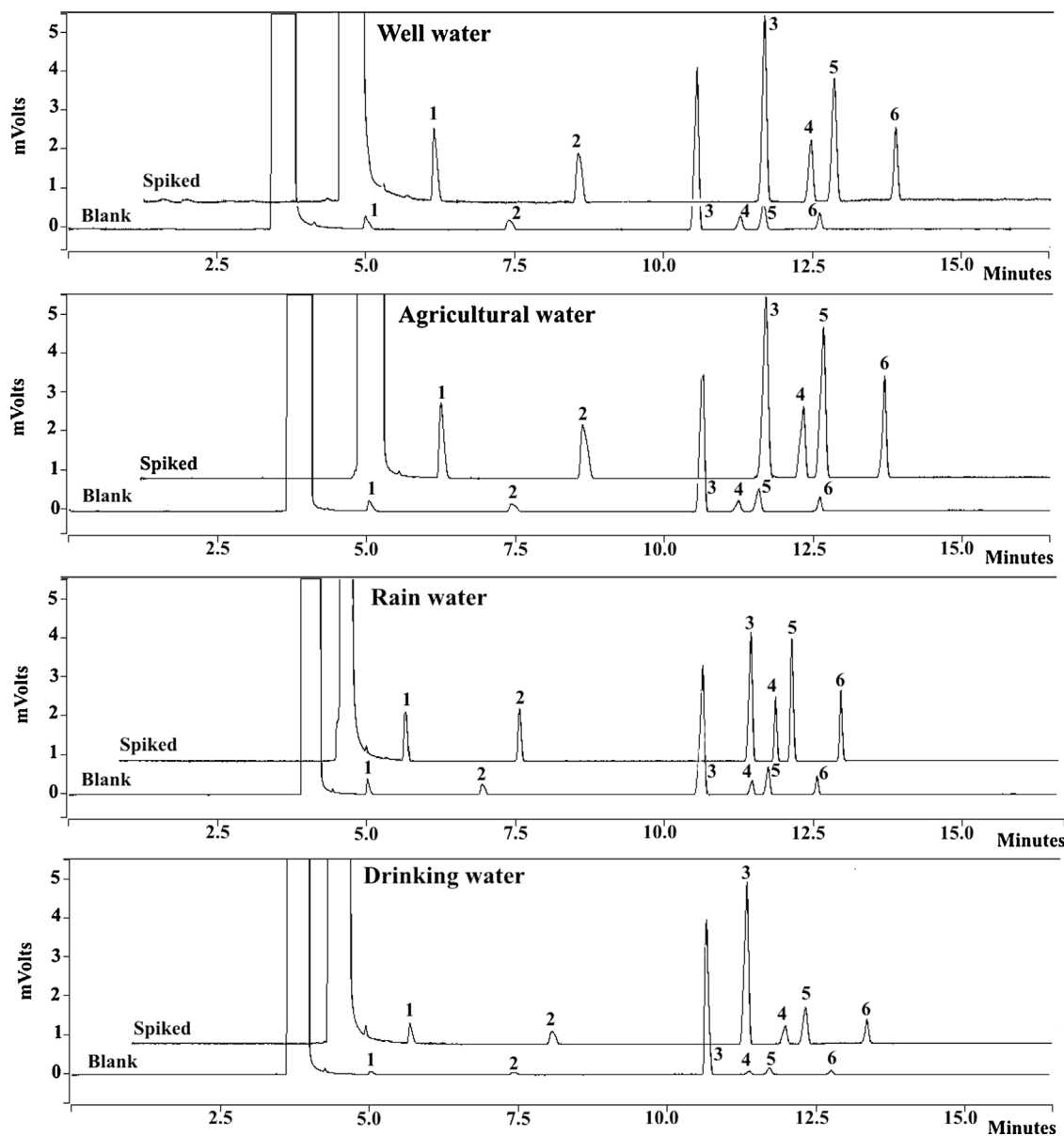


Fig. 7. Typical chromatograms obtained after μ -SPE from spiked real water samples. Peak identification: (1) benzene, (2) toluene, (3) chlorobenzene (IS), (4) ethylbenzene (5) p/m-xylene and (6) o-xylene.

real samples followed by reanalyzing the samples (Fig. 7). Indicating the effect of the sample matrix on extraction, relative recoveries are defined as follows:

$$RR\% = \left(\frac{C_{\text{found}} - C_{\text{blank}}}{C_{\text{added}}} \right) \times 100 \quad (3)$$

where C_{found} , C_{blank} , and C_{added} are the concentration of the analyte after addition of known amount of standard into the real sample, the concentration of analyte in real sample, and the concentration of known amount of standard, which was spiked into the real sample, respectively. The relative recoveries were found to range within 64.5–101.3%. These results demonstrated that β -CDP is a suitable sorbent for the μ -SPE of BTEX in environmental aqueous samples.

4. Conclusion

μ -SPE using β -CDP as a sorbent combined with GC-FID was successfully applied to determine trace amounts of BTEX in environmental water samples. Using a tea bag with its hydrophilic

nature and fast water absorption capability, one could overcome the poor wettability of the polypropylene membrane. Also tea bag filter shielded the β -CDP particles from harmful matrix effects. Therefore, the proposed procedure combined sample cleanup and preconcentration into a single step. Other advantages of the proposed μ -SPE included lower solvent consumption and hence lower waste generation. So, the proposed method has a significant potential for extraction and determination of BTEX. Further studies on μ -SPE using β -CD as a sorbent for the determination of other water contaminants are being explored.

Conflict of interest

There are no financial or commercial conflicts of interest.

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