Talanta 130 (2014) 155–163

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

New macroporous β-cyclodextrin functionalized ionic liquid polymer as an adsorbent for solid phase extraction with phenols

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ARTICLE INFO

Article history:
Received 7 April 2014
Received in revised form
26 June 2014
Accepted 28 June 2014
Available online 5 July 2014

Keywords:
Cyclodextrin
Ionic liquid
GC–FID
Solid phase extraction
Phenols

ABSTRACT

Cyclodextrin-ionic liquid polymer (βCD-BIMOTs-TDI) is a new class of macroporous material and has great potential to be used as an SPE adsorbent material for extraction of phenols in river water samples. Six phenols, as model analytes, were extracted on a βCD-BIMOTs-TDI SPE cartridge, and then, eluted with 2 mL of methanol containing 1% acetic acid. The optimum experimental condition was 15 mL of sample volume (sample at pH 6) and 2 mL of methanol containing 1% acetic acid as an eluent solvent. The eluent concentration was determined by using Gas Chromatography–Flame Ionization Detector (GC–FID). Under optimized condition, high sensitivity (detection limits 0.23–0.35 μg/L) and good recoveries (87–116%) were achieved with satisfactory relative standard deviation (RSD) (0.1–1.7%). The developed βCD-BIMOTs-TDI-SPE was then compared with other adsorbents, and the obtained results showed that the βCD-BIMOTs-TDI exhibited higher extraction recovery due to the unique structure and properties. Finally, the βCD-BIMOTs-TDI was applied as a solid phase extraction sorbent for phenols determination under optimized condition, in river and tap waters, prior to the GC–FID separation.

1. Introduction

Sample pre-treatment is very important, and it is a laborious step in chemical analysis, especially when dealing with environment sample, due to the complex matrices of environment samples and extremely low concentration of contaminants. Thus, the most common and conventional technique for the analysis of environmental samples is the solid phase extraction (SPE), which is a widely used technique for environmental sample pre-treatment due to its high recoveries, short extraction time, high enrichment factor, low consumption of organic solvent, and ease of automation [1]. In SPE, the choice of adsorbent is the main key point because it controls the parameters, such as the selectivity, affinity, and the capacity of the method. Apart from that, the SPE adsorbent type also plays a very important role on the recoveries of the target analyte in the SPE process. Therefore, during the SPE cartridge selection, the characteristics of the adsorbent and physical–chemical properties of the target analyte need to be considered in order to develop a good method [2]. However, the commonly available SPE sorbent, such as C18 silica, spherical hydrophobic polystyrene-divinylbenzene adsorbent resin (HR-X), and polystyrene-divinylbenzene adsorbent resin (HR-P), are applicable for a limited number of analytes. Furthermore, the reusability of the SPE cartridges is also a problem. Thus, a new SPE adsorbent is of high value.

Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to eight glucose units. Generally, CDs are composed of 6, 7, or 8 D-glucose units, connected by α-1,4-glucosidic linkages, which are categorized as α-, β-, and γ-CD, respectively. The inner cavity of the CDs is hydrophobic and it is able to form inclusion complexes with various molecules through host-guest interactions (Van Der Waals force, hydrophobic interaction, electrostatic affinity, dipole–dipole interaction, and hydrogen bonding) [3–6]. β-CD is the most largely produced CD used in many fields, including pharmaceuticals, food, cosmetics, chemical products, and technologies [7]. The applications include chemical separations [8,9], adsorbents [10,11], food processing [12], and pharmaceutical excipients [13].

On the other hand, ionic liquid (IL) is a kind of salt, whereby the ions are poorly coordinated. These compounds are found to be liquid below 100 °C or even at room temperature (RTILs) [5,14]. Besides, ILs basically exhibit several unique properties, such as non-flammability, low viscosity, chemical and electrochemical

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http://dx.doi.org/10.1016/j.talanta.2014.06.067
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stability and non-volatility [15]. Furthermore, many researchers are interested with ILs because they can remain in liquid state over a wide temperature range. Recently, the number of publications and reviews on ILs has increased due to the growing interest and application of ILs in analytical chemistry [16–20]. The applications of ILs in analytical chemistry have mostly been related to extractions [19] and separations [21].

The ability of ILs to self-assemble in different domains, either polar or non-polar, has made us to consider it as a templating solvent in some reactions. Thus, these properties of ILs have led us to the development of a new supramolecular based polymer [22]. Recently, new types of IL polymers have become famous because they exhibit the properties of ILs and polymers [23]. The unique properties of β-CD polymers and ILs have allowed us to functionalize β-CD with the ILs in order to develop a new generation of macroporous material to be applied in the extraction studies. The physical properties of CD can be altered by functionalising it with various precursors in order to make them suitable for a wide range of application [24,25].

To the best of our knowledge, cyclodextrin functionalized ionic liquid (CD-IL) materials have been applied as stationary phases in high performance liquid chromatography (HPLC) [26,27], as chiral selectors in capillary electrophoresis [28,29], and they have been used in a preliminary sorption study for the removal of organic pollutants and heavy metals [30]. Recently, the applications of cyclodextrin-ionic liquid polymer (CD-ILP) in SPE have been reported by Zhou et al., for the analysis of kaempferol and magnolol in real samples [31,32]. Previously, we have successfully synthesized, characterized, and applied new macroporous CD-ILP (βCD-BIMOTs-TDI) for the removal of phenols [33,34]. Even though the CD based materials have been applied as SPE adsorbents for various analytes [35,36], the application of CD-ILP in SPE for phenols has yet to be reported. Thus, in this work, we demonstrated a new SPE method using new macroporous βCD-BIMOTs-TDI powder as an adsorbent. Due to high toxicity and the widespread of environmental occurrences, phenols were selected as model analytes in this study [37–39]. Even though there have been many works that have been published on the development of new SPE sorbents for the extraction of phenols [40–43], this is the first study to report on the application of CD-ILP (βCD-BIMOTs-TDI) as an adsorbent in SPE for the determination of phenols.

2. Experimental section

2.1. Standard, reagents, and chemicals

2-chlorophenol (2-CP), 2-nitrophenol (2-NP), 2,4-dichlorophenol (DCP), 4-chlorophenol (4-CP), 4-chloro-3-methylphenol (4-CMP), and 2,4,6-trichlorophenol (TCP) were purchased from Sigma Aldrich (Steinheim, Germany) (Fig. 1), while β-CD was purchased from Acros (Hungary) (99%). 1-benzylimidazole and toluene 2,4-diisocyanate (TDI) were supplied from Sigma Aldrich. All the solvents and chemicals used were of analytical and chromatographic grades, respectively. They were used as received. Double distilled water was used throughout the study. All the reactions were performed under inert conditions. *N*,*N*-dimethylformamide (DMF) and hexane anhydrous were purchased from Merck. Chromabond C-18 sorbent, spherical hydrophobic polystyrene-divinylbenzene adsorbent resin (HR-X), and polystyrene-divinylbenzene adsorbent resin (HR-P) were purchased from Macherey-Nagel (Duren, Germany). HPLC grade of solvents were purchased from Fisher Scientific (Leicestershire, UK). The standard stock solutions of phenols (1000 mg/L) were prepared in methanol and stored in a dark amber glass at 4 °C to prevent degradation. The working solution was freshly prepared by diluting the stock solutions with water. p-Toluene sulfonic anhydride was prepared according to a literature procedure [44], and was used without further purification.

2.2. Instruments

Agilent 7890A GC system with an Agilent 5975C Series GC/FID from Agilent Technologies Inc. (Santa Clara, CA, USA) was used to analyse the phenols. HP-5MS GC column (30 m × 0.32 mm i.d. and 0.25 μm film thickness) was used. Helium, as a carrier gas, was used at a flow rate of 1.0 mL/min. βCD-BIMOTs-TDI and βCD-TDI were characterized using several techniques. The Fourier Transform Infra-Red (FT-IR) spectra were recorded on a Perkin–Elmer RX1 FT-IR between 4000 cm^{-1} and 400 cm^{-1} with a resolution of 2 cm^{-1}. The samples were adequately mixed with KBr powder and pressed into disks. The morphology of the samples was obtained from the Scanning electron microscope (SEM) Leica S440. The Brunauer–Emmett–Teller (BET) analysis was determined from low-temperature nitrogen adsorption isotherms at 77.40 K using Quantachrome Autosorb Automated Gas Sorption System. Typically, at least 1 g of the sample was used each time during the analysis. The average pore diameter and pore volume of the samples in dry state were measured from the adsorption branch of the isotherms by Barret–Joyner–Halenda (BJH) model, while the surface area was obtained via Brunauer–Emmett–Teller (BET) method.

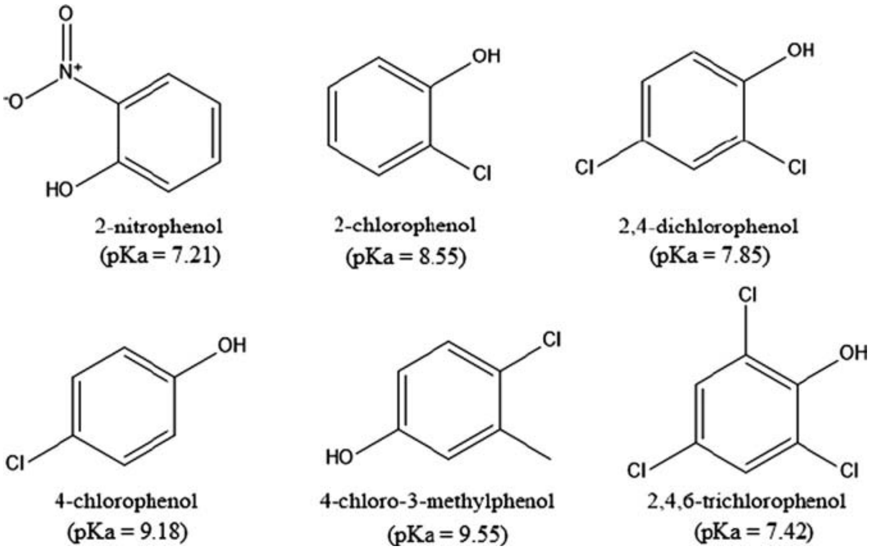
2.3. Chromatographic conditions

Both the injection port and detector temperatures were set at 260 °C. The gas chromatography temperature profile was set at 35–220 °C, starting at 35 °C (held for 1 min) and ramped at 35–220 °C/min (held for 8 min). The sample (1 μL) was injected manually into the injection port under splitless mode.

2.4. Synthesis of the adsorbents

The βCD-BIMOTs-TDI adsorbent was prepared according to our previous work [33,34], as shown in Scheme 1. First, 6-*O*-monotosyl-6-deoxy-β-cyclodextrin (β-CDOTs) was synthesized according to the method proposed by Zhong and his co-workers [44]. The reaction was carried out, by reacting β-CDOTs with 1-benzylimidazole (BIM) in the DMF solvent. Benzylimidazole can easily undergo nucleophilic substitution, since tosyl is a good leaving group. The preparation of monofunctionlized β-cyclodextrin with BIM (βCD-BIMOTS) was carried out according to the following procedure [29]: Appropriate amounts of BIM (1.23 g, 7.8 mmol) and CDOTs (1.00 g, 0.78 mmol) were dissolved in excess amount in anhydrous DMF (40 mL) and the solution was stirred at 90 °C in an inert atmosphere. The resultant solution was cooled to room temperature after two days, and was slowly added into acetone. The obtained mixture was stirred for 30 min, and thereafter, filtered and washed again with acetone. The final product was recrystallized three times from hot water in order to get the final product, which was yellowish precipitate.

Lastly, the insoluble modified βCD-BIMOTs-TDI adsorbent was prepared according to the polymerization process, adopted from the method of Mahlambi et al., [30]. Briefly, βCD-BIMOTs (0.69 mmol) was dissolved in 30 mL of anhydrous DMF, followed by the addition of toluene 2,4-diisocyanate (TDI) (6.9 mmol) drop wise at room temperature, and the mixture was stirred for 24 h at 70 °C. Unmodified βCD-TDI polymer was prepared by using the same method as above, by reacting 0.88 mmol of βCD with 8.8 mmol of TDI. The obtained polymers were then precipitated by the addition of excess acetone and thereafter, filtered and washed with acetone. Finally, the obtained polymers were washed with doubly distilled water in order to remove unreacted cross linkers and were dried overnight under reduced pressure prior to use.



2-nitrophenol (pKa = 7.21)
2-chlorophenol (pKa = 8.55)
2,4-dichlorophenol (pKa = 7.85)
4-chlorophenol (pKa = 9.18)
4-chloro-3-methylphenol (pKa = 9.55)
2,4,6-trichlorophenol (pKa = 7.42)

Fig. 1. Types and structures of phenols used in this study.

2.5. *The solid phase extraction (SPE) procedure*

βCD-BIMOTs-TDI (100 mg) was placed in a 3 mL SPE polypropylene cartridge using upper and lower frits to avoid adsorbent loss. 12-port SPE vacuum manifold from Thermo Fischer Scientific (Waltham, MA, USA) was used to place the filled SPE cartridge. Prior to extraction, the cartridges were conditioned by passing 5 mL of methanol and 5 mL of water, respectively. 15 mL of spiked sample (5 mg/L of each phenol) was passed through the cartridge at a flow rate of 0.5 mL/min for optimization process. The prepared sorbent material in the cartridge was not allowed to dry at any moment. After the sample loading procedure, the SPE cartridge was then dried by passing air for 30 min. The retained phenols were then eluted from the adsorbent with 2 mL of methanol containing 1% of acetic acid, and finally, injected to GC–FID for analysis. For comparison purpose, the βCD-TDI SPE, C-18 SPE, HR-X SPE, and HR-P SPE were packed in 3 mL cartridges for extraction and a similar procedure as the βCD-BIMOTs-TDI SPE was followed.

2.6. *The determination of phenols in real samples*

Tap water samples were collected from a water tap in the lab (Universiti Malaya). Meanwhile, river water samples were collected in glass bottles from Taman Jaya, Petaling Jaya, Kuala Lumpur, Malaysia. The collected samples were filtered using 0.45 μm Milipore cellulose membrane, right after sampling. The pre-cleaned bottles were covered with aluminium and stored in the dark at 4 °C prior to analysis. In order to access the matrix effects, 0.5 mg/L and 1 mg/L of phenols were spiked to the river and tap water and their concentrations were determined by SPE using the βCD-BIMOTs-TDI adsorbent.

3. Results and discussion

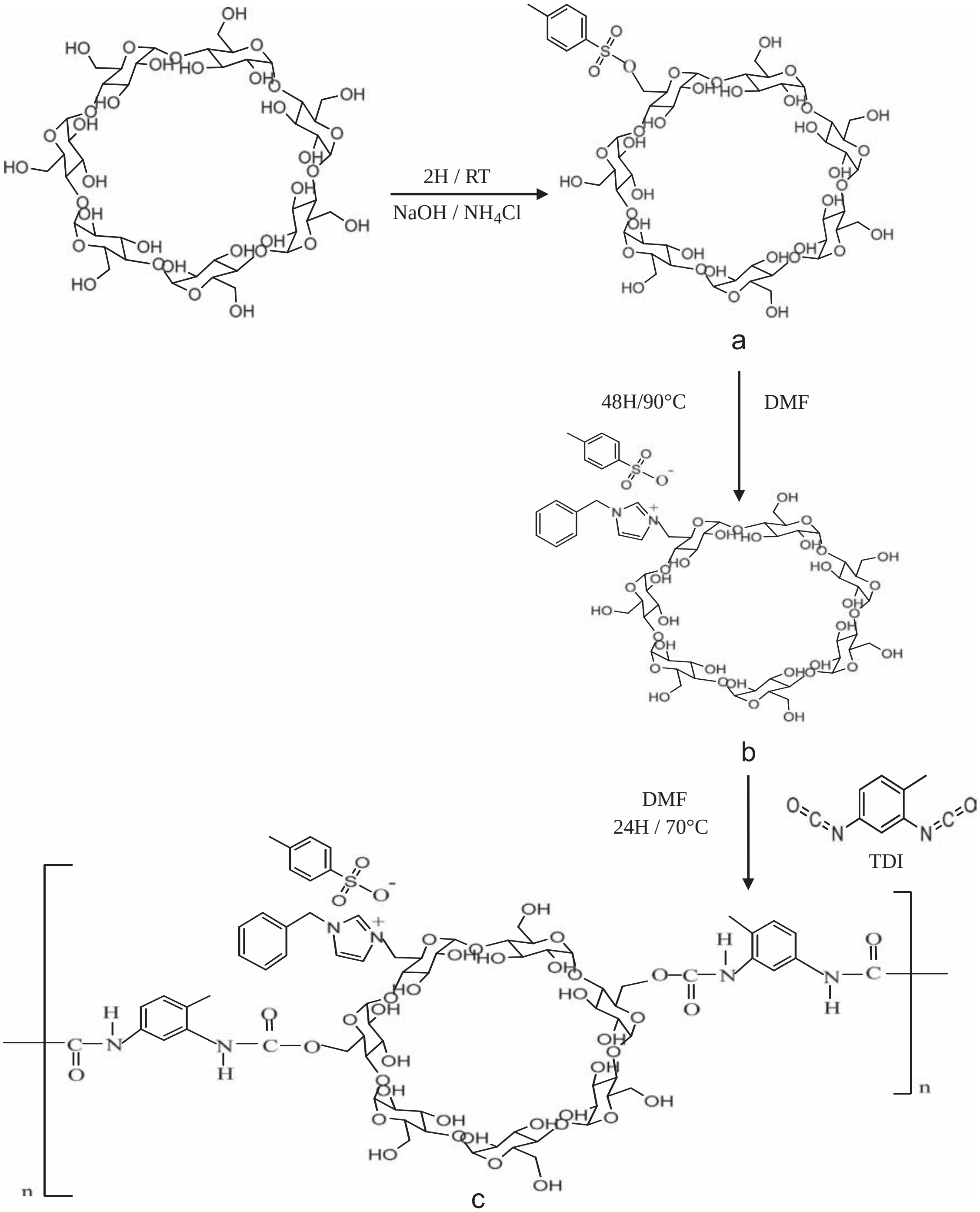
3.1. *Characterization of polymers*

The physicochemical properties of βCD-BIMOTs-TDI and βCD-TDI polymers are shown in Table 1. The FTIR spectra of (a) βCD-BIMOTs-TDI, and (b) βCD-TDI are shown in Fig. SI1 (Supporting Information). In the spectrum of βCD-BIMOTs-TDI, the presence of imidazole could be clearly seen at 3302 cm^{-1}. Apart from that, upon cross-linking with TDI, the peak at 2270 cm^{-1}, which corresponded to the isocyanate group, disappeared and the presence of carbamate linkage (NHCO) was clearly observed in the spectra of the polymers. Therefore, we can conclude that the polymerization process between βCD-BIMOTs and βCD with TDI had been complete [45]. The N_2 adsorption/desorption isotherm for βCD-BIMOTs-TDI exhibited type-II isotherm with H_3 type hysteresis loop, as shown in Fig. SI2 [46], while typical type-IV isotherm was obtained for βCD-TDI with H_3 type hysteresis loop. The pore size distribution for dry βCD-BIMOTs-TDI was calculated using the Barret–Joyner–Halenda model (BJH) and it showed that the βCD-BIMOTs-TDI was a macroporous material with 77.6 nm of pore size and 0.02435 cm^3/g of pore volume. In comparison, the βCD-TDI represented micropores with 1.585 nm of pore size and 0.02188 cm^3/g of pore volume. Prior to functionalization, the surface area of βCD-BIMOTs-TDI was found to be lower (1.254 m^2/g) compared to βCD-TDI (2.401 m^2/g). The surface morphologies of the polymers were investigated with Scanning Electron Microscope (SEM). Referring to Fig. 2a, the βCD-BIMOTs-TDI exhibited a totally different and unique crystalline structure with macropores in between, and this observation was supported by the findings from the BET result, while the βCD-TDI (Fig. 2b) was found to be in “shrinking” crystal structure with micropores on the surface.

3.2. *SPE optimization*

3.2.1. *Sample pH*

The extraction of phenols depends on the pH value of the sample solution because it is presented in different states according to different pH medium [47]. Moreover, as the solubility of the acidic/basic target analytes is affected together with dissociation equilibrium, an adjustment of the pH enhances the extraction process [48]. Therefore, in this study, the effect of sample pH on the recoveries was investigated in the range of 3 to 10, as shown in Fig. 3a. The obtained result illustrated that the sample pH greatly affected the adsorption of all the phenols for βCD-BIMOTs-TDI within the examined pH ranges. The best result was observed at pH 6, with recoveries of 80%, 43%, 88%, 75%, 84%, and 57% for 2-CP, 2-NP, DCP, 4-CP, 4-CMP, and TCP, respectively, and therefore, pH 6 medium was selected for the entire extraction process in this work. The obtained results can be explained by using the adsorption mechanism, which is dominated by the inclusion complex, hydrogen bonding, and Van Der Waals force [49]. Furthermore, neutral phenols are able to form inclusion complexes with hydrophobic cavity of CD [50], and in this study, the inclusion complex formation



Scheme 1. Synthesis pathway of (a) β-CDOTs, (b) βCD-BIMOTs and (c) βCD-BIMOTs-TDI.

Table 1
Physiochemical properties of βCD-BIMOTs-TDI.

Characteristics	βCD-BIMOTs-TDI	βCD-TDI
Specific surface area (m^2/g)	1.254 m^2/g	2.401 m^2/g
Pore size (nm)	77.6 nm (macropore)	1.585 nm (micropore)
Pore volume (cm^3/g)	0.02435 cm^3/g	0.02188 cm^3/g
N–H and O–H stretch	3302	3307
Absence of isocyanate group	2270	2270
Aromatic group in TDI	1600, 1450	1450
NHCO, carbamate linkage	1535, 1651	1653, 1534
C–N stretch	1153	–
N_2 adsorption/desorption isotherm	Type-II isotherm with H3 type hysteresis loop	Type-IV isotherm with H3 type hysteresis loop

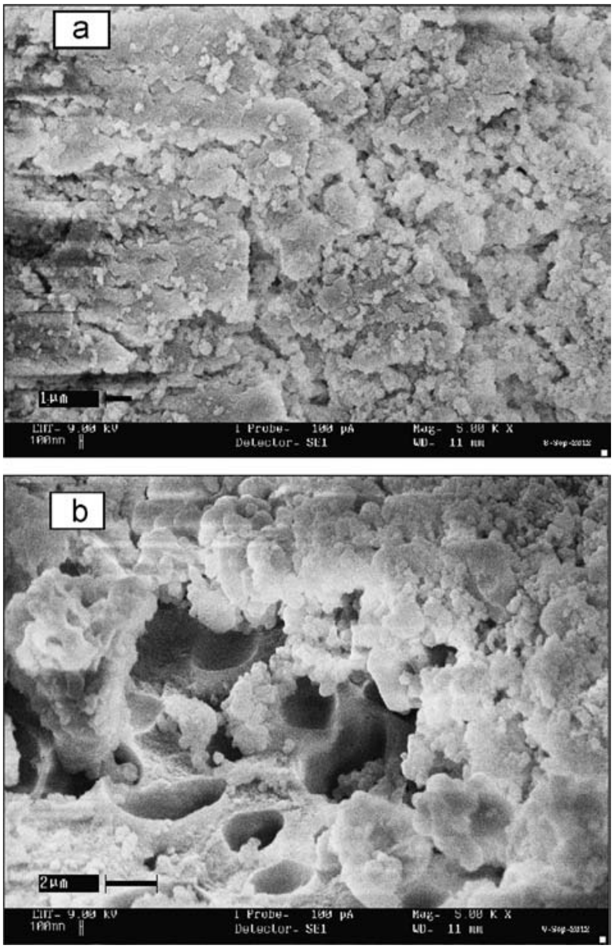


Fig. 2. SEM analysis of (a) βCD-TDI and (b) βCD-BIMOTs-TDI (Mag 5.00 KX).

could be the main interaction since the cavity of β-CD was maintained during the polymerization process apart from other interactions. The inclusion complex formation between the modified CD (βCD-BIMOTs) with the DCP had been proven in our previous work using ^{1}H NMR and 2D NMR experiments [34]. In addition, strong π–π interaction between the imidazolium ring of IL and phenol molecules also resulted in higher extraction recovery at pH 6 [34].

Apart from that, low and high pH medium were not suitable for the extraction process in this study because at low pH medium, the phenols were in protonated form, meanwhile, at high pH medium, they were in deprotonated form. It is well known that hydrophilic guest (protonated or deprotonated) would not be able to form inclusion complex with CD [49], thus, neutral pH medium was the most suitable, even though strong π–π interaction between imidazolium ring of the IL and the phenol molecules was present at both high and low pH medium. Furthermore, chlorophenols and nitrophenols were found to be ionisable when $\mathrm{pH} > \mathrm{p}Ka$ (the pKa values are listed in Fig. 1). Therefore, pH 6 was the best condition for this extraction process.

In addition, such results can be explained in accordance with the anion-exchange mechanism of phases based on benzylimidazoliumtosylate functionalized on β-CD. The ionization of the test compounds was suppressed, minimizing the ionic interaction at low pH medium, while at high pH, the phenols were fully negatively charged, and this favoured their interaction with the positively charged IL. However, due to high concentration of hydroxyl groups, which competed with the phenol molecules, there were lower adsorption and recoveries of phenols on βCD-BIMOTs-TDI [47]. Therefore, the recoveries were also in accordance with the ability of anion-exchange, and therefore, pH 6 medium was used for the entire extraction process.

3.2.2. *Sample loading volume*

The optimization process was carried out in order to investigate the effect of sample volume; the cartridge was loaded with 1–75 mL aqueous solution of phenols. Basically, for SPE satisfactory, the recoveries should obtain high sensitivity and enrichment factor. Thus, it was necessary to determine the breakthrough volume. As shown in Fig. 3b, the recoveries increased as the sample volume increased, but optimum percentage of removal was observed at 15 mL of sample volume. Therefore, 15 mL of sample volume was regarded as the breakthrough volume. The recoveries were low at low sample volume due to the limited phenols aqueous medium to adsorb the βCD-BIMOTs-TDI, while at high sample volume, the recoveries were also low due to the fact that in the presence of larger amounts of solvent, it would result in less interaction between the phenols and βCD-BIMOTs-TDI, and hence, resulted in lower adsorption and recoveries [47]. In addition, low recoveries at high sample volume could be also due to the sorbent breakthrough that was exceeded [48]. As a result, on the basis of optimization, a sample volume of 15 mL was selected as the optimal sample volume for the extraction process.

3.2.3. *The elution step*

In SPE, the eluting step is very important in order to desorb the retained phenols on βCD-BIMOTs-TDI with a suitable solvent. In this study, seven eluting solvents of different polarities, namely methanol, dichloromethane, hexane, ethanol, acetonitrile, ethyl acetate, and acetone, were investigated to find out the best eluting solvent. Strong elution solvents were able to displace all the analytes from the sorbent in a small volume [51]. So, polar solvents, such as methanol, acetonitrile, ethanol, and acetone, were the best candidates as the solvent strengths were higher compared to non-polar solvents (dichloromethane, hexane, and ethyl acetate). As shown in Fig. 3c, hexane showed poor eluting capability towards all the studied phenols and it indicated the strong affinity of phenols for βCD-BIMOTs-TDI. As shown in Fig. 3c, higher extraction recovery was achieved with methanol for all the studied phenols in the range of 76–113% compared to other solvents. This has been due to the properties of the methanol, which is a protic solvent and is able to elute polar phenols that may have hydrogen bonding with the hydroxyl/carboxyl groups on the βCD-BIMOTs-TDI's surface more effectively than aprotic solvent, such as acetonitrile [52]. Therefore, methanol was the most effective eluent as it gave the highest recoveries for all the studied phenols.

The eluent volume was optimized from 2 mL to 20 mL; the efficient elution could only be achieved with no less than 2 mL of methanol. The recoveries for all the phenols decreased as the eluent volume increased as the sample was diluted. Thus, 2 mL of methanol was used as eluent solvent for the extraction of the phenols.

3.2.4. *The washing step*

The βCD-BIMOTs-TDI sorbent was rinsed with hexane after the sample was loaded into the cartridges since hexane has poor eluting capability of phenols from βCD-BIMOTs-TDI sorbent, and therefore, it was used as a washing solvent in order to find out if the washing step increased the recovery of the retained phenols, and to displace any undesired matrices without displacing the analyte of interest. Furthermore, the collected washing solvent was also analysed with the GC–FID and the results indicated that the hexane solution did not elute the phenols effectively from the

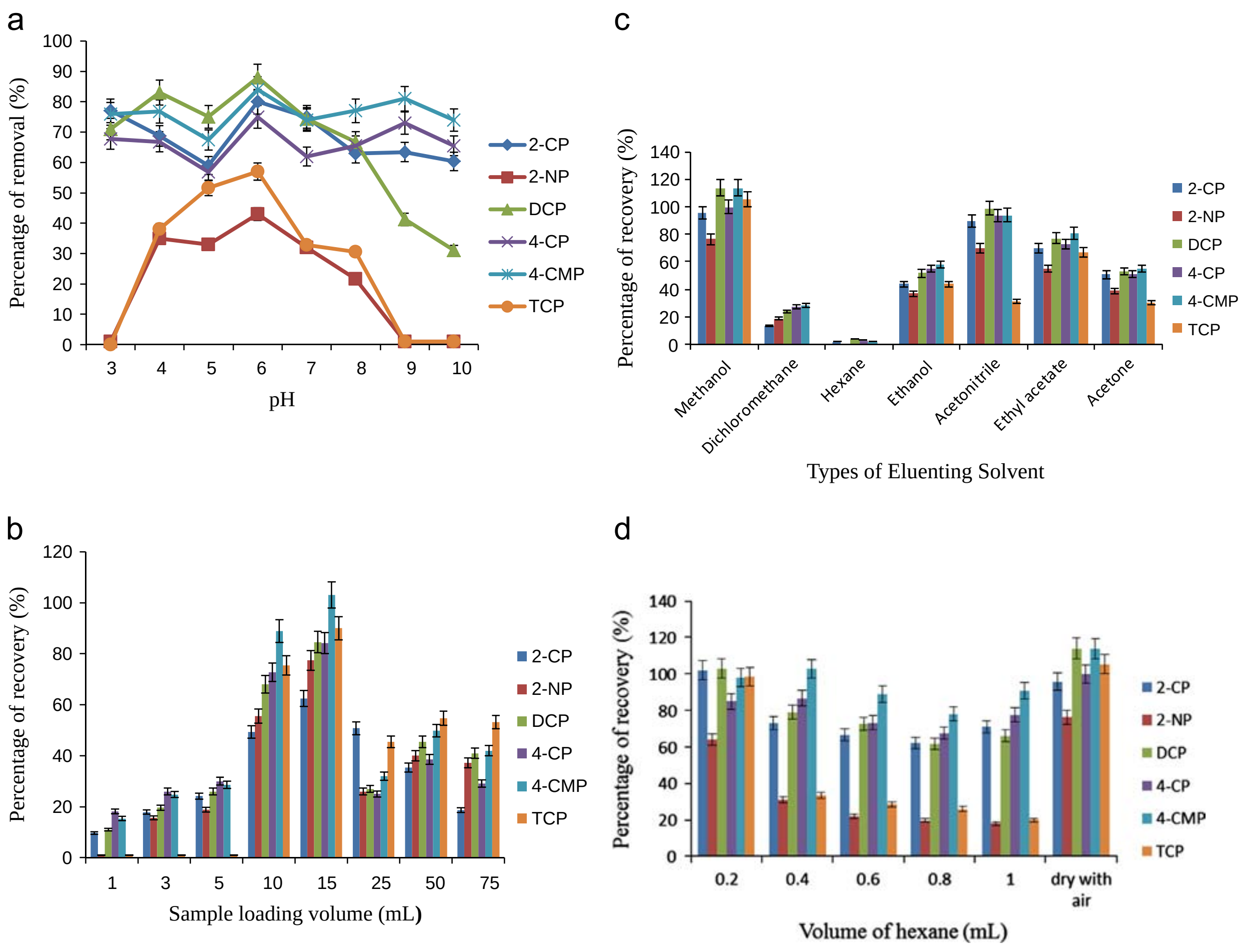


Fig. 3. (a) Effect of sample pH of analytes mixture on the recovery of phenols, (b) effect of different sample loading volume on recovery of phenols, (c) effect of eluting solvent on recovery of phenols, (d) effect of washing on the recovery of phenols.

cartridge. Therefore, hexane was used as a washing solvent in this study since it was a weak solvent and could not displace the phenols during the extraction process [53].

As shown in Fig. 3d, the volume of hexane was optimized from 0.2 mL to 1 mL, and the result showed that washing with 0.2 mL of hexane yielded higher percentage of recovery. Meanwhile, the drying step was introduced prior to the elution step to replace the washing solvent since the drying step reduced the volume of the solvent that retained in the sorbent after the sample loading step. Thus, the sorbent was allowed to dry with air for 30 min, which was considerably sufficient to remove the entire sample solvent which might be trapped in the sorbent pores. As expected, the extraction recoveries for all the studied phenols had been higher compared to the washed sorbent with solvent. Therefore, the 30-min drying step was used throughout the subsequent analysis.

3.2.5. *The effect of modifier*

A study on the effect of modifier was carried out in order to identify if it increased the extraction recoveries of the retained phenols on βCD-BIMOTs-TDI, especially 2-nitrophenol. Thus, the effect of modifier was looked into with the addition of 1% to 20% of acetic acid in 2 mL of elution solvent (methanol). The obtained result is shown in Fig. 4a, whereby 1% of acetic acid gave the highest extraction recovery for all the studied phenols. In addition, a significant difference could be observed from Fig. 4b, whereby, a comparison was done with and without the addition of 1% of acetic acid in the 2 mL of eluent solvent (methanol). The significant result could be seen, especially in the extraction recovery of 2-NP, which was increased up to 114%. Therefore, the addition of acetic acid in the eluent solvent as a modifier played an important role in desorbing phenols from the βCD-BIMOTs-TDI. This is because acetic acid would compete with the phenols for the functional groups in the binding sites, but too much of acetic acid would not benefit the elution step [40]. The complete elution of the analytes also guaranteed the reusability of this SPE cartridge. Thus, between the extraction processes, the cartridges were washed with methanol containing 1% of acetic acid and water to ensure that the cartridges could be made available immediately for the next extraction.

3.2.6. *Comparison with other adsorbents*

For the purpose of comparison, the SPE performance of βCD-BIMOTs-TDI adsorbent with unmodified βCD-TDI and some commonly available adsorbent materials, such as C-18 silica, spherical hydrophobic polystyrene-divinylbenzene adsorbent resin (HR-X) (spherical particles 85 μm, pore size 55–60 Å, surface area 1000 m^2/g), and polystyrene-divinylbenzene adsorbent resin (HR-P) (specific surface 1200 m^2/g, particle size 50–100 μm), was evaluated. In order to conduct these comparisons, the same amounts (100 mg) of different adsorbents were packed in 3 mL SPE cartridges. Optimization of extraction condition was carried out for βCD-TDI, C18 silica, HR-P, and HR-X adsorbents. The optimized condition was applied to extract the phenols using SPE, and the result is shown in Fig. 5. The obtained result showed that the βCD-BIMOTs-TDI sorbent yielded the highest recoveries (103–114%) of phenols among these studied sorbents. This result

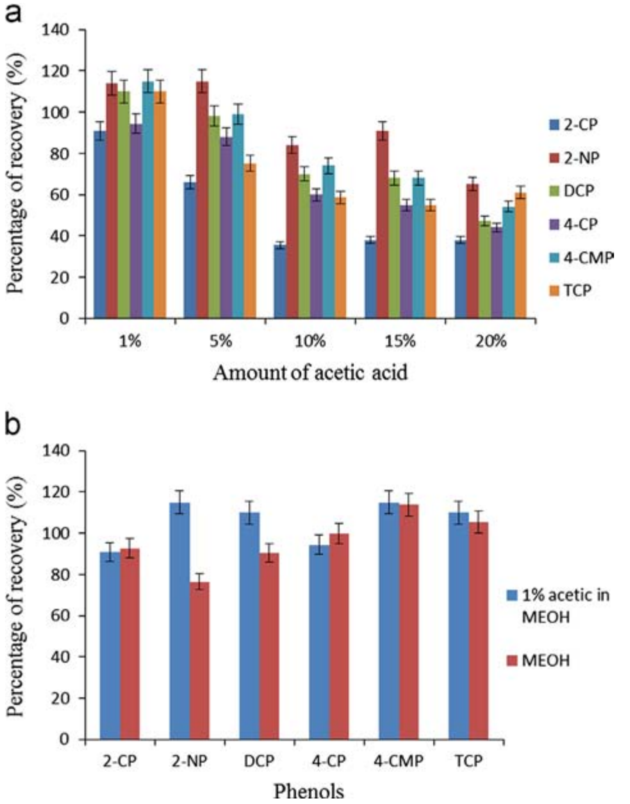


Fig. 4. (a) Effect of modifier on recovery of phenols, (b) comparison with and without addition of modifier on recovery of phenols. Extraction condition: 5 mL methanol ± 5 mL water as conditioning solvent, sample at pH=6, and 2 mL of methanol as elution solvent.

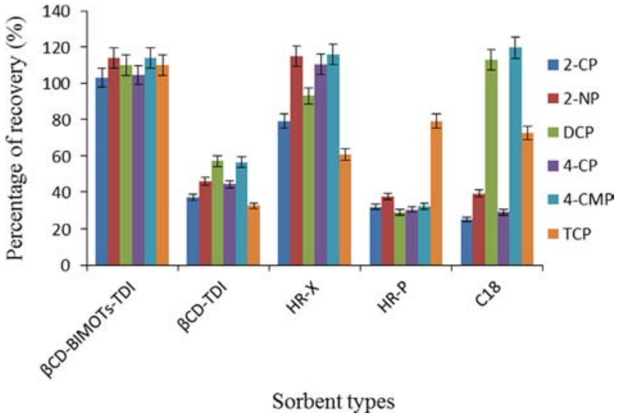


Fig. 5. Comparison of the performance of βCD-BIMOTs-TDI with other adsorbents (βCD-TDI, HR-X, HR-P and C-18) for the SPE of six phenols. The SPE cartridges were packed with 100 mg adsorbent in all cases. Extraction condition: 5 mL methanol ± 5 mL water as conditioning solvent, 15 mL of sample solution at pH 6 containing 5 mg/L of each phenol, and 2 mL methanol containing 1% of acetic acid as eluent solvent.

definitely justified the worth of βCD-BIMOTs-TDI as an SPE adsorbent.

The recovery of HR-X was also higher among all the studied phenols, in the ranges of 60.6–115%. Notably, no phenols were found in the washing solutions for HR-X, indicating that HR-X had good sorption capacity for the phenols, but lower recoveries were obtained compared to βCD-BIMOTs-TDI sorbent due to too stable adsorption and strong affinity of phenols towards the HR-X adsorbent.

The extraction process was easier to be conducted with C18 silica compared to βCD-BIMOTs-TDI adsorbent, but the adsorption was poorer. Phenols could be detected in the washing solution after the phenols were loaded on the C18 cartridge, indicating that 100 mg of the C18 silica had been insufficient for the retention of phenols, especially for 2-CP, 2-NP, and 4-CP, as their recoveries were too low (25%, 38%, and 29%) compared to TCP, CMP, and DCP that showed that C18 silica had poor sorption capacity for polar compounds. Higher sorption capacities of C18 towards TCP, CMP, and DCP were observed due to the increase in the number of chloro substituent, which further increased the hydrophobicity [54]. Thus, the obtained results of the present study clearly indicated that the hydrophobic interaction was predominant between C18 silica and the phenols. In order to increase the adsorption capacity with C18 silica, the mass of the adsorbent must be increased, but it would increase the cost of the analysis and it was unfavourable for instrument miniaturization, and meanwhile, the performance of HR-P was even poorer than the C18 silica as this could be due to the shortage of sorption capacity.

The performance of βCD-TDI sorbent was tested to investigate the effectiveness of the modified βCD-BIMOTs-TDI. The extraction recoveries were low (32–57%) for the βCD-TDI adsorbent. The presence of IL ring in the βCD-BIMOTs-TDI enhanced the selectivity of the phenols towards the βCD cavity compared to the unmodified βCD-TDI. Since strong π–π interaction and inclusion complex formation were the main interactions between the βCD-BIMOTs-TDI and the phenols, especially in the βCD-TDI sorbent, only weak inclusion interaction was present between the adsorbent and the analyte. Thus, the extraction recovery was low for the βCD-TDI compared to βCD-BIMOTs-TDI. This unique characteristic makes βCD-BIMOTs-TDI a powerful adsorbent material for the extraction of phenols.

3.3. Analytical performance of the proposed method

The optimized parameters for the extraction of phenols using βCD-BIMOTs-TDI were sampled at pH 6, 5 mL methanol+5 mL water as conditioning solvent, 15 mL sample loading volume, and 2 mL of methanol containing 1% of acetic acid as the elution solvent prior to the GC–FID analysis. A series of experiments were designed to obtain linear ranges, precision, detection limits, and other characteristics of the developed method. Good linearity with correlation coefficient (R^2) ranging from 0.9904 to 0.9978 was obtained for this method and the results are tabulated in Table 2. Based on a signal-to-noise ratio of 3, the limits of detection (LODs) were in the range of 0.23–0.35 μg/L, while the signal-to-noise ratio of 10 and the limits of quantification (LOQs) were in the range of 0.70–1.18 μg/L. The obtained LOD value in this study had been below the legal tolerance level for each phenol in drinking water (0.5 μg/L), according to the European Community Directive [55] and Japanese Ministry of Health, Labour and Welfare, that stated the maximum contaminant level for phenols in drinking water is 5 μg/L [56]. The repeatability was obtained by performing three extractions at the concentration of 0.1 μg/L under optimal conditions with 100 mg of sorbent. The relative standard deviations

Table 2
Analytical performance data of the proposed method.

Analyte	Linear range (μg/L)	r^2	LOD (μg/L)	LOQ (μg/L)	RSD (%) ($n=3$)
2-CP	0.01–6.00	0.9916	0.35	1.18	2.9
2-NP	0.01–5.00	0.9904	0.29	0.97	3.4
DCP	0.01–6.00	0.9916	0.24	0.79	1.3
4-CP	0.02–6.00	0.9917	0.33	1.08	1.8
4-CMP	0.02–6.00	0.9955	0.23	0.70	2.2
TCP	0.02–6.00	0.9978	0.25	0.82	1.0

Table 3
The recoveries and standard deviations of phenols in real environmental samples with a spiked concentration of 0.5 mg/L and 1 mg/L for each analyte.

Analyte	Tap water		River water	
	Concentration added (mg/L)	Recovery (%)	Concentration added (mg/L)	Recovery (%)
2-CP	0.5	111.7 (0.1)	0.5	101.9 (0.6)
	1	91 (0.2)	1	107.9 (1.1)
2-NP	0.5	116 (0.4)	0.5	116.3 (0.2)
	1	100.8 (0.4)	1	98 (1.1)
DCP	0.5	104 (0.3)	0.5	96 (0.2)
	1	90 (1.1)	1	87 (1.7)
4-CP	0.5	88 (0.1)	0.5	100 (0.2)
	1	100.8 (0.2)	1	98.8 (0.5)
4-CMP	0.5	115.1 (1.3)	0.5	115.2 (0.2)
	1	93 (0.7)	1	91.5 (0.5)
TCP	0.5	99.6 (0.3)	0.5	105.6 (0.4)
	1	104 (0.3)	1	103.7 (0.5)

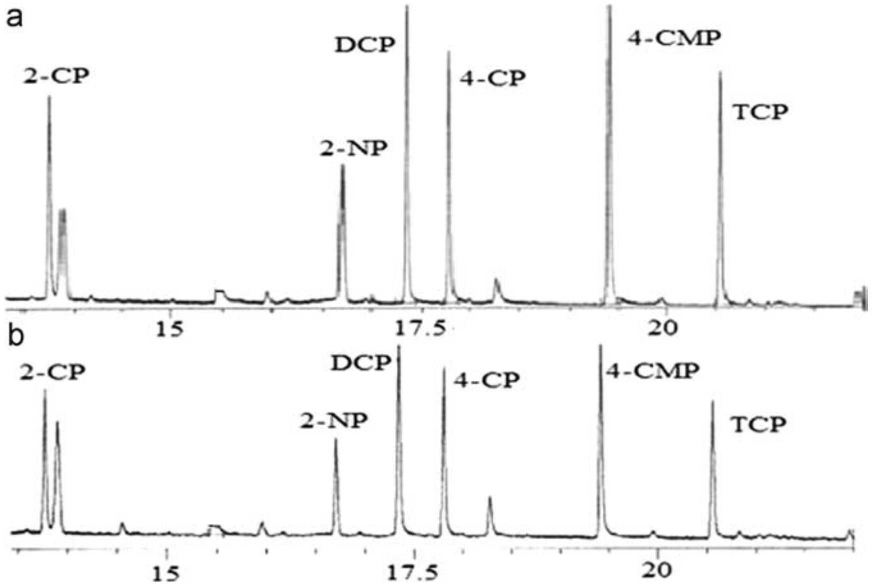


Fig. 6. Chromatogram obtained from the analysis of river water using βCD-BIMOTs-TDI SPE for phenols (Carrier Helium: 33 cm/s, constant flow, Oven: 35 °C for min, 35–220 °C at 8 °C/min: Splitless, 250 °C, FID, 300 °C, Spiking conc. (a) 1 mg/L, (b) 0.5 mg/L.

Table 4
Comparison of the represented method with other methods for the determination of phenols.

Clean-up	Determination				
	Technique	Recoveries (%)	RSD (%)	LOD (μg/L)	References
SPME (PANI, 50 °C, 50 min, NaCl)	GC–FID	69–111	8.0–15.0	0.7–58	[57]
HS-SPME	GC–FID	94–105	4.0–5.0	14–32	[58]
SPE	CE-CL	79–92	2.0	20–82	[59]
SPE	GC–MS/SIM	–	6.0	16–22	[60]
SPE	FI-Amperometric biosensor	–	2.6–3.8	19–66	[61]
βCD-BIMOTs-TDI-SPE	GC–FID	87–116	0.1–1.7	**0.23–0.35**	Current study

(RSDs) were in the range of 1.0% to 3.4% respectively, and these excellent results indicated that the developed method was simple, yet provided a sensitive procedure for the determination of phenols at trace levels.

3.4. *Real water sample analysis*

The applicability of the method for phenols was validated using real environmental aqueous samples, which were river water and tap water, with the proposed method. The pH of all the real samples was adjusted to 6 before SPE. None of the target analytes were detected in these water samples under optimized condition described and these samples were then spiked with phenols at a concentration of 0.5 mg/L and 1 mg/L in order to investigate the effect of the sample matrices. As shown in Table 3, the recoveries of the spiked phenols in the river and tap water samples were satisfactory, which were between 87% and 116%, and the relative standard deviations (RSDs) (0.1–1.7%) were lower than 5%. The typical chromatograms of river water samples at the concentration level of 0.5 mg/L and 1 mg/L for phenols are demonstrated in Fig. 6.

3.5. A comparison of the represented method with other methods

The proposed method in this study was compared with the previous study for the determination of phenols in water samples. The analytical methods developed previously are summarized in Table 4 for the determination of phenols in water. All these results indicated that the proposed method is a fast, reproducible, and provides a simple technique with low LOD and RSD values with good extraction recoveries.

4. Conclusion

In this work, the cyclodextrin-ionic liquid polymer (βCD-BIMOTs-TDI) was successfully applied as an adsorbent for SPE, coupled with GC–FID, for extraction of six selected phenols in tap and river water samples. The βCD-BIMOTs-TDI-SPE method offered an interesting and effective option for the analysis of phenols in environmental water samples. Higher recoveries were achieved with βCD-BIMOTs-TDI compared to other adsorbents due to its unique morphology and chemical structure. The βCD-BIMOTs-TDI adsorbent also exhibited some advantages, such as high sorption capacity towards phenols, good compatibly with different types of solvents, good repeatability, and no impact on sorbent drying. The performance of βCD-BIMOTs-TDI was successfully applied and compared with several other adsorbents and it exhibited low detection limit (0.23–0.35 μg/L) compared to the other previously reported methods. Thus, it is believed that this adsorbent can be a promising material for SPE. Currently, additional work is still in progress in order to extend the application of the current method.

Acknowledgements

The authors would like to seize this opportunity to express their gratitude to the University Malaya for the Research Grant (RP006A-13SUS), IPPP grant PV076/2012A, University Malaya Centre for Ionic Liquid for the funding, and High Impact Research Grant UM-MOE UM.C/625/1/HIR/MOHE/F00004-21001 from the Ministry of Higher Education Malaysia (MOHE). The authors also acknowledge the Advanced Medical and Dental Institute, University of Science Malaysia (IPPT) and MOHE for providing fellowship to one of the authors-cum-researchers, Mr. Muggundha Raoov s/o Ramachandran.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.06.067.

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