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Determination of parabens in water samples by cloud point extraction and aqueous two-phase extraction using high-performance liquid chromatography

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ABSTRACT

Five methods have been successfully developed which are the ionic liquid–two-phase extraction (IL-ATPS), ionic liquid–two-phase extraction with addition of β-cyclodextrin as modifier (IL-βCD-ATPS), cloud point extraction (CPE-DC193C), cloud point extraction with addition of β-cyclodextrin as modifier (CPE-DC193C-βCD), and cloud point extraction with addition of ionic liquid functionalized β-cyclodextrin as modifier (CPE-DC193C-βCD-IL). These methods are new, green, and simple extraction technique to couple with a reversed-phase high-performance liquid chromatography to get the optimum conditions for phase separation of parabens in water samples. The parameters, i.e. pH of the solution, water content, distribution coefficient, and preconcentration factor, are evaluated to get the optimum conditions for phase separation of parabens. The CPE-DC193C-βCD-IL method shows the highest losses of water content among other methods. It also produces the highest preconcentration factor and distribution coefficient. The lowest limit of detection of parabens in water samples is also demonstrated by the CPE-DC193C-βCD-IL method. The CPE-DC193C-βCD-IL method gives an excellent performance on the detection of parabens from water samples with limit of detections are in the range of 0.017–0.043 μg/L with the percentage recoveries 90.5–98.9%. To conclude, the CPE-DC193C-βCD-IL method is a superior method in the determination of parabens from water samples among the developed methods. The use of β-CD is an economically viable approach because it improves the performance of paraben extraction method dramatically. In addition, this surfactant is cheap and non-toxic to our environment.

Keywords: Cloud point extraction; Aqueous two-phase extraction; Paraben; High-performance liquid chromatography; β-cyclodextrin; Ionic liquid functionalized β-cyclodextrin

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1. Introduction

Separation methods based on surfactant's phase separation phenomena, cloud point extraction (CPE) have been investigated extensively. CPE has been recognized as an alternative to the conventional extraction because of its performance, low cost, and less toxic. Comparing with conventional liquid–liquid extraction, no organic solvent is used during the process of CPE, so it is economical and friendly for the environment. To achieve phase separation, almost all commercially available anionic, cationic, and non-ionic need high acid or salt concentration [1].

Moreover, the well-known non-ionic surfactants such as Triton X [2–4] and PONPE [5] series have high background absorbance in the ultraviolet or fluorescent region, due to the presence of an aromatic moiety in their structure. This prevents the chromatographic determination of organic pollutants [6]. Although the clean-up step of surfactant prior to HPLC has never been used to relieve the problem, the surfactant is not able to be removed completely and the recovery also lowered by the process [7,8]. To alleviate this problem, biodegradable surfactants, mainly ethoxylated alcohols without phenyl group and branched alkyl chains, are proposed [9]. Polysiloxane polyether surfactants are widely used in cosmetic products and pharmaceutical industries. Their biocompatibility and safety to human and friendliness to the environment have been proved for a long time [10]. In this study, the DC193C which is a polysiloxane polyether surfactant that is considered as a green surfactant will be used in the extraction of parabens in water samples.

Aqueous two-phase systems (ATPS) have been widely used with ionic liquids (ILs) in separation science [11–14] as a green, economical, and efficient method. It has attracted considerable attention because it presents the advantages such as short process time, low energy consumption, relatively reliability in scale-up, and a biocompatible environment [15]. Compared with traditional liquid–liquid extraction, ATPS contains over 70% water in each phase and low interfacial tension between them; therefore, ATPS facilitates the separation of polar solutes without the troubles of a wide range of pH adjustment and traditional volatile organic compounds (VOCs) [14,16]. In recent years, room temperature ionic liquids (RTILs) as a class of potential green solvents have been found in wide application of separation study. Therefore, our interest is to develop a new method using IL in the aqueous two-phase extraction on the determination for the paraben from water samples.

Cyclodextrin (CD) is a macrocyclic compound with seven D-glucopyranose units linked by α-1,4-glycosidic bonds. It has a hollow truncated cone with a hydrophobic cavity and a hydrophilic wall. As a molecular shape sorter, it could entrap and retain analytes with appropriate sizes and polarities in its cavity to form reversible and noncovalent inclusion complexes. Thus, it has a remarkable ability to recognize certain analytes in highly selective and sensitive manner [17]. On the other hand, the function of CDs to ionic liquid and also the interesting aspects are to be explored. This is because some studies reported that the performance of CD-IL in the adsorption/removal of pollutant is very excellent strategies [18–20]. Therefore, we grab this knowledge as a challenge to develop a new method on CD-IL using CPE method [21].

Our previous studies reported the CPE and ATPS of parabens in water samples using β-CD and βCD-IL as a modifiers [20–23]. Based on the excellent results obtained, we would like to expand research on the comparison of IL-ATPS and CPE using β-CD and βCD-IL as a modifier. We select the important parameters to be compared between these five developed methods. These parameters will lead to the achievement of high percentages recoveries of parabens extraction. Because of the awareness and concern to the amount of parabens in Malaysia's water samples, this research presents the development of a simple, fast, efficient, and green method to remove parabens in water samples. The optimum separation of five developed methods are successfully obtained and applied on the spiked parabens in water samples. Four types of water samples have been collected from various places in Malaysia which are river water, sea water, treated water, and tap water. In this article, we study the performances of the developed methods on parabens extraction. The selected parameters are water content, distribution coefficient, preconcentration factor, method validation, and percentage extraction recovery.

2. Experimental setup

2.1. Reagents and standards

Ionic liquid (1-butyl-3-methylimidazolium chloride), [C_4mim][Cl], (99.5%) is purchased from Merck (Germany). Beta cyclodextrin and potassium phosphate, K_3PO_4, are purchased from Acros Organics (USA). Methylparaben (MeP), ethylparaben (EtP), propylparaben (PrP), and benzylparaben (ArP) are purchased from Sigma-Aldrich (Germany). Silicone-ethyleneoxide copolymer (DC193C) is manufactured by Dow Corning (Shanghai, China) and supplied by Dow Corning Malaysia. Unfortunately, the information on the detailed molecular structure, the values of *x*, *y*, and molecular weight of these compounds are not provided by the manufacturer. β-CD is purchased from Acros Organics (USA) and deionized water used in mobile phase is of conductivity 18 MΩ cm. Sodium sulfate (Na_2SO_4) is obtained from Merck (Germany). Acetonitrile (HPLC grade) is purchased from Merck (Germany). Stock solutions of parabens at a concentration of 1,000 mg/L are prepared in acetonitrile because it produces good peaks in analyzing using HPLC. This acetonitrile does not interfere in the extraction recoveries. Working standard solutions are prepared by step-wise diluting with deionized water of stock solutions. pH of the solution samples is adjusted with diluted hydrochloric acid or diluted sodium hydroxide solutions.

2.2. Instrumentation

The separation and quantification of the tested parabens are carried out in Shimadzu HPLC system consisting of a pump, degasser, auto injector, column oven, ultraviolet detector, guard column, and Chromolith C_{18} column (100 × 4.6 mm, Merck, Germany). HPLC conditions are used to separate the analytes using acetonitrile and deionized water at a flow rate of 0.7 mL/min and detection of 254 nm. The isocratic elution is performed as follows: 30% acetonitrile and 70% water for 7 min.

2.3. Preparation of IL-ATPS and IL-βCD-ATPS

For the preparation of IL-ATPS method, 1.0 mL 5% (w/v) solution of $[C_4mim][Cl]$, 1.0 mL of the standard solution of parabens, and 0.5 mL of 1.5 M K_3PO_4 is added into 15-mL centrifugal tube. The pH is adjusted with diluted acid or diluted alkaline solution until the desired pH is obtained. The mixture is sonicated to ensure the solution mixes thoroughly, and two phases are formed after about two minutes.

For the IL-βCD-ATPS method, 1.0 mL 5% (w/v) solution of $[C_4mim][Cl]$, 1.0 mL of the standard solution of parabens, 1.0 mL of β-CD (10 ppm), and 0.5 mL of 1.5 M K_3PO_4 is added into 15-mL centrifugal tube. Then, the pH adjustment and two-phase formation procedure is similar to the IL-ATPS method.

2.4. Preparation for CPE-DC193C, CPE-DC193C-βCD, and CPE-DC193C-βCD-IL

In the CPE-DC193C method, a desired aqueous solution is obtained by mixing 30% (w/v) surfactant aqueous solution, 1 mL of stock solution of parabens, and 0.5 mL of sodium sulfate (1.5 M concentration) using ultrasonicator at the temperature of 30°C for 5 min. Meanwhile, for the CPE-DC193C-βCD and CPE-DC193C-βCD-IL methods, the solutions are obtained by mixing the 1.0 mL of 30% (w/v) surfactant aqueous solution, 1.0 mL of β-CD (10 ppm), 1.0 mL of βCD-IL (10 ppm), and 0.5 mL solution of sodium sulfate (1.5 M concentration). The pH of the solution is adjusted in a glass centrifuge tube prior to the blending process. Subsequently, separation of the phases is achieved by centrifugation for 10 min at 4,000 rpm or otherwise kept overnight to ensure separation between surfactant-rich phase and aqueous phase is achieved. Then, the volumes of surfactant-rich phase and aqueous are measured.

2.5. Determination of parabens in real samples using IL-ATPS, IL-βCD-ATPS, CPE-DC193C, CPE-DC193C-βCD, and CPE-DC193C-βCD-IL techniques

Tap water samples are collected from the laboratory. River water samples are collected from Bahau, Negeri Sembilan (geographical coordinate 3°1′44′′N 102°22′1′′E, Malaysia), while treated water samples are collected from a wastewater treatment plant in Kuala Lumpur (geographical coordinate 3°7′25′′N 101°39′12′′E, Malaysia), and seawater samples are collected from Perak (geographical coordinate 4°13′0′′N 100°34′0′′E, Malaysia). All water samples are filtered using a 0.45-μm nylon membrane filter to remove suspended particulate matter and stored at 4°C in the dark. Then, 1.0 mL of water samples is added in the aqueous solution for IL-ATPS, IL-βCD-ATPS, CPE-DC193C, CPE-DC193C-βCD, and CPE-DC193C-βCD-IL preparation (as mentioned in Sections 2.3 and 2.4).

3. Results and discussion

3.1. Effect of pH on the extraction recovery of paraben

The pH effect on CPE depends on the characteristics of both surfactants and analytes. In most studies, the influence of pH on the extraction recoveries is not crucial for the neutral or non-ionized compounds such as polycyclic aromatic hydrocarbons (PAHs), polycyclic biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzodioxins (PCDDs); however, a few notable exceptions have been reported [24]. For analyte possessing an acidic or basic moiety, pH plays an important role for their CPE. The ionic form of a molecule formed upon deprotonation of a weak acid or protonation of a weak base normally does not interact and bind as strongly as its neutral form with the surfactant aggregate. As a

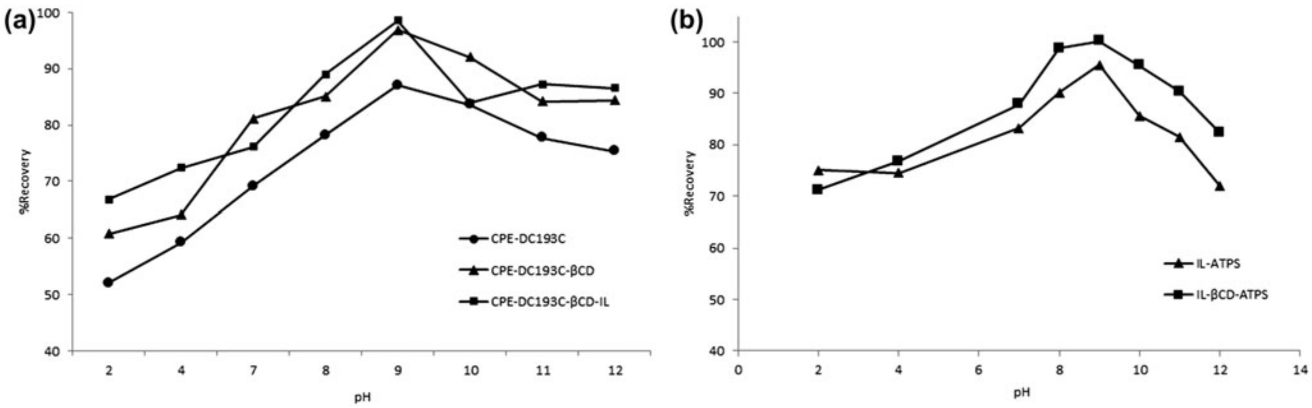

Fig. 1. Effect of pH on percentage recoveries of parabens extraction paraben using (a) CPE-DC193C, CPE-DC193C-βCD, and CPE-DC193C-βCD-IL methods and (b) IL-ATPS and IL-βCD-ATPS methods.

result, the lesser ionized form of an analyte is extracted [24].

The effects of sample pH to the recovery of paraben for the all methods are optimized over the range of 2–12. The results are exhibited in Fig. 1 where Fig. 1(a) is for CPE-DC193C, CPE-DC193C-βCD, and CPE-DC193C-βCD-IL methods, while Fig. 1(b) is for IL-ATPS and IL-βCD-ATPS methods. It is found that all methods show the highest level extraction at pH 9 for all studied parabens. The change in the extraction recoveries can be explained by considering the change in the charged of the parabens. At below pH 3, parabens are in protonated form where the extraction recovery of paraben in this form is low. While at pH 4–6.5, parabens exist mainly in neutral form. There are the increasing trends in extraction recovery at this region as paraben loses its net positive charge due to hydroxyl group becoming deprotonated.

At pH values from 7 to 9, paraben exists mostly in a negatively charged form because the hydroxyl group is now fully deprotonated. In this region, recovery percentage for all methods increases dramatically and until the maximum at pH 9. For IL-ATPS and IL-βCD-ATPS, the percentage recovery values increase because of the electrostatic attraction between deprotonated paraben of cation from imidazolium of ionic liquid. In CPE-based methods, the hydrogen bonding, electrostatic attraction, and π–π interaction could be the main interaction when paraben start to be deprotonated with the surfactant DC193C, βCD-IL, and β-CD.

When the pH is adjusted to pH 10, the recovery percentage falls low again. The decreasing trend of recovery percentage continues until pH 12 is reached. This is because at above pH 8, the process of alkaline hydrolysis of parabens takes place, leading to the corresponding alcohol and hydroxybenzoic acid [25]. This might be the reason why the percentage of recoveries of parabens start to decrease at pH 10 since all parabens compound are fully transformed to alcohol and hydroxybenzoic acid. As a result, a higher concentration of parabens could be extracted to the surfactant-rich phase. The results prove that pH play an important role in determining the optimum condition of paraben extraction.

3.2. Water content in the surfactant-rich phase

Water content in the layer of surfactant-rich phase, W_s, for the five developed methods is illustrated in Fig. 2. High W_s will interrupt the performance of extraction method because it causes difficulty in further increasing the preconcentration factor, C_F, or distribution coefficient, K_d.

Based on Fig. 2, ArP shows the highest loses of water content among all methods. CPE-DC193C-βCD-IL method produces 67% wt of water content for the ArP which is the highest followed by IL-βCD-ATPS method with 50%wt, and the lowest loses of water content is produced by CPE-DC193C method with 33%wt. This result clearly shows that the extraction methods that uses β-CD and βCD-IL produce higher loses of water in the surfactant-rich phase compared to the method without the addition of β-CD.

This is because β-CD has the ability to form inclusion complex with the hydrophobic parabens. It has the hydroxyl groups at the outer surface of the molecule, with the primary hydroxyls at the narrow side and secondary hydroxyls at the wider side, hence makes CD as water soluble but simultaneously generates an inner cavity that is relatively hydrophobic [26,27]. Thus, CD can either partially or entirely accommodate suitable size of molecules that are

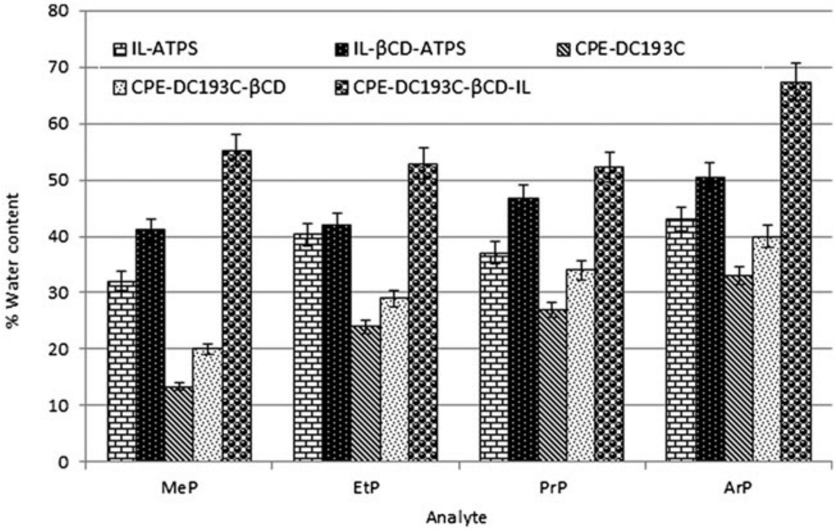

Fig. 2. Percentage of water content loses of developed method on studied parabens.

hydrophobic. In this study, ArP is the most favorable to accommodate in the inner cavity because this compound is highly hydrophobic compared to the other studied parabens. Ionic liquid that are positively charged makes an electrostatic interaction with the inner part of the β-CD that are negatively charged.

3.3. Distribution coefficient

The effect of distribution coefficient, log K_d, for all the developed methods corresponding to the studied parabens is shown in Fig. 3. It can be seen that for all parabens, the CPE-DC193C-βCD-IL method produces the highest value of log K_d of parabens in surfactant-rich phase followed by the IL-βCD-ATPS and the lowest is demonstrated IL-ATPS except for MeP. All methods show the markedly increase on the distribution coefficient when the hydrophobicity of parabens is increased except the IL-ATPS method. The IL-ATPS method shows constant value of log K_d when the hydrophobicity is increased. It can be explained clearly that the longer the chain, the higher the hydrophobicity.

Comparing among all the studied parabens, the distribution coefficients are in the order of

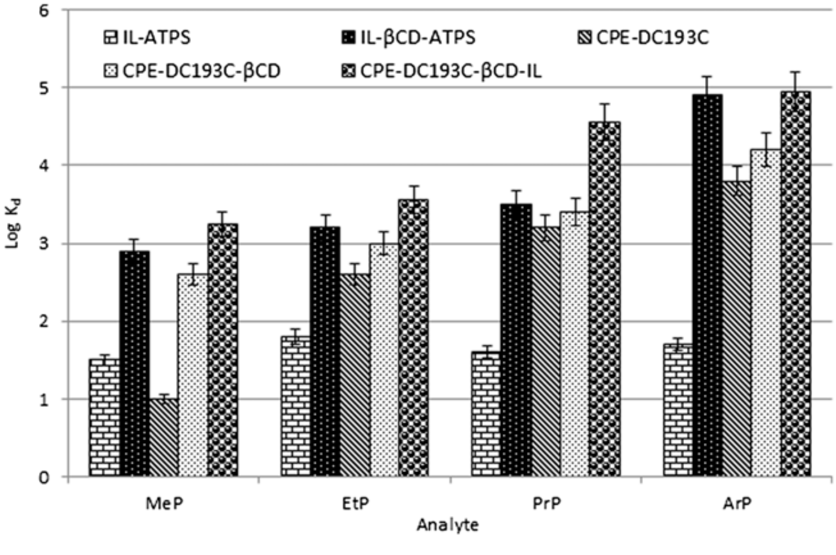

Fig. 3. Comparison of distribution coefficients, log K_d, between the developed methods for the studied parabens.

MeP < EtP < PrP < ArP for all methods except the IL-ATPS method. The methods with the addition of β-CD and βCD-IL show the highest log K_d because it has hydrophobic inner [21] cavity that can generate interactions with the hydrophobic parabens. ArP is easily absorbed into the cavity of β-CD that is relatively hydrophobic because this analyte is the least polar and least soluble in water. Therefore, we can conclude that the distribution of parabens in ionic liquid-rich phase and surfactant-rich phase methods depends on the hydrophobicity of parabens. Addition of β-CD and βCD-IL as a modifier increases the ability to form phase separation between ionic liquid-rich phase and aqueous phase.

3.4. Preconcentration factor

Fig. 4 illustrates the preconcentration factor of the parabens for the developed methods. The results clearly show that the preconcentration factor of the paraben for all the methods in the order of highest to lowest is the ArP, PrP, EtP, and MeP. The CPE-DC193C-βCD-IL method shows the highest preconcentration factor while CPE-DC193C is the lowest for all parabens except MeP. The CPE-DC193C-βCD-IL produces excellent results because of the low water content in the surfactant-rich phase, Vs, which reduces the volume of final surfactant-rich phase. The higher preconcentration factor is attributed to the smaller phase volume of the surfactant-rich phase/IL-rich phase; thus the volume of injected sample in HPLC is highly concentrated and produced good results [3,4].

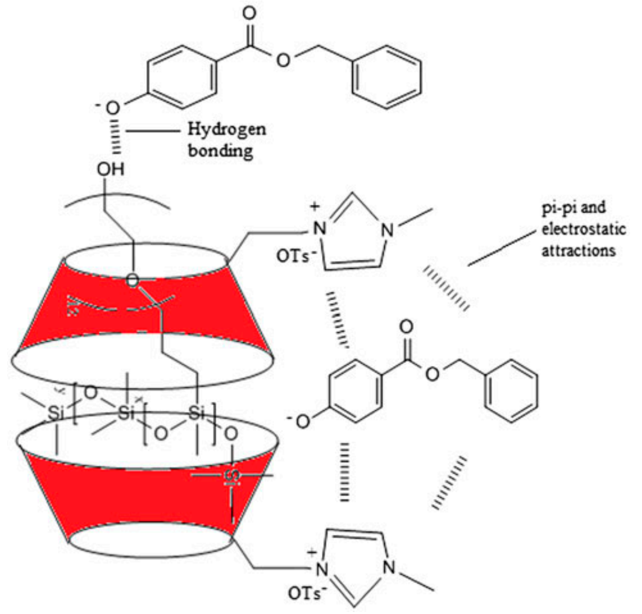

Fig. 5. Schematic illustration of the complexation of ArP and DC193C with βCD-IL [21].

Hence, the possible formations of the inclusion complex structure of the complexation of ArP and DC193C with βCD-IL are shown in Figs. 5 and 6 and have been proposed by taking account of the hydrogen bonding between DC193C and deprotonated ArP, π–π interaction, electrostatic attraction between the imidazolium ring and ArP, as well as the inclusion complexes between βCD-IL with DC193C and βCD-IL

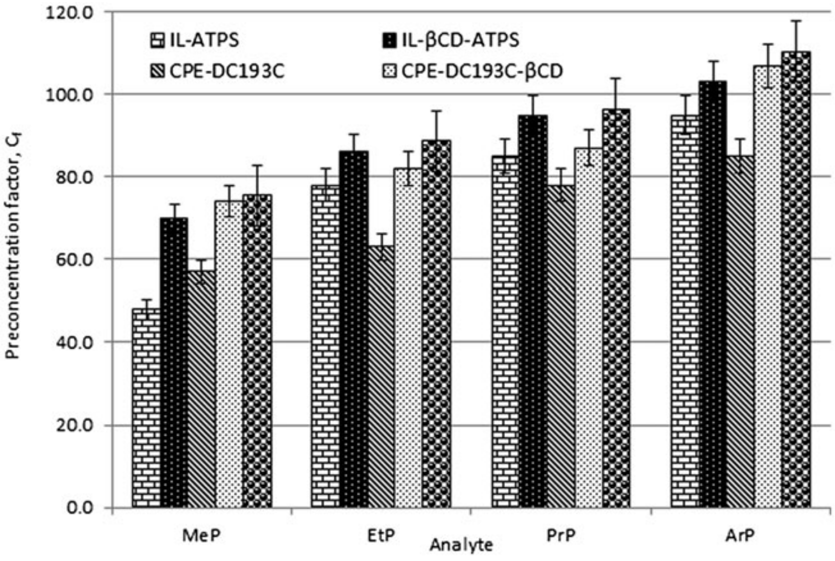

Fig. 4. Preconcentration factor on developed method of paraben extraction.

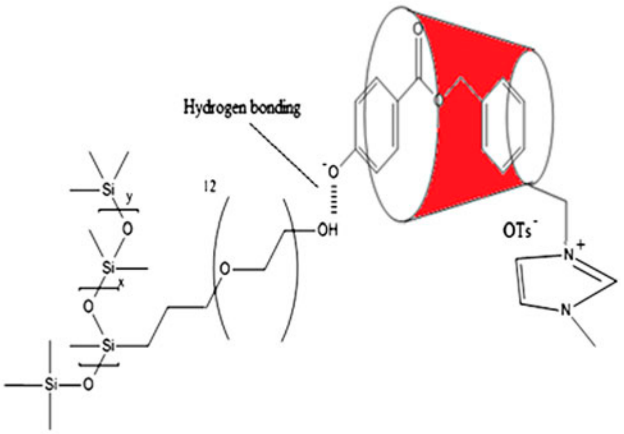

Fig. 6. Schematic illustration of the complexation of ArP and DC193C with βCD-IL [21].

Table 1
Limits of detection of developed method on determination of parabens from real water samples

Method	LOD (μg/mL)			
	MeP	EtP	PrP	Arp
IL-ATPS	0.038	0.0195	0.071	0.053
IL-βCD-ATPS	0.0037	0.0028	0.0011	0.0032
CPE-DC193C-βCD	0.017	0.033	0.043	0.029
CPE-DC193C-βCD-IL	0.00018	0.00012	0.00024	0.00063
CPE-DC193C	0.17	0.25	0.2	0.18

with ArP [21,28]. Detailed discussion about the proposed mechanism will be obtained in our previous study [21].

3.5. Method validation

The limit of detections (LOD) of the parabens is determined from spiked solution of analytes under the optimized condition. The results obtained from the five developed methods are tabulated in Table 1. A linear range of each paraben is from 0.10 to 10 μg/L. It is shown that the CPE-DC193C-βCD-IL method has a superior precision, and hence a better performance on parabens detection. The experimental results demonstrated that the detection limits for the studied parabens using CPE-DC193C-βCD-IL method were lower compared to other methods. The addition of β-CD and βCD-IL improves the sensitivity of the developed methods due to higher distribution coefficient and preconcentration factor compared to the methods without β-CD. It can be concluded that the proposed methods give similar and some higher limit of detections as compared to the other alternative procedures [29–31]. Furthermore, the cost of acquisition, total extraction time, and solvent consumption for the present methods are lower than those methods. Moreover, the complexity of the analytical systems employed [32] and sample pretreatment required [33,34] in those procedures are comparable with the developed methods.

The spiked parabens concentrations in the real samples for all methods are 0.01 μg mL^{-1}. The developed methods are applied to recover parabens from several water samples, i.e. river, treated, sea, and tap waters. The results are summarized in Table 2. Based on the table, percentage of recoveries for all methods with addition β-CD and βCD-IL are more than 90% with relative standard deviations (RSD) of less than 4%. This shows that the addition of β-CD and βCD-IL improves the selectivity of the developed method. To conclude, the developed method of CPE-DC193C-βCD-IL has the highest recovery compared to other methods for the recovery of parabens from aqueous solutions. Thus, it is feasible to be used for monitoring parabens compound in environmental water samples.

Applying CPE-DC193C method, the lowest recovery percentage is obtained from seawater sample among the other water samples. This is probably due to the electrolyte factor (salt concentration) from seawater that interrupts the CPE-DC193C method. Fortunately, this matrix effect only involves two analytes, MeP and EtP. This problem has been solved using

Table 2
Recovery of method developed of parabens in spiked water samples

Method	%Recovery (RSD%)			
	River water	Tap water	Treated water	Seawater
IL-ATPS	88.6–91.7	90.1–95.8	91.7–96.1	87.2–92.8
IL-βCD-ATPS	91.3–97.2	94.3–99.2	96.0–98.8	96.0–97.3
CPE-DC193C-βCD	90.5–98.9	90.9–97.9	90.3–95.2	90.5–93.7
CPE-DC193C-βCD-IL	97.4–98.9	92.3–97.8	92.9–100.0	91.2–98.2
CPE-DC193C	89.5–97.7	80.6–96.3	85.6–94.3	71.2–87.9

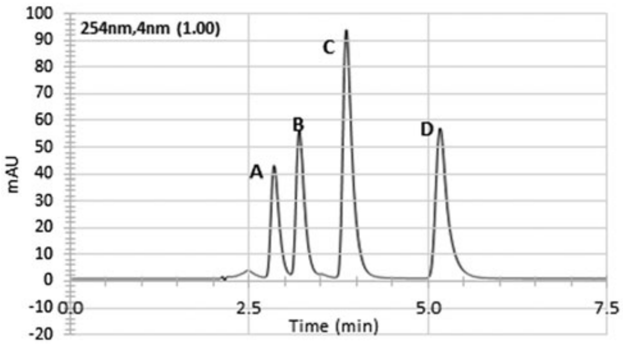

Fig. 7. Chromatogram of seawater sample spiked with the four studied parabens. A = methyl paraben, B = ethylparaben, C = propylparaben, D = benzylparaben.

CPE-DC193C-βCD and CPE-DC193C-βCD-IL systems where the results show that the recovery percentage of parabens extraction in seawater samples is higher compared to CPE-DC193C. Thus, the presence of modifiers βCD-IL and β-CD is significant in improving the CPE systems investigated. Fig. 7 shows the chromatogram of seawater sample spiked with the four studied parabens. These results have shown that developed method is feasible to be used for monitoring parabens compound in environmental water samples.

4. Conclusions

This study demonstrates the CPE-DC193C-βCD-IL consisting of βCD-IL as a modifier is suitable for the extraction of parabens from various water samples compared with the other developed methods. βCD-IL and βCD as modifiers give the improvements to the selectivity and sensitivity of CPE-DC193C. Comparing these two modifiers, βCD-IL shows the excellent performance in the CPE-DC193C method. The addition of βCD-IL improves the sensitivity of the developed method because of the detection limits for the studied paraben using CPE-DC193C-βCD-IL method were lower compared to the other methods. In addition, the preconcentration factor and loses of water content in CPE-DC193C-βCD-IL method are also the highest. This is because the complex formations from βCD-IL, surfactant molecules, and paraben in the surfactant-rich phase are extra large in the micelles during the CPE process.

So, the remaining spaces for the water inside or among the micelles are efficiently compressed. Therefore, the amount of water content that has been extracted in the surfactant-rich phase is less compared to the other methods. On the other hand, the addition of βCD-IL also improves the selectivity of the method. For example, the matrix effect that causes the low parabens recovery is totally reduced with addition of βCD-IL in the CPE-DC193C-βCD-IL method. Hence, the recovery of parabens is dramatically improved. Moreover, the distribution coefficient of paraben in surfactant-rich phase also according the hydrophobicity of parabens except IL-ATPS method. It is shown that βCD-IL produces the higher distributions of parabens in surfactant -rich phase. Comparing all methods, it is an economically viable option when using βCD and βCD-IL because it is capable of improving the performance of CPE and IL-ATPS methods dramatically, since these chemicals are cheap and non-toxic to our environment.

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