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Cloud point extraction of methylphenol in water samples with low viscosity of non-ionic surfactant Sylgard 309 coupled with high-performance liquid chromatography

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ABSTRACT

A cloud point extraction method is developed for the extraction of methylphenol from various water samples using the non-ionic surfactant, Sylgard-309. Methylphenol in the water is a toxic element that is dangerous to humans. Hence, the treatment of water containing methylphenol is necessary. The method's optimum conditions are 2.0 M salt concentration and 10% of surfactant concentration at room temperature. The limit of detection and limit of quantification of the method is 0.109 ppm and 0.365, respectively. The extraction recoveries of methylphenol in water samples (tap water, lake water, river water and sea water) are in the range of 90–99% with the relative standard deviations of less than 1.5%.

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KEYWORDS

Cloud point extraction; methylphenol; non-ionic surfactant; water samples; low-viscosity surfactant; low cloud point temperature

Introduction

Methylphenol is one of the most detected pollutants in water because it is widely used in many industrial processes.^[1] It is an organic compound which is bonded directly to hydroxyl group, and has limited solubility in water (8.3 g/100 mL). The compound of methylphenol is very toxic, has a diverse effect on the taste and odour of water at low concentration^[2] and low biodegradability.^[3] The compound of methylphenol is the waste product from the production of medicines, pesticides, perfumes, photographic film developer, dyes and petrochemical industry.^[4] The occurrence of methylphenol in water system is currently a major issue of global concern due to its harmful impact of to the environment.^[5] Methylphenol can affect human carcinogen even at low concentrations.^[1] US Environmental Protection Agency (EPA) and European Union (EU) have listed methylphenol as one of the major pollutants in the aquatic environment.^[6] In Malaysia, the acceptable limit of methylphenol concentration in the waste water is 0.001 mg/L.^[7] The European Community (EC) Directive specifies the legal tolerance level of 0.5 µg/L for each phenol in water intended for human consumption.^[8] Hence, the treatment of wastewater containing methylphenol is a necessity.

Cloud point extraction (CPE) is a potential alternative treatment method for methylphenol. The advantages of CPE compared with other techniques are the use of

relatively nontoxic surfactants instead of toxic organic solvent, low cost, modest energy consumption, higher extraction efficiency and environmental friendliness.^[9–11] CPE as an effective extraction method uses less solvent and only requires a very small amount of relatively non-flammable and non-volatile surfactant that is environmentally friendly. In recent years, molecularly imprinted nanoparticles has been widely used for nanosensor applications because of its high temperature resistance, extreme resistance and impermeability properties.^[12] Molecularly imprinted nanoparticles have been reported for determination of organic pollutant in wastewater treatment.^[13–17]

Our previous study demonstrated that CPE method using surfactant DC 193C for the extraction of phenol is an excellent method.^[18,19] In this paper, we would like to take a challenge to develop a new CPE method using a brand new surfactant, 3-(3-hydroxypropyl)-heptamethyltrisiloxane ethoxylated acetate, which is also called Sylgard 309. This non-ionic surfactant is used as a CPE solvent for extraction of methylphenol in water samples. This surfactant has low viscosity, rapid wetting, high penetration and low surface tension, properties which can produce higher efficiency in the extraction. It is a new surfactant that has never been used in any study. It is chosen because it offers the advantages such as low viscosity, low cloud point temperature, high water solubility and environment

friendliness compared with DC 193C.^[18,19] The developed method is tested on water samples from a few locations in the area of Kuala Terengganu, Malaysia.

This research involves one of the most crucial problems of environmental issue, that is water pollution. The organic pollutants that exist in water are the toxic elements that are strongly adsorbed to sediments, offering a potential risk to deposit-feeding invertebrates, and ultimately to consumers of higher up coastal food chains. This study develops a simple, fast, green, effective and low-cost technique to extract and remove the organic pollutants from the water samples.

Several parameters have been optimized using CPE methods such as the effect of salt concentration, surfactant concentration, pH, extraction time, temperature and water content. Our literature search reveals that this is the first attempt to extract and separate methylphenol in the CPE method utilizing non-ionic surfactant Sylgard 309 as the solvent extractant.

Experimental

Reagents and solutions

Non-ionic surfactant Sylgard 309 was obtained from Dow Corning (Shanghai, China). The structure is shown in Fig. 1. Methylphenol was obtained from Sigma Aldrich (St. Louis, MO, USA). Analytical-grade sodium hydroxide, hydrochloric acid (37%) and acetonitrile were purchased from Merck (Darmstadt, Germany). All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. Sodium sulphate (Na_2SO_4) was obtained from Sigma Aldrich. A stock standard solution of methylphenol (1000 mg/L) was prepared in HPLC-grade acetonitrile and stored in a fridge at 4°C. It is brought to ambient temperature prior to use.

Instrumentation

The separation and quantification of the tested methylphenol were carried out in a Shimadzu HPLC system. The system consists of a pump, degasser, auto injector, column oven, ultraviolet detector, guard column and SUPELCO Ascentis® C18 column (15 cm × 4.6 mm, 5 μm, Sigma-Aldrich). HPLC conditions to separate the analytes using acetonitrile and deionized water are at flow rate of 1.00 mL/min and detection of 280 nm.

Procedure for cloud point extraction (CPE)

In the CPE method, the desired aqueous solution was obtained by blending 30% (w/v) surfactant aqueous solution, 2.5 mL stock solution of methylphenol and 0.5 mL solution of sodium sulphate (0.5, 1.0, 1.5, 2.0 and 2.5 M) in a centrifuge tube. The solutions were then mixed using ultrasonicator for 5 min. The cloud point temperature was determined by measuring the temperature of the solution when it became turbid. The surfactant-rich phases were isolated before being injected into the HPLC system.

Method validation

Tap water samples were collected from the Analytical Laboratory, Universiti Malaysia Terengganu (geographical coordinates: 5° 4' 11" N, 103° 08' 9" E, Malaysia). River water samples were collected at Jalan Biawak, Universiti Malaysia Terengganu (geographical coordinates: 5° 4' 07" N, 103° 09' 1" E, Malaysia), while lake water samples were collected at Pusat Pengajian Pembangunan Sosial dan Ekonomi, Universiti Malaysia Terengganu (geographical coordinates: 5° 4' 12" N, 103° 08' 7" E, Malaysia) and sea water samples were collected at Pantai Tok Jembal, Kuala Terengganu (geographical coordinate: 5° 4' 10" N, 103° 09' 4" E, Malaysia). All water samples were filtered using a 0.45 μm nylon membrane filter to remove the suspended particulate matters

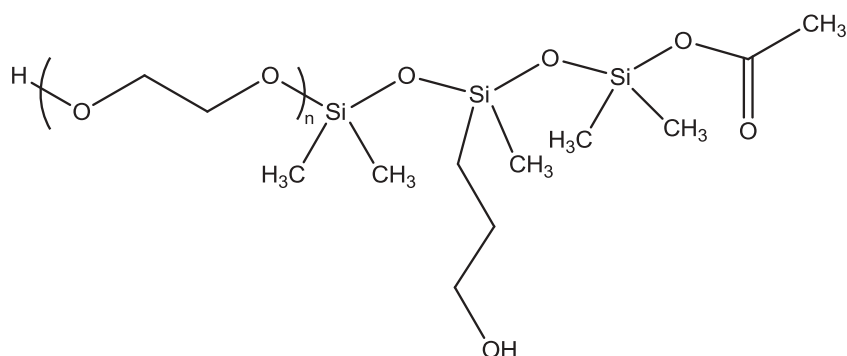


Figure 1. Structure of Sylgard 309 non-ionic surfactant.

and stored at 4°C in the dark. Then, 0.2 mL of each water sample was added to the CPE method preparation and analysed using HPLC-UV.

Results and discussion

Effect of salt concentration

Salts are important in the extraction recovery of methylphenol because salts promote the separation of two phases in CPE. The salts increase the density of the aqueous phase,^[20] and the addition of salts in real water samples may influence the extraction process. Sodium sulphate, Na₂SO₄, salt is chosen because it is chemically stable and does not decompose even if heated. It also does not react with oxidation and reduction agents at normal temperature. Na₂SO₄ is a neutral salt with pH 7 when dissolved in water. In this study, different concentrations of Na₂SO₄ ranging from 0.5 to 2.5 M are added to the CPE solution. Figure 2 shows the effects of Na₂SO₄ on the CPE method to extract methylphenol from water samples.

The extraction recovery increases when the Na₂SO₄ concentration is increased from 0.5 to 2.0 M. The results show that the electrolyte salt causes an increment in the dehydration of micelle in surfactant-rich phase.^[21] Since Na₂SO₄ salt acts as a drying agent, it has a very high capacity and very efficient capability in controlling the surfactant loss during CPE method. The salts cause dehydration to occur for both surfactant and methylphenol by breaking the hydrogen bonds with water molecules.^[18,22] At 2.0–2.5 M of salt concentration, the extraction recovery of methylphenol shows a declining trend. This is because at 2.5 M concentration, the solution starts to form precipitation. At the high salt concentration, Na₂SO₄ molecules are unable to break the hydrogen-bonded water molecules between surfactant and methylphenol.^[18] This is because when

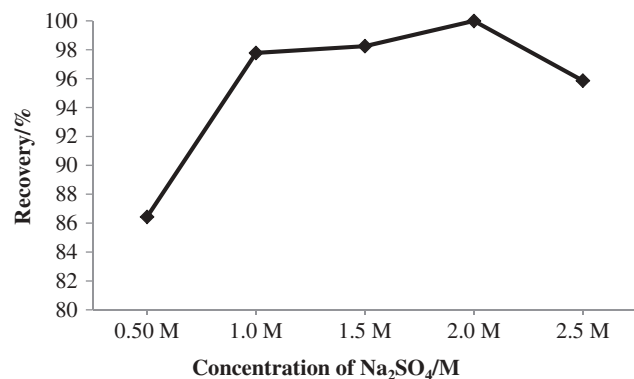


Figure 2. Effect of Na₂SO₄ on the extraction recovery of methylphenol.

the concentration is higher than 2.0 M, the surfactant-rich phase will be on the surface of the solution, making it more difficult to have better separation between the two phases.

Similar results were reported by Saraji and Bakhshi,^[11] where the peak area value of analytes decreases with the increase of sodium chloride, NaCl, concentration. Therefore, 2.0 M salt concentration is adopted as the optimum salt concentration to achieve the best analytical signals and highest extraction recovery for methylphenol extraction.

Previously, Zain *et al.*^[19] have investigated the effect of salt in CPE method including NaCl, NaOH, KCl, KI, Na₂SO₄ and K₃PO₄. It is reported that, only Na₂SO₄ salt can form the two-phase system when the concentration of salt is in the range of 0.5–1.0 mg/L. However, the other salts are unable form the two-phase system at concentration of ≤2.0 mg/L. This is because SO₄²⁻ ions are kosmotropic which exhibit a stronger interaction with water molecule than the water with itself.^[23] In addition, it is capable of breaking water–water hydrogen bonds and are beneficial to the phase separation formation. Thus, Na₂SO₄ salt is chosen due to its ability to produce two phases of separation in CPE.

Effect of surfactant concentration

The effects of non-ionic surfactant Sylgard 309 concentration are studied in order to get the maximum enrichment factor that produces the small phase volume ratio.^[24] The smaller phase volume ratio of surfactant-rich phase leading to higher concentration of analyte are obtained. The effects of Sylgard 309 surfactant concentration are studied at different concentrations 10%, 20%, 30%, 40% and 50% (w/v).

Figure 3 illustrates the effect of non-ionic surfactant concentration on the extraction recovery of methylphenol. It can be clearly seen that the extraction recovery of

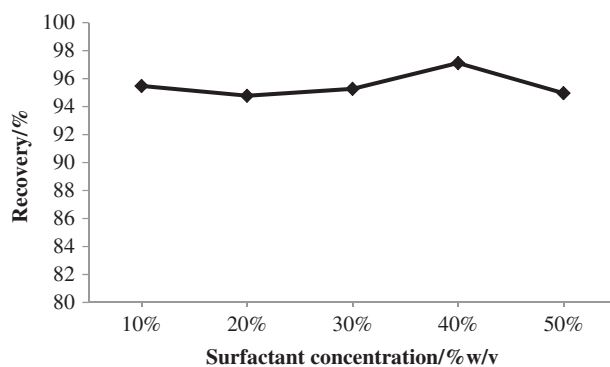


Figure 3. Effect of surfactant concentrations on extraction recovery of methylphenol.

methylphenol slightly increases from 20% to 40% (w/v) when the concentration of surfactant is increased. This is probably due to the increase in the viscosity of the surfactant-rich phase where viscosity of the surfactant Sylgard 309 will interrupt in the CPE phase separation and decrease the volume of surfactant-rich phase.

The small volume of surfactant-rich phase gives a good extraction recovery of methylphenol. The obtained results show an absolute extraction recovery of methylphenol ranging from 94% to 97%. This is probably due to excellent performance of Sylgard 309 non-ionic surfactant which is water soluble. This surfactant also has low viscosity of polyether liquid composition. These properties of surfactant enhance the performance to entrap methylphenol in the surfactant-rich phase. Therefore, 10% of surfactant Sylgard 309 concentration is selected as the optimum surfactant concentration.

Similar study was conducted by Kiran *et al.*^[25], using TX-100 as surfactant agent, for extraction of chromium (III) and (IV) in various environmental samples. The surfactant concentration is optimized from 1 to 6 g/L. From their study, TX-100 is chosen for the formation of surfactant-rich phase due to its low cloud point temperature and high density of the surfactant-rich phase. It shows the optimum surfactant concentration of 3.0 g/L is selected because the highest possible extraction recovery are obtained.

Effect of temperature

The optimization of temperature is important in order to get the equilibrium temperature in CPE method. Liang and Yang^[24] explained that temperature is a significant parameter in the determination of copper in food and water samples using CPE method. When the CPE method is at equilibrium temperature, the best separation is achieved.^[26]

In this study, the dependency of CPE extraction and phase separation of methylphenol is investigated at the temperature ranging from 30°C to 70°C.

The results are illustrated in Fig. 4. The extraction recoveries are in the range of 84–97% and the highest is obtained at room temperature. This result proves that CPE is a highly efficient extraction and fast separation method for organic compounds. This is because the separation between surfactant and aqueous phase easily occurs at room temperature without heating process. Therefore, room temperature is selected as the working equilibrium temperature for methylphenol extraction.

Noorashikin *et al.*^[18] conducted a similar study which concluded that there is also no significant effect of temperature on extraction recovery of phenol. This is

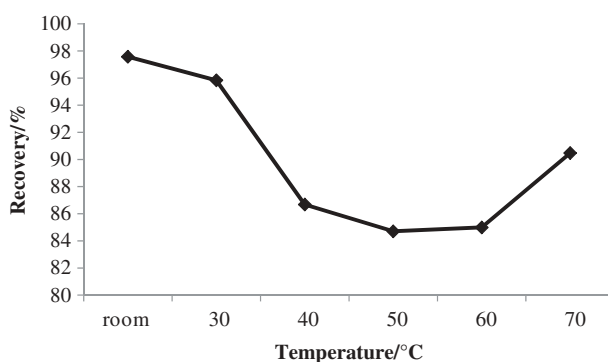


Figure 4. Effect of temperature on the extraction recovery of methylphenol.

because of their plateau result on the extraction recovery of phenol, which was obtained from temperature of 30°C to 70°C. From their results, room temperature was taken as the optimum temperature. Thus, the study proved that the temperature of extraction has insignificant effect on dehydration of the micelle and the volume of surfactant-rich phase.

Effect of extraction time

The effect of extraction time of methylphenol using CPE method is studied in the range of 5–60 min. In this work, it is desirable to have the shortest extraction time to complete the reaction and efficient separation of phases. The percentage of extraction recovery depends on the time that the analyte have to interact with the micelles and get into their core.^[27]

Figure 5 shows the effect of extraction time on extraction recovery of methylphenol. It can be seen that the extraction time of 5 min has the highest recovery of 89%. It is a sufficient time to complete the phase separation between surfactant-rich phase and aqueous phase of methylphenol because within 5 min under

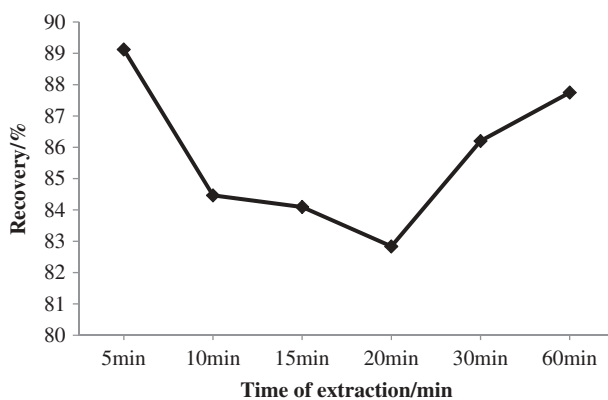


Figure 5. Effect of extraction time on the extraction recovery of methylphenol.

thermostatic water bath at 30°C, the salt molecules undergo partial dehydration. Which occurred by the breaking of the hydrogen bonding with water molecules of surfactant and methylphenol. The breaking increases the size of micelle thus enhancing the analyte to be more soluble.

The extraction times from 10 min onwards show an inconsistent trend of extraction recovery, due to the interruption of salts in the surfactant-rich phase. Hence, 5 min is chosen as the extraction time of methylphenol for the CPE method. Thus, the transfer of analytes from aqueous phase to surfactant-rich phase is fast and the equilibrium state is quickly achieved.^[28]

Effect of pH

The pH effect on CPE depends on the characteristics of both surfactants and analytes. pH plays an important role in CPE method for analytes that possess an acidic or a basic moiety. As illustrated in Fig. 6, the effect of pH on extraction recovery of methylphenol is studied in the range of pH 2 to pH 14.

From the figure, it is clearly shown that there is a decreasing trend of extraction recovery of methylphenol at pH 2 to pH 6. At this condition, the solution is in acidic form. The low extraction recoveries at pH <6 are because methylphenol species are protonated, leading to the increase of the ionic characteristic of methylphenol in the hydrophobic micelles.^[18] Therefore, only a small amount of methylphenol is extracted in the surfactant-rich phase due to less interaction between methylphenol and surfactant Sylgard 309, resulting low percentage extraction recovery.

The extraction recovery of methylphenol increases from pH 6 to pH 7 in which methylphenol existed in neutral form at this condition. This is due to good interaction between the uncharged methylphenol with Sylgard 309. Xie *et al.*^[29] reported that deprotonation of weak acid or protonation of weak base does not interact

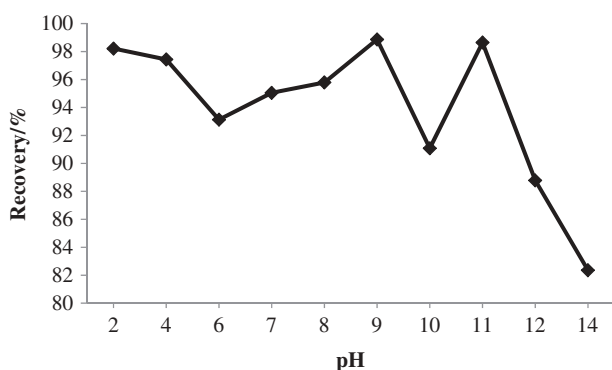


Figure 6. Effect of pH on the extraction recovery of methylphenol.

and bind as strongly as it is in neutral form with the surfactant aggregate. The recovery of methylphenol increases while at pH 9 to pH 10, the extraction recovery declines due to the formation of phenolate ions that interrupts the CPE method. However, at pH 10 to pH 11, the extraction recovery increases. From the results, the effect of pK_a value of methylphenol ($pK_a = 10.0$) to the pH of the CPE solution is insignificant.^[30]

At pH 11 to pH 14, the extraction recovery of methylphenol markedly decreases. This is because under basic condition, methylphenol is in deprotonated form causing less interaction between methylphenol and Sylgard 309 surfactant. Thus, the concentration of methylphenol in the surfactant-rich phase decreases. To conclude, the effect of pH to the extraction recovery of methylphenol is insignificant.

Effect of phase volume ratio

The phase volume ratio, R_v , is defined as the ratio between the volume of surfactant-rich phase, V_s , and the aqueous phase, V_w . It is calculated using the following formula:

$$R_v = \frac{V_s}{V_w}$$

Figure 7 shows the effect of surfactant concentration in phase volume ratio. It can be seen that the phase volume ratio increases with the increase of surfactant concentration. This is because the concentration of surfactant in dilute phase remains nearly constant thereby increasing the volume of the surfactant-rich phase.^[20] The interaction among the Sylgard 309 surfactant micelles increases leading to dehydration from external layers of micelles. Therefore, it results in a decrease of surfactant-rich phase volume and an increase in an aqueous phase volume ratio. In this study, the 10% (w/v) surfactant concentration is

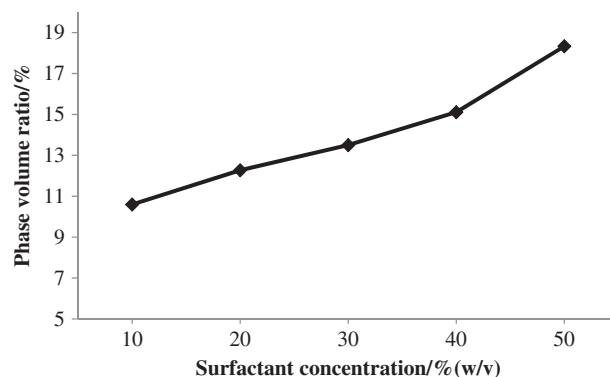


Figure 7. Effect of phase volume ratio.

selected because it gives the optimum volume of surfactant-rich phase for the HPLC analysis.

Effect of interference study

The effects of different cations and anions on the extraction of methylphenol in CPE method are studied. An ion is considered to be an interferent when it causes an error greater than $\pm 5\%$ in this study.^[31,32] In order to examine the selectivity of the CPE method, sample solution containing methylphenol and individually spiking Na^+ , K^+ , Cl^- , Br^- , CO_3^{2-} , OH^- , I^- and NO_2^- ions are extracted under an optimized CPE.

Table 1 shows the effect of selected ions on the extraction of methylphenol. The results reveal that all of the ions do not interfere in the extraction of methylphenol even when the concentration of each ion achieves 50 ppm. Hence, the interference by the addition of ion presence at moderate concentration is considered as insignificant.

Water weight loss in the surfactant-rich phase

Water content study is conducted to assess the amount of preconcentration water in the surfactant-rich phase. This study is important because the presence of water in CPE method affects the extraction recovery of methylphenol. According to Yao and Yang,^[33] the performance of CPE is limited by the water content in the surfactant-rich phase because lower amount of water in surfactant-rich phase results in higher concentration of analyte.

Figure 8 shows the water content in the surfactant-rich phase corresponding to the concentration of surfactant Sylgard 309. It can be seen that the water content decreases from 1.66% to 0.016% when the surfactant concentration is increased from 10% to 30% (w/v). The highest loss of water content is at 30% (w/v) surfactant concentration because the solute–solute interaction between the surfactant itself probably has a greater contribution than the solute–water interaction^[11] and hence high percentage of methylphenol extraction recovery is obtained.

Table 1. Interference of ions to the extraction recovery.

Ions	Concentration (ppm)	Extraction recovery (%)
Na^+	50	84.90
K^+	50	81.30
Cl^-	50	86.10
Br^-	50	84.90
CO_3^{2-}	50	81.30
OH^-	50	85.50
I^-	50	80.00
NO_2^-	50	84.80

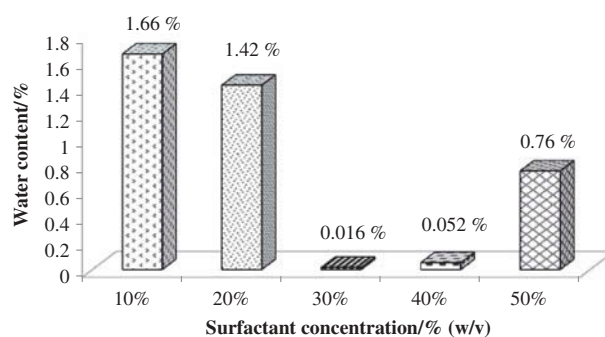


Figure 8. Water content in surfactant-rich phase using CPE method.

A similar study conducted by Noorashikin *et al.*^[18] reported that the percentage water content in surfactant-rich phase using CPE-SNIS- β CD method demonstrates a decreasing trend in extraction of parabens from water samples. This is because the amount of hydrophilic surfactant becomes higher in the solution. Therefore, lower amount of water is detected in the surfactant-rich phase, as molecule of surfactant favour is likely to interact with the surfactant itself rather than with water molecules.

Method validation

Water samples are collected from various types of water matrices such as tap water, river water, lake water and sea water in the area in Gong Badak, Kuala Terengganu, Malaysia. Prior to the analysis, all the water samples are successively passed through 0.45 μm nylon filter to remove the possible suspended particulate matter and stored at the dark place before extraction. The developed CPE method for methylphenol extraction exhibits a better performance with lower limit of detection (LOD) and limit of quantitation (LOQ) of 0.109 ppm and 0.365 ppm, respectively.

As tabulated in Table 2, all the real water samples show the excellent recoveries in the range of 90–99% with relative standard deviations (RSD) of less than 2%. The result shows the good accuracy of the CPE method and its independence from the matrix effects. This outstanding extraction recovery confirms the validity of

Table 2. Methylphenol extraction recovery from spiked water samples and extraction concentration from unspiked water samples.

Water samples	% Recovery (RSD %) in spiked water samples	Concentration of methylphenol without spiked water sample (ppm)
Tap water	91.50 (0.45)	1.40
River water	93.46 (1.31)	1.36
Lake water	98.15 (0.78)	0.84
Sea water	98.06 (0.28)	0.49

Table 3. Comparison of the developed method with our previous method for the determination of methylphenol in water samples.

Types of surfactant	Extraction techniques		
	CPE-UV	CPE-HPLC-UV	
	DC 193C	Sylgard 309	
LOD (ppm)	0.08	0.11	
RSD (%)			
	Lake water	0.08	0.78
	River water	0.04	1.31
	Sea water	0.08	0.28
	Tap water	0.07	0.45
Recovery range (%)	78–97	90–99	
Reference	(18)	Current work	

^aCPE, cloud point extraction; UV, ultraviolet–visible detector; HPLC-UV, high-performance liquid chromatography, UV, ultraviolet detection; LOD, limit of detection; RSD, relative standard deviation.

the CPE method in real water samples. Sea water has the high extraction recovery compared with our previous method, CPE-DC 193C, that showed the recovery of 78%. This is because salts in sea water are entrapped by the CPE method which enhances the recovery. In conclusion, CPE method is feasible to be used for monitoring methylphenol compound in environmental water samples.^[18]

Besides, high recoveries are obtained using the developed method of CPE from unspiked water samples of methylphenol. The highest concentrations of methylphenol are extracted from tap water with 1.40 ppm followed by 1.36 ppm from river water, 0.84 ppm from lake water and 0.49 ppm from sea water. The result proves that developed method of CPE is successful for extraction of methylphenol in water samples.

Comparison of the developed method with other CPE method

Table 3 presents a critical comparison of the developed method with our previous method.^[18] Apparently, this developed method has the highest range of extraction recovery percentage and these characteristics are comparable or even better than our previous method.

Conclusions

In this study, the CPE method offers several advantages such as being very simple, low cost, sensitive, selective, effective and less toxic to the environment. To the best of our knowledge, this is the first report on the use of non-ionic surfactant of Sylgard 309 in the CPE that is applied for the extraction of methylphenol species in water samples. Experimental results show that high recoveries can be obtained at the optimized parameters. Furthermore, the non-ionic Sylgard 309 surfactant in the CPE has a great potential to be explored for the

extraction of organic pollutant in the water samples. It is because of the unique structure of molecules that could entrap hydrophobic as well as hydrophilic substances. Besides, it has low water content which enhances the extraction efficiency.

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