Optimization of a greener method for removal phenol species by cloud point extraction and spectrophotometry

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Highlights

- The optimize method of the cloud point extraction (CPE) has been developed by using nonionic DC193C surfactant and UV–Vis spectrophotometer.
- Performance of nonionic DC193C surfactant has been studied in detail for several parameters that affected the extraction efficiency.
- The different on the hydrophobicity of phenolic compounds have been studied.
- Application of the developed method with environment water samples.

Abstract

A greener method based on cloud point extraction was developed for removing phenol species including 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and 4-nitrophenol (4-NP) in water samples by using the UV–Vis spectrophotometric method. The non-ionic surfactant DC193C was chosen as an extraction solvent due to its low water content in a surfactant rich phase and it is well-known as an environmentally-friendly solvent. The parameters affecting the extraction efficiency such as pH, temperature and incubation time, concentration of surfactant and salt, amount of surfactant and water content were evaluated and optimized. The proposed method was successfully applied for removing phenol species in real water samples.

Introduction

Phenol and its derivatives such as 4-nitrophenol (4-NP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) are found in aquatic environment as a result of the common availability of the by-products of many industrial processes [1,2]. These compounds are generated in the production of plastic, dyes, drugs, pesticides, antioxidants and paper in the petrochemical industries.

Most of them are very toxic and have diverse effects on the taste and odor of water at low concentration. Nowadays, phenol and its compounds become particularly of interest and concern in accordance to the US Environmental Protection Agency (EPA) and European Union which are included in their lists of aquatic environment [3–5]. Additionally, these compounds can persist under a certain environmental condition, at ppm levels in ground
water for a number of days or weeks depending on the temperature and pH [1]. Thus, many researchers are very concerned in removing the phenol species rather than in determining them in the water samples.

The most common methods that have been used in research work for removing phenolic species in water samples are the membrane separation process [6,7], oxidation [8,9], ozonation [10,11] as well as the adsorption [12–14] on different adsorbents. In contrast, a simple, fast, economical, greener, sensitive and selective analytical methods are required for removing phenol species from the water sample [15]. Based on that, few researchers have discovered recently about the principles and advantages of the cloud point extraction (CPE) as the new extraction method. It is found that the CPE methodology which is simple, cheap, highly efficient, and has lower toxicity offers an alternative to a more conventional extraction system [15–17].

Surfactants are amphiphilic molecules, having two distinct structure moieties, a hydrophilic head and one or two hydrophobic tails. This latter part is generally a hydrocarbon chain with different numbers of carbon atoms. The hydrocarbon may be linear or branched aliphatic chains and it may also contain aromatic rings [18,19]. The hydrophobic tails can entrap and thus isolate the hydrophobic substances. This ability has been extensively used in the cloud point extraction [20]. At certain temperature, an aqueous solution of the non-ionic surfactant micellar system becomes turbid. This temperature is known as the cloud point temperature (CPT) [21–23]. Above the cloud point temperature, the solution separates in two phases: first off, the surfactant rich phase, which has a small volume compared to the solution and which is also called the coacervate phase while the other phase is the aqueous phase containing surfactant concentration slightly above the critical micelle concentration (CMC) [24–26].

There are many potential advantages to replace the volatile organic compounds (VOCs) with water or various types of aqueous solution. The most obvious are low cost, reduced flammability, reduced toxicity, and reduced environmental risk as a result discharge of the supporting phase. Therefore, relatively few articles have focused on the use of aqueous polyethylene glycols (PEGs) solution. PEGs (also called dimethicone copolysols, silicone glycols, and silicone surfactants) are one class of amphiphilic materials having water soluble and a silicone soluble portion in one molecule. DC193C fluid which is non-ionic surfactant based on silicone PEGs copolymer [27].

PEGs have been recognized as an alternative approach to replacing VOCs due to a number of advantages, e.g. non-toxic, odorless, colorless, non-irritating and the fact that they do not evaporate easily. In addition, PEGs are considered inert as they are not reacting to other materials. They are also soluble in many organic solvents. They have been an important and growing class of raw materials used in the cosmetic, food and pharmaceutical industries; their biocompatibility and safety to human and their friendly nature to the environment have been proven for a long time [28,29]. As reported by Chen (2005), even if the PEGs are discharged to the environment; the environment would suffer from no significant effect. Moreover, the US FDA has permitted this surfactant for internal consumption [27]. Therefore, due to the advantages of DC193C surfactant, phenol species are more concerned in removing them in the water samples compared to recover the non-ionic surfactant of DC193C from water samples.

There are several types of surfactant that had been used as extractant such as Triton X, Tergitol and PONPE series in CPE. Triton X-114 is well known for micelle formation compared to other classes of non-ionic surfactant. However, its aromatic chromophore has strong UV absorbance or fluorescence signals which becomes obstacles in UV and fluorescence detectors [26]. Therefore, DC193C fluid non-ionic surfactant was used to overcome this problem. Furthermore, it has more flexible polysiloxane chains without any aromatic structure and becomes more compact micelle structures which offer low water content in the surfactant rich phase; thus, enhancing the extraction efficiency [30].

In the present work, the feasibility of employing the CPE as a simple and effective method has been adopted to remove phenolic species from water samples using DC193C as a non-ionic surfactant. Several parameters used in the cloud point extraction method of DC193C have been optimized such as the effect of pH, concentration and amount of surfactant, equilibration temperature and time, concentration of salt and analyte and water content. This is the first attempt of DC193C surfactant used in the CPE for removing phenolic species from water samples by the spectrophotometric method. Due to this fact, DC193C has high flexible polysiloxane chains with low cohesive energy, which offers more conformations than the conventional surfactants, resulting in compact micelle structures as well as low water content in the surfactant rich phase [28,30]. Therefore, it was selected to be used in this study. Meanwhile, spectrophotometry was preferred because of its simplicity, low cost and rapid analysis.

### Experimental

#### Apparatus

A Shimadzu (Kyoto, Japan) Model UV-1650 UV–Vis spectrophotometer was used for the measurement of the phenolic compounds. A wise bath® was used to be maintained at the desired temperature. The pH values of the sample solutions were determined by pH meter (Hanna instrument). 15 ml calibrated centrifuge tubes were used (Copen, Malaysia).

#### Reagents

Dow Corning DC193C, also known as polyethylene glycol (PEG) silicone, was supplied by Dow Corning (Shanghai, China). Fig. 1 shows the chemical structure of the PEG. The values of x, y and molecular weight of these compounds were available from the manufactures. Fig. 2 shows the absorption of the UV–Vis spectra for 4-Nitrophenol (molecular weight: 139.11, λmax: 318 nm), 2,4-dichlorophenol (molecular weight: 163, λmax: 285 nm) and 2,4,6-trichlorophenol (molecular weight: 197.45, λmax: 295 nm) that were purchased from Aldrich. Standard stock solutions of chlorophenols (1000 mg L

#### Procedure

An aliquot of 1.0 mL of a sample or standard solution containing the analyte (10 mg L

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**Fig. 1.** The structure of silicone surfactant (DC193C).
1.5 mol L\(^{-1}\) of Na\(_2\)SO\(_4\) at pH 7.0 were mixed in tapered glass tubes and the phase separation was induced by heating the content in a water bath at 50 °C for 15 min. The separation of the phases was achieved by centrifugation for 2 min at 1500 rpm. On cooling in an ice-bath for 5 min, the surfactant rich phases became viscous. Then, the surfactant rich phase at the top layer could be separated by using a syringe, thereby minimizing the possibility of cross-contamination of analytes from the corresponding aqueous phase. Subsequently, 2.0 mL of de-ionized water was added to the surfactant rich phase in order to decrease its viscosity. It will also make the final volume feasible to transfer into the optical cell for the measurement each phenol species spectrophotometrically at the respective absorption maxima against a reagent blank prepared under similar conditions.

**Water content**

The water content of the surfactant rich phase after the extraction was measured by drying the surfactant rich phase at 353 K until no mass was observed. The water content was obtained by calculating the weight differences of the surfactant rich phase before and after drying. All the data given in this study were the average of triple measurements.

**Analysis of water sample**

Water samples were taken from two selected lakes in urban areas in Kuala Lumpur which were Taman Jaya Lake and Taman Titwangsa Lake (Malaysia). Prior to the analysis, lake water samples were successively passed through filters by using 0.45 μm nylon filter to remove the possible suspended particulate matter and to be stored in the refrigerator at 4 °C before extraction. An appropriate amount of standard solutions at two different level concentrations (400 and 1200 μg L\(^{-1}\)) of 2,4-DCP was added to the real water sample for recovery test. The same procedure was carried out for 2,4,6-TCP and 4-NP.

**Results and discussion**

**Characterization of non-ionic DC193C surfactant**

Most of the previous works involving the cloud point extraction utilized alkylphenyl poly(oxyethylene) ethers (PONPE-7.5 or Triton X-114) [26]. However, the silicone surfactant symbolized by DC193C was employed in this study because of its possession of several desirable features which make it particularly suitable for use in a routine cloud point extraction work as mentioned below:

(i) The surfactant becoming commercially available in a highly purified homogenous form.
(ii) It is not hazardous compared to other surfactant such as Triton X and most importantly.
(iii) No aromatic moiety to interfere with possible analyte UV absorbance or fluorescence detection modes.

**Parameters that optimize CPE**

The main variables affecting the extraction process, such as pH, concentration and amount of surfactant, equilibration temperature and time, concentration of salt and analyte were optimized. The extraction efficiency of the phenol species by surfactant from the sample was calculated as [31]:

\[
\text{Extraction efficiency, } (\%) = \left( \frac{C_v}{C_0} \times \frac{V_s}{V_0} \right) \times 100
\]

where \(C_v\) represents the phenol species concentration in the surfactant rich phase of volume \(V_s\); \(C_0\) represents the phenol species concentration in the sample-surfactant mixture of volume \(V_0\).

**Effect of pH**

In the cloud point extraction, the pH is the most crucial factor regulating the partitioning of the target analytes in the micellar phase for organic molecules. In this work, the effect of pH on the efficiency of the extraction was studied within pH range from 2.0 to 9.0 and the results were obtained and latter shown in Fig. 3.

Fig. 3 illustrates the dependence of the extraction efficiencies against pH that were obtained for 2,4-DCP (\(pK_a\) 7.7), 2,4,6-TCP (\(pK_a\) 7.4) and 4-NP (\(pK_a\) 7.2). It can be seen from Fig. 3, that the maximum extraction efficiencies for the three phenol species were achieved at pH 7.0, where the uncharged form of target analyte prevails [19,32]. The extraction efficiencies of the three phenol species were less in acidic pH and increased as the pH increased. The three phenol species were protonated at lower pH (less than \(pK_a\) value) and their ionic characteristics increased, leading to less solubilization of the phenol species in the hydrophobic micelles due to the interaction of the protons with polyethylene oxide. At higher pH > 7 (above \(pK_a\) value), the extraction efficiency for the three phenol species decreases, and this may be because of the formation of phenolate ion. According to Frankewich and Hinze (1994), the ionic form of a neutral molecule formed upon the deprotonation of a weak acid (or protonation of a weak base) normally does not interact with, and bind, the micellar aggregate as strongly as does its neutral form due to the non-dissociated type of non-ionic surfactant [33]. Therefore, pH 7.0 was selected as the optimal pH for the three phenol species.

![Fig. 2. The absorption of the UV–Vis spectra for individual phenol species at the respective absorption maxima in the surfactant rich phase after CPE.](image)

![Fig. 3. Effect of pH on the extraction efficiency. Conditions: 10 mg L\(^{-1}\) of phenol species concentration, 0.5 (v/v%) DC193C, 1.5 mol L\(^{-1}\) Na\(_2\)SO\(_4\) at 50 °C.](image)
Effect of DC193C concentration

It is desirable to use minimum amount of surfactant for maximum extraction of phenol species. The amount of DC193C not only affected the extraction efficiency, but also the volume of the surfactant rich phase. A successful CPE should be maximizing the extraction efficiency by minimizing the phase volume ratio ($V_n/V_o$). The effect of DC193C concentrations on extraction efficiency was evaluated in the range 0.1–0.8 (v/v%) for the three phenol species. The plot of the extraction efficiency of the three phenol species in the surfactant rich phase after CPE versus DC193C concentration was demonstrated in Fig. 4. The extraction efficiency and volume of the surfactant rich phase ($V_r$) increased on the increasing DC193C concentration up to 0.5 (v/v%) and remained constant up to 0.8 (v/v%) for the three phenol species. An increase in the surfactant amounts also increases the volume of the surfactant rich phase to maintain the material balance, as the concentration surfactant in the dilute phase remains almost constant. Therefore, by increasing DC193C concentration, the number of hydrophobic micelles increased and caused responsive increase of the extractability of DC193C [34]. The extract was therefore more diluted when higher amounts of surfactants were used, resulting in the loss of sensitivity with the increase of DC193C concentration above 0.5 (v/v%), due to the increased viscosity of the surfactant rich phase. At concentration below this value, the extraction efficiency of the phenol species was low because there are few molecules of the surfactant entrapping the phenol species quantitatively. Thus, to fulfill the “environmentally benign” extraction, a low concentration of DC193C, 0.5 (v/v%), was selected for use in this experiment for three phenol species.

Effect of amount DC193C

Fig. 5 depict the effect of the variation of DC193C amount on the percentage extractions of the three phenol species. Different volumes of the DC193C (0.5 v/v%) ranging from 0.1 to 1.0 mL were used in this study. As shown in Fig. 5, the percentage extractions for the three phenol species increased by increasing the DC193C amount up to 0.5 mL and suddenly decreased at higher amounts of 0.5 v/v%. This is because of the fact that the analytical signal is observed to deteriorate due to the increase in the final volume of the surfactant. Therefore, 0.5 mL of 0.5 v/v%. DC193C was used as the optimum amount for the three phenol species.

Effect of equilibrium temperature and time

It is desirable to have the lowest possible equilibration temperature and shortest incubation time, which compromise the completion of the reaction and efficient separation of phase. In the CPE process, the cloud point can alter with the increasing length of the hydrocarbon and sometimes dramatically, in the presence of acids or bases, salts and organic additives [35].

In this work, the temperature of the thermostatic bath was varied from 25 °C to 80 °C (Fig. 6). It is found that the temperature of 50 °C was adequate for all phenols. As shown in Fig. 6, the extraction efficiencies were found to gradually increase when the temperature increased from 25 °C to 50 °C and almost constant up to 80°C for the three phenol species. The temperature affects interactions in both phases, decreasing the hydration of solutes i.e., phenols and surfactant in the aqueous phase and surfactant rich phase. Due to that, depending upon the experimental conditions, an increase of the temperature can cause an increase or a decrease of phenols recovery [36]. It is well known that, critical micelle concentration (CMC) decreases at higher temperature. Moreover, the non-ionic surfactant becomes relatively more hydrophobic at higher temperature because of an equilibrium shift that favors the dehydration of the ether oxygens. This leads to an increase in the number of concentration of micelles. Therefore, the solubilization capability of the micellar solution increases with temperature leading to an increase in the phenol extractions. At an elevated temperature, the interaction among the DC193C micelles increases leading to the dehydration from the external layers of micelles resulting in a decrease in the volume of surfactant rich phase volume ($V_n$) [37]. Unfortunately, for a thermally labile compound, the lowest possible equilibration temperature should be used to avoid unstable decomposition of the compound at an elevated temperature.

**Fig. 4.** Effect of concentration surfactant on the extraction efficiency. Conditions: 10 mg L$^{-1}$ of phenol species concentration, pH 7.0, 1.5 mol L$^{-1}$ Na$_2$SO$_4$ at 50 °C.

**Fig. 5.** Effect of amount surfactant on the extraction efficiency. Conditions: 10 mg L$^{-1}$ of phenol species concentration, pH 7.0, 0.5 (v/v%) DC193C, 1.5 mol L$^{-1}$ Na$_2$SO$_4$ at 50 °C.

**Fig. 6.** Effect of temperature on the extraction efficiency. Conditions: 10 mg L$^{-1}$ of phenol species concentration, pH 7.0, 0.5 (v/v%) DC193C, 1.5 mol L$^{-1}$ Na$_2$SO$_4$. 

ture [38]. Therefore, the equilibrium temperature at 50 °C was selected as an operating temperature in this study for three phenol species.

The dependence of the extraction efficiency upon the incubation time was also studied in the range of 5–30 min at 50 °C. Fig. 7 displays that the incubation time of 15 min was sufficient to complete the quantitative extraction of three phenol species. The extraction efficiency declined as the incubation time exceeded 15 min, which was probably due to the stability of the phenol species and the decreasing surfactant [39]. Hence, 15 min at 50 °C was chosen as an incubation time for the three phenol species for the CPE process.

**Effect of ionic salt**

The phase separation in the CPE was commonly induced by heating the mixture containing the surfactant up to a temperature above the cloud point. However, anlate that is sensitive to this kind of approach, due to inherent volatility, and solution heating might actually lead to analyte losses. In this sense, the salting-out effect of salt was adopted as an alternative to induced phase separation in the aqueous solutions of DC193C.

It has been reported that the addition of electrolytes may accelerate the separation of the two phases of the CPE procedure [40,41]. This is because salt acts as “drying agent”, causing the partial dehydration to occur for both surfactant and phenols by the breaking of hydrogen bonds with water molecules. This obviously results in a significant reduction of the cloud point in a way that phase separation already occurs at room temperature [42].

In this work, salts which were used in the CPE included NaCl, Na2SO4, NaOH, K2PO4, KCl and KI. The effect of salting-out electrolytes is mainly due to the dehydration of the PEG chain by cation and increasing water molecule self-association by anions. However, the CPE systems had different behavior against the salt type. Na2SO4 can form the two-phase system when the concentration of the salt is in the range of 0.5–2.0 mg L−1. However, the other salt cannot form the two-phase system at concentration ≤2.0 mg L−1 such as NaCl, NaOH, K2PO4, KCl and KI. This phenomenon is probably a solvophobic one. The kosmotropic ions, e.g. SO42−, OH−, Na+ and PO43−, which exhibit a stronger interaction with water molecule than water with itself are therefore capable of breaking water–water hydrogen bonds and beneficial to the phase separation formation. However, the chaotropic ions, e.g. Cl−, K+ and I−, have the opposite effect because of their exhibiting weaker interactions with water than water itself and thus interfering little in the hydrogen bonding of the surrounding water. The effect of the cation nature is usually smaller than that of the anion. According to Ferreira and Teixeira (2010), the salting-out ability of the cations follows the Hofmeister series (Na+ > K+) and can be related to the ions from Gibbs’ free energy of hydration (∆Ghydr). Comparing the cation ∆Ghydr (−89.6 kcal mol−1 for Na+ and −72.7 kcal mol−1 for K+) it is possible to confirm that (Na+) is the most kosmotropic ion. Kosmotropic ions have large negative ∆Ghydr due to the resulting structured water lattice around the ion, and therefore the salting-out effect of Na+ is greater than K+ [43]. Therefore, Na2SO4 has been chosen due to its ability to form the two phases of separation.

As shown in Fig. 8, the extraction efficiencies of the three phenol species increase with the increasing Na2SO4 concentration from 0.5 to 1.5 mol L−1 and become constant above 1.5 mol L−1. After adding the concentration of salt up to 2.0 mol L−1, the concentration of salt becomes saturated, causing no changes on the extraction efficiencies, compared to the concentration of salt at 1.5 mol L−1 for the three phenol species. This approach was compatible with the UV–visible detection even by adding salts under saturated conditions to the surfactant solution [44]. In general sulfate ion (SO42−); as it is well established fact that anion has marked influence compared to that of cation. It has a strong influence on the structure of the water and the hydrogen bonding between the real oxygen of polyethylene oxide (PEO) chain and water. The following explanation for the PEO–sulfate ion interaction in water can be given: The water surrounding the sulfate ion is polarized on the ionic field, resulting in a low free energy, while the water in the PEO hydration shell is in a high free energy state because of its unfavorable entropy contribution. As a sulfate ion approaches the PEO, the amount of the intervening water decreases, leading to a repulsive force between the sulfate ion and PEO (since the PEO is far less polarizable than water). This progressive dehydration of PEO disrupts hydrogen bonds between the ether oxygen of the copolymer molecules and water or transformation of a polar PEO conformation to a non-polar gauge formed at higher salt concentration [45]. Therefore, 1.5 mol L−1 was selected as an optimum concentration of salt. It is fact that the addition of Na2SO4 electrolyte increased the size of the micelle and aggregation number, thus, enhancing the analyte to be more soluble in the surfactant rich phase so more water goes to the dilute phase due to the salting-out effect. The added sulfate ions also decrease the self-association of water molecules, the hydration of the PEO chain and the surfactant solubility in water, causing decreases in the CPE [46]. It has been mentioned that adding too much Na2SO4 is not always favorable. The addition of excessive Na2SO4 to the micellar solution will lead to the very low CPT and, thus, render the formation of the unwanted and very viscous surfactant rich phase. The salting-out effect was also correlated with the water content in the surfactant
rich phase. The more concentration of Na₂SO₄, it will contribute to the occurrence of the dehydration process less water content in the surfactant rich phase [47].

Effect of concentration analytes

Fig. 9 shows the extraction efficiency of phenol species versus initial concentration of phenol species in the range of 2.0–20.0 mg L⁻¹. The extraction efficiencies decrease with the increment in the concentration of solute and it appears to be constant from 16.0 mg L⁻¹ to 20.0 mg L⁻¹ for the three phenol species. As shown in Fig. 9, both chlorophenols (2,4-DCP and 2,4,6-TCP) had obtained 100% of extraction efficiencies at 2.0 mg L⁻¹. Meanwhile, about 80% extraction efficiency was achieved for 4-NP at 2.0 mg L⁻¹. At a constant operating temperature (50 °C), the concentration of surfactant in both the aqueous and rich surfactant phases remains constant. Hence, the three phenol species solubilization capacity of the surfactant micelles remains almost invariant in both phases. Therefore, with further increase in phenol species concentration this leads to the unsolubilized excess phenol species and which were retained in the aqueous phase that account for a decrease in the extraction efficiencies of the three phenol species [18].

Interference study

In order to investigate the selectivity of the method, a 1 mL of sample solution containing 10 mg L⁻¹ of 2,4-DCP and 500 mg L⁻¹ of Na⁺, K⁺, Cl⁻, Br⁻, CO₂⁻, OH⁻, I⁻ and NO₃⁻ was extracted under a specific experimental condition. The same procedure was carried out for 2,4,6-TCP and 4-NP. The results given in Table 1 reveal that there is no significant interference by the diverse ions present at moderate concentration.

Water content in surfactant rich phase

Water content in the surfactant rich phase is another factor to be focused on, in improving the extraction efficiency. In fact, about 80 wt% water content is still present in the surfactant rich phase after the CPE process; even the phase extraction process was straightened by the high speed centrifugation operation. The high water content in the surfactant rich phase has limited the performance of the CPE to a large extent, which further causes the difficulty in the distribution coefficient and extraction efficiency [30]. Fig. 10 shows the comparison of the percentage water content in the surfactant rich phase between the CPE process with DC193C and Triton X. Based on the result, Triton X obtained the higher percentage of water content in the surfactant rich phase compared to DC193C after the CPE process for three phenol species. The percentage of water content in surfactant rich phase for DC193C were about 58 wt% (2,4-DCP), 56 wt% (2,4,6-TCP) and 67 wt% (4-NP), respectively. Meanwhile for Triton X, the percentage of the water content in the surfactant rich phase was above 80 wt% for three phenol species. Referring to the structure of DC193C (Fig. 1), more conformation of the PEG dimethicone molecule was present in the formation of micelles and surfactant rich phase during the CPE process in order to make the arrangement of molecule more compact due to the flexible long silicone chain structure. Thus, the spaces remained for the water inside or among the micelles were efficiently compressed compared to the structure of Triton X [30]. Therefore, the surfactant of DC193C was favorable for the excellent performance of CPE.

Another factor that contributes to the specificity of the interphase transfer in the micelle extraction system was the influence of the analyte molecule structure and their hydrophobicity on its distribution between the aqueous and the surfactant rich phase [48]. As illustrated in Fig. 10, the surfactant rich phase has the highest water content for the least hydrophobic 4-NP compared to 2,4-DCP and 2,4,6-TCP which are more hydrophobic. The least hydrophobic molecule of 4-NP has the potential to solute in the aqueous phase that causes the spaces to remain for the water inside the micelles were not efficiently compressed. Meanwhile, the surfactant rich phase becomes more hydrophobic when more hydrophobic analytes for both chlorophenols are bound into the micelle core. Trichlorophenol is more hydrophobic than dichlorophenol due to the increasing numbers of chlorine atoms in the molecular structure. Thus, the solubilization increases in the hydrophobic micelles instead of the aqueous phase. As a result, the percentage of the water content in the surfactant rich phase decreased on the increasing of molecule hydrophobicity according to the following order;

$$2,4,6\text{-TCP} > 2,4\text{-DCP} > 4\text{-NP}$$

![Fig. 9. Effect of concentration analytes on the extraction efficiency. Conditions: pH 7.0; 0.5 (v/v%) DC193C, 1.5 mol L⁻¹ Na₂SO₄ at 50 °C.](image)

![Table 1](image)

<table>
<thead>
<tr>
<th>Ions</th>
<th>Concentration (mg L⁻¹)</th>
<th>Extraction efficiency (%)</th>
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<tr>
<td></td>
<td></td>
<td>2,4-DCP</td>
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<tr>
<td>Na⁺</td>
<td>500</td>
<td>80</td>
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<tr>
<td>K⁺</td>
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<td>Cl⁻</td>
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<td>NO₃⁻</td>
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![Fig. 10. Water content in the surfactant rich phase obtained by the CPE process with DC193C and Triton X at 0.5 (v/v%) surfactant concentration.](image)
In addition, the concentration of non-ionic DC193C surfactant is also one of the factors that affect the percentage of water content in the surfactant rich phase as shown in Fig. 11. The percentage of water content decreases as the concentration of DC193C increases from 0.1 to 0.5 v/v% and almost constantly up to 0.8 v/v% for the three phenol species studied. This is due to the increasing number of hydrophobic micelles which results in the extraction efficiency of three phenol species [46]. This finding has been supported by the results obtained as shown in Fig. 4. From this, we can conclude that the lowest percentage water content in the surfactant rich phase, the higher the extraction efficiency in the phenol species.

**Method validation**

Under the optimized conditions, the calibration graphs were constructed by plotting the absorbance signal against the concentrations of each analyte subjected according to the general procedure for the CPE. The measurement of each analyte spectrophotometrically at the respective absorption maxima against a reagent blank prepared under similar conditions. The calibration data are summarized in Table 2.

**Application real samples**

The calibration graphs in the range 0.4–2.0 mg L\(^{-1}\) were constructed by plotting the absorbance signal against the concentration of each phenol species subjected according to the general procedure under the optimized conditions. The developed method has been applied to evaluate its feasibility by spiking each phenol to the water sample. The results were summarized in Table 3 and the recoveries for all phenol species were calculated to be in the range of 69–97%. Therefore, the method can be considered as a reliable method for the removal of phenol species in water samples.

**Conclusion**

The CPE technique offers several advantages such as the fact that its cost is low, it is sensitive, selective and it provides safety with good extraction efficiency. To the best of our knowledge, this is the first report on the use of non-ionic surfactant of DC193C in the CPE that is applied for the removal of the three phenol species (2,4-DCP, 2,4,6-TCP, 4-NP) in aqueous samples. Experimental results show that high recoveries can be obtained at the optimized parameters: DC193C, 0.5 mL of 0.5 v/v%; for Na\(_2\)SO\(_4\), 1.5 mol L\(^{-1}\); equilibration temperature, 50 °C and incubation time, 15 min for three phenols. Furthermore, the non-ionic DC193C surfactant in the CPE has a great potential to be explored for removing the organic pollutant in the water samples based on their unique structure molecules that could entrap hydrophobic and as well as hydrophilic substances. Besides, it has low water content which enhances the extraction efficiency. In addition, a non-ionic surfactant of DC193C used in the CPE makes the micellar extraction procedure simple, greener and economical as highly desired for the removal technique.

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