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Determination of phenol in water samples using cloud point extraction and UV spectrophotometry

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ABSTRACT

A cloud point extraction method is developed using silicone-ethylene oxide surfactant, DC193C to extract phenol compound in the environmental water samples. The parameters such as the effect of salt concentration, pH, temperature, surfactant concentration, and water content are evaluated. The nonionic surfactant, DC193C is chosen because it is well known as an environmental friendly solvent. The developed method obtains the high recoveries of phenol extraction from water samples with the percentage recoveries at 78–97% with the limit of detection is 0.076 mg/L. The phenol is measured using UV–vis spectrophotometer at 260 nm. The proposed method is successfully applied to the environmental water samples such as river water, lake water, sea water, and tap water for phenol extraction with satisfactory results.

Keywords: Cloud point extraction; Phenol; Nonionic surfactant; Water samples; UV–vis spectrophotometry

1. Introduction

Phenols are used in a multitude of consumers' products resulting in ubiquitous human exposure. Phenol also extensively found in the effluents from dyestuffs, petrochemicals, pesticides, and pharmaceuticals [1]. The relatively high solubility in water makes phenol possible to be transported favorably in the environment. It has been classified in the list of prior pollutants by most national environmental protection agencies (EPA) owing to their potential harm to the environment and mutagenic and also carcinogenic effects to human health at relatively low concentrations. The US EPA, the Central Pollution Control Board (CPCB) and the European Union (EU) have set an effluent standard of 1.0 mg/L of phenol and their derivatives for the save and sanitary discharge of industrial and agricultural effluents [1]. Phenol influences the objectionable taste and odor of drinking water at the concentration of 0.005 mg/L [1]. Moreover, fatal doses can be absorbed through the skin and chronic phenol exposure would damage organs including spleen, pancreas, and kidneys. Acute poisoning would cause severe gastrointestinal disturbances, lung edema, circulatory system failure, kidney malfunction, and convulsions [1].

For the sake of public health and environmental safety, many studies have focused on the efficient

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elimination of phenol from aqueous solutions such as photocatalytic oxidation [2], electrolysis [3], sorption [4], biodegradation [5], and membrane [6]. Among these methods, sorption technique has been widely used in the preconcentration and solidification of aromatic pollutants due to its low-cost, easy operation, and wide adaptability [1]. However, the limited capabilities and efficiencies hinder their practical applications in real work. Therefore, the development of an efficient, fast, low-cost, and greener extraction method to extract phenols in water samples is of great importance.

CPE methods have been used where they are able to extract and preconcentrate a wide range of organic compounds from the aqueous phase. Moreover, some of the surfactants in CPE are toxic and dangerous to humans and the environment. Therefore, we should find a green surfactant to protect the environment and human health. A silicone nonionic surfactant so-called DC193C in what follows is a water-soluble surfactant that may be considered as a green surfactant and can be used directly for HPLC/UV without giving any obstacles to the detector [7]. Consequently, it is an alternative which able to overcome the problem from most of the nonionic surfactants used in HPLC/UV or UV instruments.

The novelty of this study is the introduction of a role of nonionic surfactant, DC193C in cloud point extraction (CPE) to extract phenol from water samples. Here, DC193C surfactant is proposed as nontoxic solvents for the extraction of phenol species in CPE. It has been an important and growing class of raw materials used in the cosmetic, food, and pharmaceutical industries. In addition, their biocompatibility and safety to human and environment have been proved for a long time. As reported by Chen (2005), even the DC193C surfactant discharged to the environment, there is no significant effect to the environment. Moreover, the US FDA permitted this surfactant for internal consumption [8]. This study is important because the application of CPE with DC193C technique results in a fast extraction, high preconcentration factor, and avoidance of using toxic and environmentally unfriendly organic solvents. Thus, it is advantageous compared to other techniques. Based on our previous study [9–11], since extraction of parabens using DC193C gives promising results, we would like to explore the application of DC193C in the extraction of phenol from water samples. It is a challenge to determine the efficiencies of silicone nonionic surfactant DC193C to extract many more organic pollutants in water samples. The parameters, i.e. salt concentration, pH of the solution, temperature, and surfactant concentration are screened to attain the optimum conditions for phase separation of phenol. The performances of the DC193C method are evaluated using water content and recovery percentage of phenol extraction in water samples.

2. Materials and methods

2.1. Reagent and standards

The silicone nonionic surfactant-ethylene oxide copolymer called DC193C was manufactured by Dow Corning (Shanghai, China) and supplied under the name DC193C by Dow Corning Malaysia. The cloud point is 95–100˚C. Flash point, closed cup = 113˚C. Kinetic/kinematic viscosity = 260 cST (centistoke). Unfortunately, the information on the detailed molecular structure and the values of x and y are not provided by the manufacturer. The molecular weight of these compounds is 3,100 g/mol. Phenol crystal solid was purchased from Sigma Aldrich (Germany). Acetonitrile (HPLC grade) and sodium sulfate (Na_2SO_4) were purchased from Merck (Germany). The deionized water used in mobile phase is of conductivity 18 MX cm. Stock solutions of phenol at a concentration of 1,000 mg/L are prepared in acetonitrile. Working standard solutions are prepared by stepwise diluting with deionized water of stock solutions. The 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 phenol is carried out using Shimadzu UV–vis spectrophotometer (Kyoto, Japan) model UV-1650 at 260 nm.

2.3. General procedure for extraction of phenol using the CPE method

A desired aqueous solution is obtained with the mixture of 30% wt (w/v) surfactant concentration in aqueous solution, 1 mL of stock solution of phenol at 0.01 ppm and 0.5 mL of sodium sulfate solution using an ultrasonicator for 5 min. The pH solution is adjusted in a glass centrifuge tube prior to the extraction process. Subsequently, the separation of the phases is achieved by centrifugation for 10 min at 4,000 rpm or otherwise kept overnight to ensure separation between the surfactant-rich phase and water is achieved. Then, the volumes of the surfactant-rich phase and the water are measured. The surfactant-rich phase is isolated and mixed with 0.5 mL of acetonitrile before being analyzed using UV–vis spectrophotometer. To measure the water content of the surfactant-rich phase, the surfactant-rich phase is dried at 75˚C until no loss of mass is observed and the water content is obtained by calculating the weight difference of the surfactant-rich phase before and after drying. All the data given are the average of triple measurements.

2.4. Preparation of CPE in real samples

Tap water samples are collected from the laboratory. River water samples are collected from two rivers and named as River A (geographical coordinate 5˚19´50.5˝N, 103˚07´20.1˝E) and River B (geographical coordinate 5˚27´58.8˝N, 103˚01´07.1˝E). The other samples are sea water samples (geographical coordinate 5˚25´44.6˝N, 103˚04´22.0˝E) and lake water samples (geographical coordinate 5˚22´04.3˝N, 103˚06´06.8˝E). All water samples are filtered using a 0.45-lm nylon membrane filter to remove the suspended particulate matter and then stored at 4˚C in the dark. The samples are analyzed according to the method explained in sub-Section 2.3.

3. Results and discussion

3.1. Effect of salt concentrations on cloud point temperature

Fig. 1 shows the effects of Na_2SO_4 on the extraction recovery of phenol. An increasing trend on extraction recovery is observed as the salt concentration is increased from 0.5 to 1.5 M. The recovery percentage of phenol extraction shows a consistent values when the salt concentration is increased from 2.0 to 2.5 M. At this concentration, the salt solution starts to form precipitates. This is probably because at high salt concentration, salt molecules are unable to break the hydrogen bonding with water molecules between surfactant and phenol. The constant extraction recovery after 2.0 M salt is because the concentration of salt becomes saturated and causing no changes in the extraction recovery compared to the extraction recovery of phenol at 1.5 M of salt concentration [11].

Similar results have been obtained in the previous research where it was reported that the addition of electrolytes may accelerate the separation of the two phases of the CPE method [12,13]. This is because salt acts as a “drying agent” that causing the partial dehydration to occur for both surfactant and phenol by the breaking of hydrogen bonds with water molecules. These results show a significant reduction of the cloud point in a way that phase separation already occurs at room temperature.

The similar study was conducted by Zain et al. [11] which used different types of salts, i.e. Na_2SO_4, NaCl, NaOH, K_3PO_4, KCl, and KI. The obtained results showed that Na_2SO_4 form two-phase system when the concentration of the salt was in the range of 0.5–2.0 mg/L and the other salts such as NaCl, NaOH, K_3PO_4, KCl, and KI does not form two-phase system at concentration ≤2.0 mg/L. Hence, it shows that CPE method has different behavior with different types of

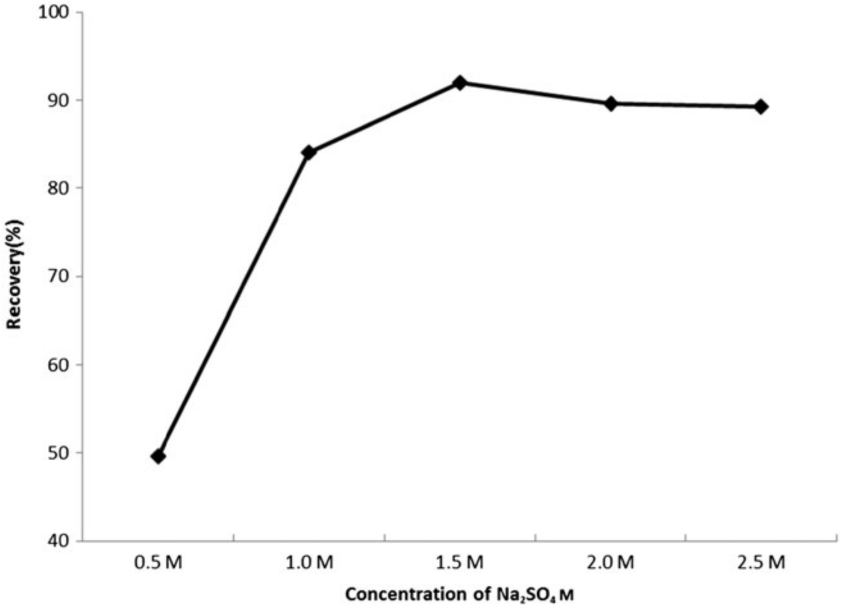

Fig. 1. Effects of Na_2SO_4 on the extraction recovery of phenol.

salt. This might happen due to the solvophobic in which the kosmotropic ions, such as OH^- or Na^+, exhibit stronger interaction with water molecules than its own water molecules and are capable of breaking water–water hydrogen bonds. This is beneficial to the phase separation formation. Sulfate ion will give strong influence on the structure of the water and hydrogen bonding. Thus, comparing the result that is obtained in this research to the previous research [14], it shows that Na_2SO_4 gives a significant effect to the optimization of salt concentration. Therefore, 1.5 M of Na_2SO_4 is selected as an optimum concentration of salt.

The addition of salt as an electrolyte increases the size of the micelle and aggregation number, thus, enhancing the analyte to be more soluble in the surfactant-rich phase. As a result, water goes into the dilute phase due to the salting-out effect. The addition of sulfate ions also decreases the self-association of water molecules, and the surfactant solubility in water causing a clear separation between surfactant-rich phase and aqueous phase layer in the CPE. Adding more salt forms more viscous surfactant-rich phase. The higher concentration of salt contributes to the occurrence of the dehydration process and consequently less water content in the surfactant-rich phase [15].

3.2. Effect of surfactant concentration on the extraction recovery of phenol

The effect of the surfactant concentration is studied using nonionic surfactant, DC193C at different concentrations which are 10% (w/v), 20% (w/v), 30% (w/v), 40% (w/v), and 50% (w/v). Fig. 2 illustrates the effect of surfactant concentration on the extraction recovery of phenol. The results clearly prove that the extraction recovery of phenol species significantly increases when the surfactant concentration is increased from 10 to 30% (w/v). While at the surfactant concentration from 30 to 50% (w/v), only a slight increment in the extraction recovery is observed.

The increases in recovery percentage from 10 to 50% (w/v) are probably due to the increase in viscosity of the surfactant-rich phase. It shows that the volume of surfactant rich decreases when the surfactant concentration is increased. The small volume of the surfactant-rich phase gives a high recovery percentage of phenol extraction. Similar observation was obtained from our previous experiment, where the results showed that the recovery percentage of parabens that had been extracted increased as the volume of surfactant-rich phase was decreased [10]. At concentrations lower than 10% (w/v), the extraction recovery of phenol is low because of only some molecules of surfactant entrapping phenol in the surfactant-rich phase. The low concentration of surfactant is expected as inadequate to entrap the phenol in surfactant-rich phase, leading to low recovery of phenol extraction in the CPE method. According to Mortada et al. [16], the extraction recovery of the complexes is low when it is at lower concentration, due to the inadequacy of the assembly to entrap the complex.

Therefore, 30% (w/v) of surfactant concentration DC193C is selected as the optimum amount of surfactant concentration for phenol species because it gives high recovery percentage of phenol extraction. Thus, this amount is also adequate for the CPE method. Similar process was conducted by Khammas et al. [17] with the utilization of surfactant Triton X-10. The results showed that the high concentration of surfactant increases the volume and viscosity of the surfactant-rich phase. In addition, it leads to poor sensitivity.

Yurtman-Gunduz et al. [18] conducted a study using Triton X-100 as a surfactant agent. The concentration is optimized from 0.1 until 0.3% (w/v). The results showed that the increment in surfactant concentration until 0.16% (w/v) led a constant value of recovery and it is considered as a complete extraction. When the surfactant concentration is low, the extraction recovery is also low because it is difficult to entrap the hydrophobic area of the surfactant. This report has similar trend with our study, where it can be seen that the percentage of recovery increases when the surfactant concentration is increased until reaching the optimum condition. After the optimum condition, the percentage of recovery will only increase slightly or consistent when the surfactant concentration is increased. This is because the CPE method has reached the optimum condition at 30% (w/v) of surfactant concentration DC193C.

3.3. Effect of temperature on the extraction recovery of phenol

Fig. 3 depicts the effect of temperature on the extraction recovery of phenol. It shows that the temperature does not give a significant effect on the extraction recovery of phenol. This is because of the plateau results on the extraction recovery of phenol are obtained from all the studied temperature (30, 40, 50, 60 and 70°C and room temperature). For analytical targets, cloud point temperature is taken at room temperature because during the centrifugation process, a decrease in temperature causes loss in extraction

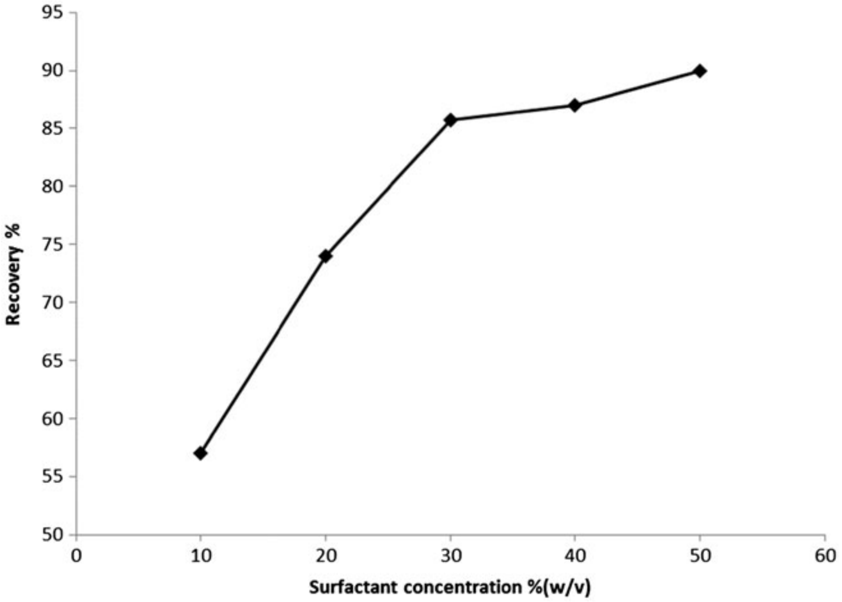

Fig. 2. Effect of surfactant concentration on the extraction recovery of phenol.

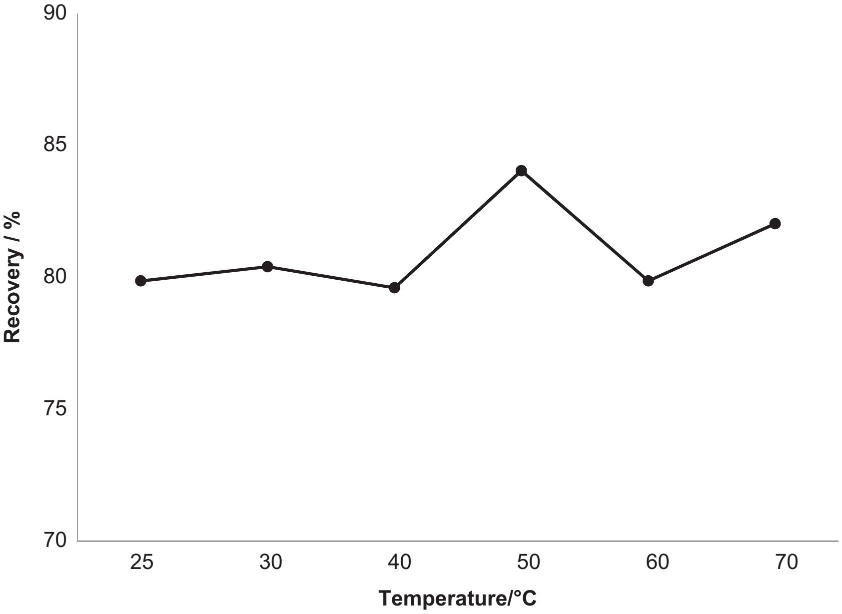

Fig. 3. Effect of temperature on extraction recovery of phenol.

recovery [19]. Thus, the result proves that the temperature does not give significant effect on the dehydration of the micelle and volume of surfactant-rich phase. It also shows that the surfactant DC193C can undergo dehydration at room temperature. To conclude, the temperature setting during CPE is not quite necessary and room temperature is chosen as the optimal temperature for this study.

3.4. Effect of pH in the Extraction of Phenol Using CPE Method

pH is the most important factor in the CPE method where it will regulate the partitioning of the target micellar phase for organic molecules. The effect of pH on the extraction recovery is studied in the range of pH 2–7. As illustrated in Fig. 4, the extraction

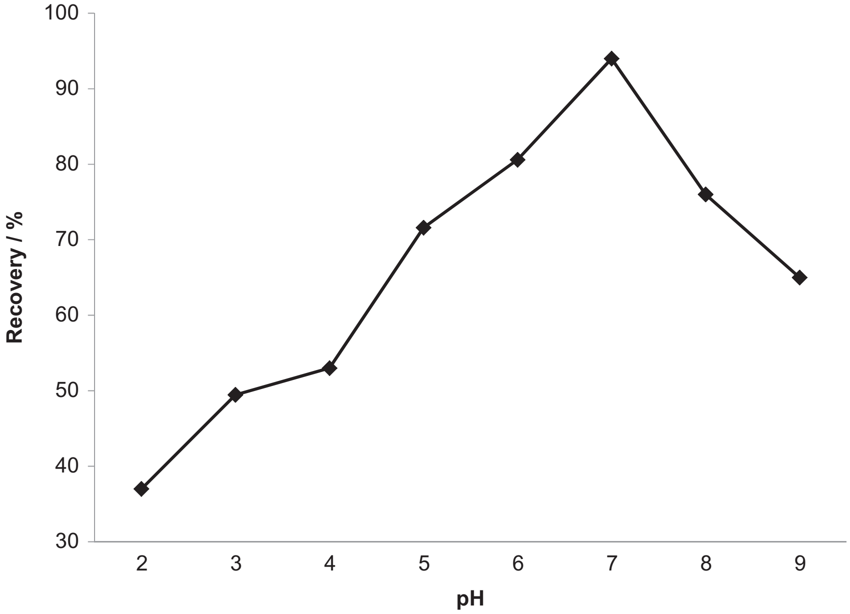

Fig. 4. Effect of pH on the extraction recovery of phenol.

recoveries of phenol gradually increased from pH 2 to 7. The highest extraction recovery of phenol is 92% at pH 7. After pH 7, the percentage of recovery starts to fall to 76 and 65% at pH 8 and 9, respectively. At $pH < 3$, the extraction recoveries are very low. The results clearly show that the trend of the extraction recovery of phenol is low at acidic and basic condition, and high at neutral condition.

Fig. 5 shows protonation and deprotonation of phenol in different pH ranges. The low extraction recoveries at $pH < 3$ is because phenol species are protonated at lower pH (less than pK_a values which is at $pH < 3$) and their ionic characteristics of phenol increase, leading to less solubilization of the phenol in the hydrophobic micelles. Since the phenol is in protonated form, the interaction between phenols and surfactant DC193C becomes less leading to low complexation [20]. Due to the less interaction between phenol and the surfactant DC193C, only a little amount of phenol is extracted in the surfactant-rich phase, resulting to low percentage of extraction recovery. The similar results were obtained in our previous study [10] which reported that below pH 3, parabens is in the protonated form, and hence the extraction recovery of paraben is low.

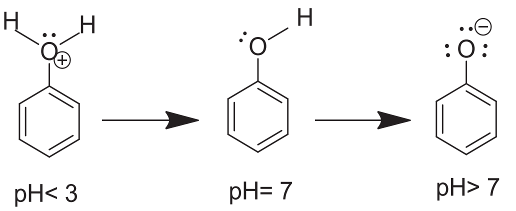

Fig. 5. Protonation and deprotonation of phenol in different pH ranges.

The extraction recovery shows the highest percentage of phenol extraction at pH 7 (Fig. 4) in which phenol existed in the neutral form (Fig. 5). This is due to the good interaction between phenol and DC193C where the uncharged form of target analyte prevails. Thus, higher amount of phenol is successfully extracted in the surfactant-rich phase. At $pH > 7$, the extraction recovery shows a decreasing trend. This trend occurs due to the formation of the phenolate ions [11]. Under basic condition, phenol is in deprotonated form which causing less interaction between phenol and DC193C. Thus, the amount of the extracted phenol in the surfactant-rich phase decreases.

Based on the previous research on the investigation of the parabens in water samples [9], the extraction performance reached a better level at pH 9 for all the studied parabens. Thus, it can be concluded that the pH plays an important role in determining the optimum condition to extract phenol or paraben. Therefore, based on this optimization, we decided to use pH 7 as the optimal condition for this study.

3.5. Water content in the surfactant-rich phase

Water content is another factor that will affect the extraction recovery. The higher the water content, the lower the performance of CPE. According to Yao and Yang [21], the performance of CPE is limited by the water content in the surfactant-rich phase. This will cause the difficulty in the distribution coefficient and extraction of phenol. The lower amount of water content in the surfactant-rich phase will affect the concentration of analyte.

Fig. 6 shows the water content in the surfactant-rich phase by the CPE process with DC193C at different surfactant concentrations. A decreasing trend of water content is observed when the surfactant concentration is decreased from 10 to 50%. It is a good trend of water content corresponding to the surfactant concentration. This is because lesser water content in the surfactant-rich phase leading to a better performance of the surfactant in the CPE method. Thus, high percentage recovery of phenol will be extracted in the surfactant-rich phase. The low volume of water contents produced in surfactant-rich phase is also due to the presence of salt [7]. The introduction of salt can increase the incompatibility between the water structures in hydration shells of the analytes and surfactant macromolecule. These in turn reduce the concentration of free water in surfactant-rich phase and consequently reduce the volume of the phase.

According to Yao and Yang [21], water is still the main part of the surfactant-rich phase after the phase separation, which has already became an obstruction in further improving the preconcentration factor and distribution coefficient. Based on the flexible long silicone chain structure, more conformations of PEG/PPG-18/18 dimethicone molecules are possibly to present in the formation of micelles and surfactant-rich phase during the CPE process. In order to make the arrangement of molecules to be more compact, the remaining spaces for the water inside or among the micelles are efficiently compressed. This result concludes that the surfactant DC193C is feasible in the CPE process because it produces a small percentage of water content in the surfactant-rich phase.

3.6. Method validation of CPE method in water samples

Table 1 shows the recovery and concentration of phenols in spiked and without spiked of water samples applied in four types of water matrices (river water, tap water, lake water and sea water). Satisfactory results are obtained within the study range in all the water samples and displayed a significant difference in the extraction recoveries between the four water samples. The spiked phenol in the real water samples is 5 ppm. It shows that the developed CPE method for phenol exhibits a better performance on lower limit of detection, 0.076 ppm.

Based on the results obtained in Table 1, all the studied water samples give good percentage of recoveries in the range of 78–97% with relative standard deviations (RSD) of less than 1%. The recovery

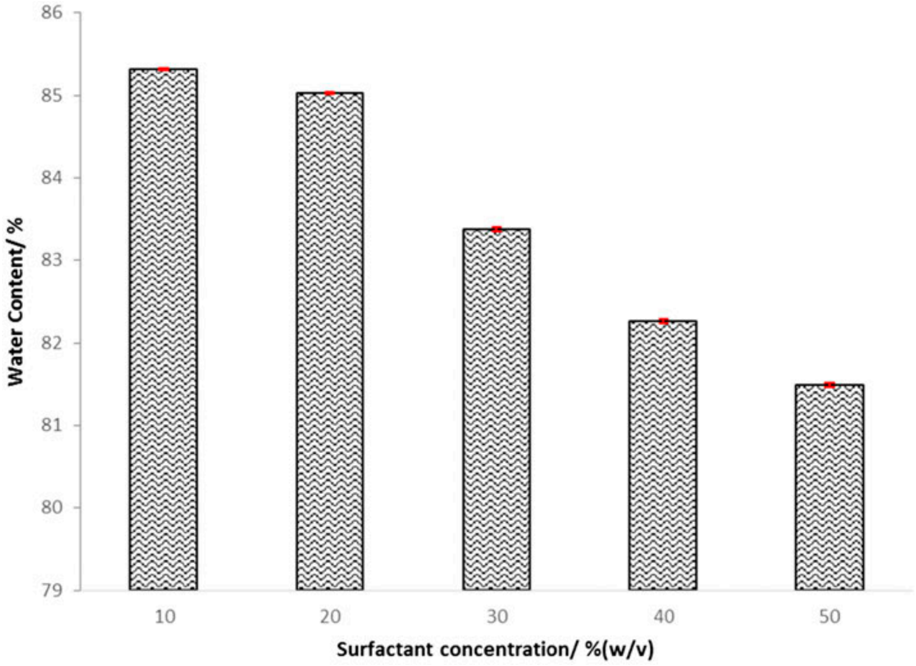

Fig. 6. Water content in the surfactant-rich phase by the CPE process with DC193C at different surfactant concentration.

Table 1
Recovery and concentration of phenols in spiked and without spiked of water samples

Water samples	% Recovery (RSD %) in spike water sample	Concentration of phenol without spiked water sample, ppm (RSD)
Sea	78 (0.075)	3.92 (0.030)
River A	97 (0.043)	3.07 (0.037)
River B	82 (0.011)	1.41 (0.035)
Lake	79 (0.075)	3.81 (0.018)
Tap	78 (0.069)	2.65 (0.049)

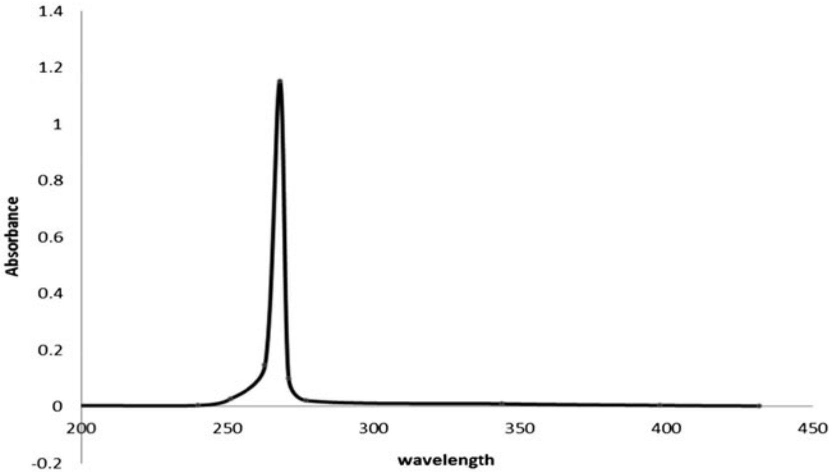

Fig. 7. The absorption of the UV–vis spectra for phenol at the respective absorption in the surfactant-rich phase after CPE method.

percentage of phenol extraction can be characterized as the percentage of phenol extracted from bulk solution into the surfactant-rich phase. The lowest recovery percentage is obtained for sea and tap water sample and the highest concentrations of phenol extracted from River A samples. It is clear that the sea water sample shows the lowest recovery percentages because salts in the sea water samples may interrupt the CPE method. This result is similar to our previous research [10] which reported that the interruption is due to electrolyte factor of salt that affecting the CPE method. These results have shown that the method developed is feasible to be used for monitoring phenol compound in environmental water samples.

On the other hand, higher recoveries are obtained using the developed method of CPE from the water samples without spiked of phenol. It is shown that the highest concentrations of phenol are extracted from sea water with 3.92 ppm followed by 3.81 ppm from lake, 3.07 ppm from River A, and 2.05 ppm from tap water. Fig. 7 shows the absorption of the UV–vis spectra for phenol at the respective absorption in the surfactant-rich phase after CPE method.

4. Conclusion

This study has demonstrated that CPE using non-ionic surfactant DC193C is an excellent method to extract phenol from various water samples. This study proves that DC193C is able to extract many more organic pollutants in water samples include parabens and phenol. It is economically viable method because of the uses of cheap and nontoxic chemicals to our environment.

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