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Study of removal of phenol species by adsorption on non-ionic silicon surfactant after cloud point extraction methodology

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ABSTRACT

In the present study, CPE was carried out to extract phenol species from aqueous solution using the non-ionic silicone surfactant of DC193C. The non-ionic silicone surfactant of DC193C was chosen because of it is well known as an environmentally friendly solvent. The adsorption mechanism between the non-ionic silicone surfactant of DC193C and phenol species was studied. Our results indicate that, the adsorption of the phenol species from aqueous solution on the DC193C surfactant was in proportion to their hydrophobicities, according to the following order; 4-NP < 2,4-DCP < 2,4,6-TCP. The data of the equilibrium concentration and amount of adsorption in the CPE system for the three phenols species follow the Langmuir-type isotherm. On some assumptions, a developed Langmuir isotherm was used to calculate the feed surfactant concentration required for the removal of the three phenol species up to the extraction efficiency of 90%. The developed correlations may be useful to design a cloud point extractor of a desired efficiency. Thermodynamic parameters including the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were also calculated. These parameters indicated that the adsorption of the three phenol species solubilized into the non-ionic DC193C surfactant is feasible, spontaneous, and endothermic in the temperature ranging from 298 to 353 K.

Keywords: Non-ionic surfactant DC193C; Adsorption; Cloud point extraction; Phenol species; Langmuir isotherm; Spectrophotometry

1. Introduction

Phenol and phenolic derivatives belong to a group of common environmental contaminants. They are widely distributed in natural waters because of their wide use in many industrial processes such as the manufacture of plastics, dyes, drugs, and pesticides [1–3]. Phenolic compounds are main pollutants in surface waters or groundwater, thus, they are considered as priority pollutants due to their toxicity and possible accumulate in the environment. They give an unpleasant taste and odor to drinking water and can exert negative effects on different biological processes. The presence of these compounds at low concentration can be an obstacle to the use (and/or) reuse of water.

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Toxicity generally increases with the degree of chlorination and it has been reported that the OH group plays an important role in the toxicity of chlorophenols to fish [4,5]. Due to their toxicity and adverse effect upon human and biota, the United States Environmental Protection Agency, has classified them as priority pollutants. The maximum allowed concentration of phenols in water is 0.1 mg L^{-1} [6–8]. Therefore, the removal of phenolic pollutants from aqueous solution is necessary for environment protection and has been investigated by various physical, chemical, and biological methods.

The toxicity of phenols, even at a trace level, attracts the environmental scientists to develop suitable technologies for their removal from aqueous solution. The various techniques that proved effective for phenols removal from aqueous solution are membrane separation process [9,10], biological degradation [11,12], chemical oxidation [13,14], and adsorption [15–17]. Among these techniques, adsorption is a most versatile and superior method for the removal of toxic pollutant. Adsorption process is known to be cost-efficient, easy, and effective at moderate and low concentrations, rapid, and reproducible for the removal of pollutant, and works without the addition of chemicals or UV radiation. These are the major advantages of adsorption technique [18].

As the temperature of an aqueous non-ionic surfactant solution is increased or some additives are added, the solution turns cloudy and phase separation occurs. The solution may separate into a surfactant-rich phase (coacervate phase) and a dilute phase. A solute that originally exists will unevenly partition itself into those two phases. The temperature at which phase separation occurs is known as cloud point [19–21]. This technique is known as cloud point extraction (CPE). CPE has been recognized as an alternative approach to the conventional liquid–liquid extraction due to a number of advantages, i.e. low cost, environmental safeties, short analysis time, high capacity, and high recovery for a wide variety of pollutants [22–24]. Recently, great attention has been attracted for its great potential in separation of biological material, removal of toxic solutes from polluted water [25]. Micelles of such well-known non-ionic surfactants have a non-polar core (hydrophobic tail) and extended polar layer (hydrophilic head), where both extractants and extracted complexes can be solubilized. It is important to study the mechanism of interaction between the surfactant and solute for obtaining a more suitable, efficient, cheap type of surfactant. The CPE is proposed to be a process of interaction between solute and micelles of surfactant, where the interaction can be treated as an adsorption of solute on the surface of the micelles or some other sites within micelles. The micelles of surfactant are the adsorption center. The micelles of surfactant have the ability to adsorb an analyte inside their central core or outer palisade layers; this can be suggested by the monolayer coverage of the solute on the surface of the micelle. Therefore, this type of adsorption can be expressed by Langmuir isotherm [26].

Despite the drawbacks associated with the use of non-ionic surfactants with an aromatic moiety in their structure (i.e. Triton X-100 and PONPE series), they have been the most frequently employed in CPE schemes. They feature high background absorbances in the ultraviolet region or fluorescence detection modes that might interfere when handling with these instruments. In addition, a high temperature is required for two liquid phase formations that prevent them to be used in the extraction of thermally labile analyte. Therefore, non-ionic silicone surfactant of DC193C extraction has been proposed to overcome some of the above-described limitations [27]. The DC193C fluid which is the non-ionic silicone surfactant is based on polyethylene glycols (PEGs) and is also called silicone surfactant [28]. PEGs offer several advantages, i.e. the fact that they are non-toxic, odorless, colorless, non-irritating, and that they do not evaporate easily. Moreover, PEGs are considered inert as they are not reacting to other materials. They are also soluble in many organic solvents. Due to their advantages, 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 [29,30]. As reported by Chen et al. [26], even if the PEGs are discharged to the environment, the environment would suffer from no significant effects. Therefore, the US FDA has permitted this surfactant for internal consumption [28].

In our previous work, the surfactant-rich phase technique has been adopted to extract the phenol species using the non-ionic silicone surfactant of DC193C. The effects of different operating parameters, i.e. pH, concentration of non-ionic surfactant, temperature, incubation time, concentration of salt and analytes, interference study, and water content on the extraction of the phenol species have been studied in detail [31]. From the experimental data, a solubilisation isotherm is developed to quantify the amount of phenols solubilisation. The thermodynamic parameters are also developed to establish the possible mechanism of phase separation. The performance of the non-ionic silicone surfactant of DC193C is investigated to extract different phenols from the aqueous solution. To the best of our knowledge, this is the first report on the use of the non-ionic silicone 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 for the adsorption study. In this work, the adsorption behavior of the three phenol species on the non-ionic silicone surfactant of DC193C was studied at fixed surfactant concentration. The equilibrium data is tested with Langmuir isotherm model. The amount of surfactant required for the removal of solute up to a desired level can be calculated using values of *m* and *n* that were calculated using the linear model of Langmuir isotherm. Thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°) are calculated to know the nature of adsorption. This fundamental study will be helpful for further application for removing pollutants in aqueous solution using non-ionic silicone surfactant of DC193C.

2. Experimental

2.1. Chemical and reagent

Dow Corning DC193C, also known as 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 manufacturers. The 4-nitrophenol (molecular weight: 139.11 g/mol, λmax: 318 nm), 2,4-dichlorophenol (molecular weight: 163 g/mol, λmax: 285 nm), and 2,4,6-trichlorophenol (molecular weight: 197.45 g/mol, λmax: 295 nm) were purchased from Aldrich. Standard stock solutions of chlorophenols (1,000 mg L^{-1}) were prepared in methanol and 4-nitrophenol (1,000 mg L^{-1}) in distilled water. Working solutions were prepared daily by an appropriate dilution of the stock solutions. For all the experiments, surfactant and phenol species were used without further purification. HCl and NaOH were used for pH adjustment. Na_2SO_4 was prepared by having it dissolved in an appropriate amount in distilled water.

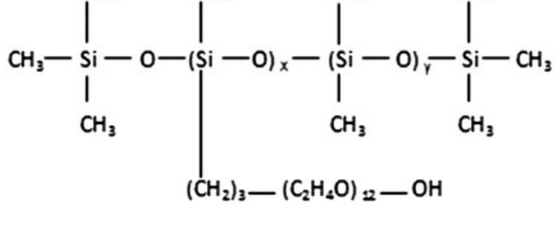

Fig. 1. Structure of silicone surfactant (DC193C).

2.1.1. Apparatus

A Shimadzu (Kyoto, Japan) Model UV-1650 UV–vis spectrophotometer was used for the measurement of the phenol species. A wise bath® was used, maintained at the desired temperature. The pH values of the sample solutions were determined by the pH meter (Hanna instrument). Fifteen-milliliter calibrated centrifuge tubes were used (Copen, Malaysia).

2.1.2. CPE procedure

An aliquot of 1.0 mL of standard solution containing the analyte (10 mg L^{-1}), non-ionic surfactant of DC193C (0.16 mol L^{-1}) and 1.5 mol L^{-1} of Na_2SO_4 at pH 7.0 was 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 different concentrations of the phenol species were in the range of 2.0–20.0 mg L^{-1} for the isotherm study. Meanwhile, the experiment was conducted at varying temperatures from 25 to 80°C for the thermodynamic study. The separation of the phases was achieved by centrifugation for 2 min at 1,500 rpm. On cooling in an ice-bath for 5 min, the surfactant-rich phases had become viscous. Then, the surfactant-rich phase at the top layer could be separated 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 and aqueous phase in order to decrease its viscosity. It will also make the final volume feasible to be transferred into the optical cell for the measurement of each phenol species in the surfactant-rich phase and aqueous phase spectrophotometrically at the respective absorption maxima against a reagent blank prepared under similar conditions. The extraction efficiency of the phenol species by surfactant from the sample was calculated as Eq. (1) [32];

$$\text{Extraction efficiency\%} = \frac{C_s V_s}{C_o V_o} \times 100 = \frac{C_o V_o - C_w V_w}{C_o V_o} \times 100 \tag{1}$$

where C_o represents the phenol species concentration in the initial sample of volume V_o, C_w represents the phenol species concentration in the aqueous phase of volume V_w, and C_s, represents the phenol concentration in the surfactant-rich phase of volume V_s.

3. Results and discussion

3.1. Effect of pH

In the CPE, 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 are shown in Fig. 2.

Fig. 2 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. 2 that the maximum extraction efficiencies for the three phenol species were achieved at pH 7.0, where the uncharged form of target analyte prevails [33,34]. 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 [35], 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 binds the micellar aggregate as strongly as does its neutral form due to the non-dissociated type of non-ionic surfactant [35]. Therefore, pH 7.0 was selected as the optimal pH for the three phenol species.

3.2. Effect of electrolyte concentration

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, analyte 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 induce 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 [36,37]. 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 [38].

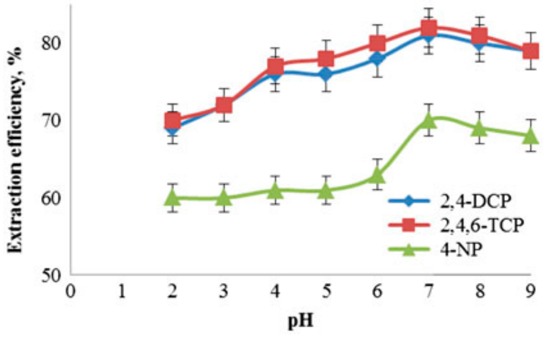

Fig. 2. Effect of pH on the extraction efficiency. Conditions: 10 mg L^{-1} of phenol species concentration, 0.5 (v/v%) DC193C, 1.5 mol L^{-1} Na_2SO_4 at 50˚C.

In this work, salts which were used in the CPE included NaCl, Na_2SO_4, K_3PO_4, 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 behaviors against the salt type. Na_2SO_4 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 salts cannot form the two-phase system at concentration ≤2.0 mg L^{-1} such as NaCl, K_3PO_4, KCl, and KI. This phenomenon is probably a solvophobic one. The kosmotropic ions, e.g. SO_4^{2-}, Na^+, and PO_4^{3-}, 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 [39], 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 (ΔG_{hyd}). Comparing the cation ΔG_{hyd} (−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 ΔG_{hyd} due to the resulting structured water lattice around the ion, and therefore the salting-out effect of Na^+ is greater than K^+ [39]. Therefore, Na_2SO_4 has been chosen due to its ability to form the two phases of separation.

As shown in Fig. 3, the extraction efficiencies of the three phenol species increase with the increasing Na_2SO_4 concentration from 0.5 to 1.5 mol L^{-1} and become constant above 1.5 mol L^{-1}. After increasing the concentration of salt up to 2.0 mol L^{-1}, the

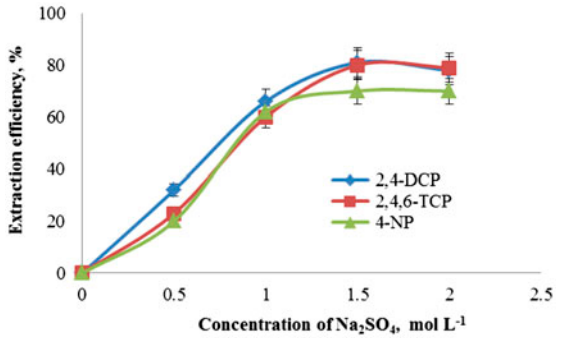

Fig. 3. Effect of concentration salt on the extraction efficiency. Conditions: 10 mg L^{-1} of phenol species concentration, pH 7.0, 0.5 (v/v%) DC193C at 50˚C.

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 [40]. Therefore, 1.5 mol L^{-1} was selected as an optimum concentration of salt. It is fact that the addition of Na_2SO_4 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 [41].

3.3. Solubilization isotherm

Adsorption isotherms are useful for understanding the mechanism of the adsorption. Adsorption properties and equilibrium parameters, commonly known as adsorption isotherms, describe how the adsorbate interacts with adsorbents, and contributes toward a comprehensive understanding of the nature of interaction. Isotherms study helps to provide information about the optimum use of adsorbents. Thus, in order to optimize the design of an adsorption system for the removal of phenol species from aqueous solutions, it is essential to establish the most appropriate correlation for the equilibrium curve. There are several isotherm equations available for analyzing experimental sorption equilibrium parameters. However, the most common types of isotherms are the Langmuir and Freundlich models [42]. The Langmuir sorption isotherm has been successfully applied to many pollutant sorption processes. It has also been the most widely used model to describe the sorption of a solute from an aqueous solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites on the surface of the sorbent. It is then assumed that once a sorbate molecule occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force and area. The driving force is the concentration in the solution, and the area is the amount of bare surface [4,26]. The Langmuir-type adsorption isotherm model has been used to explain the solubilization of the three phenol species in the DC193C surfactant for the CPE system due to its success in describing many adsorption processes. Eq. (2) gives the expression of the well-known Langmuir model.

$$q_e = \frac{mnC_e}{1 + nC_e} \tag{2}$$

where q_e is the moles of phenol species solubilized per mole of the DC193C surfactant at equilibrium (mol mol^{-1}). C_e is the dilute-phase equilibrium (mol L^{-1}) of the phenol species. The constants m and n are the Langmuir constants, m signifies he solubilization capacity (mol mol^{-1}), and n is related to the energy of solubilization (L mol^{-1}).

The constants m and n are the Langmuir constants signifying the solubilization capacity (mol mol^{-1}) and energy of solubilization (L mol^{-1}), respectively [43,44]. Values of m and n for each phenol species can be calculated by the regression analysis using experimental data. Fig. 4(a), (b), and (c) show, the solubilization isotherm of 2, 4-DCP, 2, 4, 6-TCP, and 4-NP, respectively, which is illustrated by plotting $1/q_e$ vs. $1/C_e$. The equilibrium data for the sorption of 2,4-DCP, 2,4,6-TCP, and 4-NP over the entire concentration range were fitted to the Langmuir isotherm. A linear plot was obtained when $1/q_e$ was plotted against $1/C_e$ over the entire concentration range as shown in Fig. 5(a)–(c). The Langmuir model parameters and the statistical fits of the sorption data to this equation are given in Table 1.

3.4. Evaluating the values of m and n

The Langmuir equation can be linearized into the following form;

$$\frac{1}{q_e} = \frac{1}{m} + \frac{1}{mnC_e} \tag{3}$$

where q_e is the moles of phenol species solubilized per mole of the DC193C surfactant at equilibrium (mol mol^{-1}), C_e is the equilibrium concentration (mol L^{-1}) of the phenolic species, and m and n are constants representing the maximum adsorption capacity and energy, respectively.

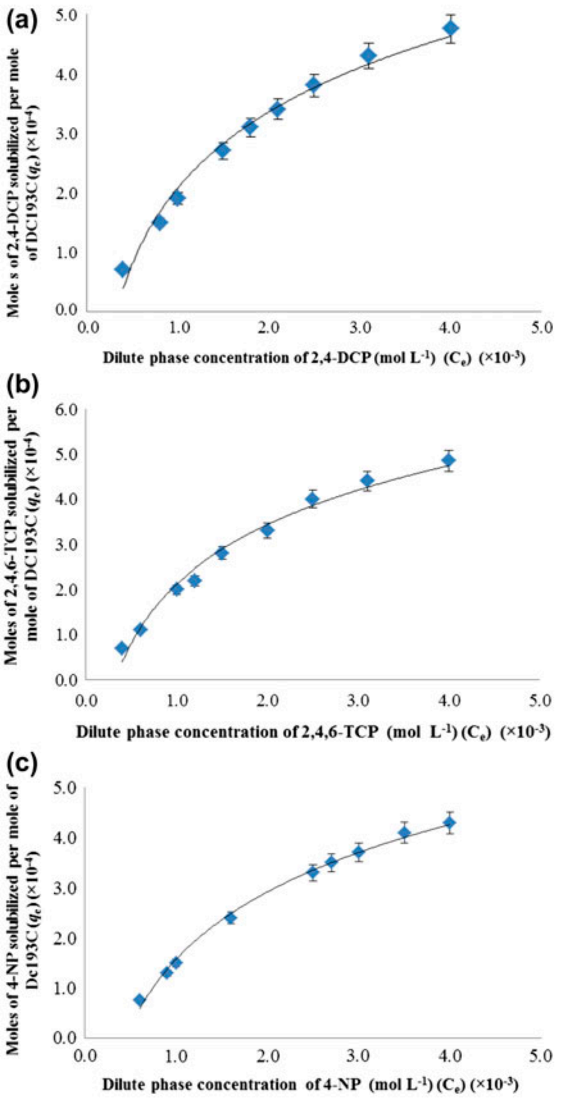

Fig. 4. Solubilization isotherm of the three phenol species over the DC193C surfactant: (a) DC193C-DCP, (b) DC193C-TCP, and (c) DC193C-NP.

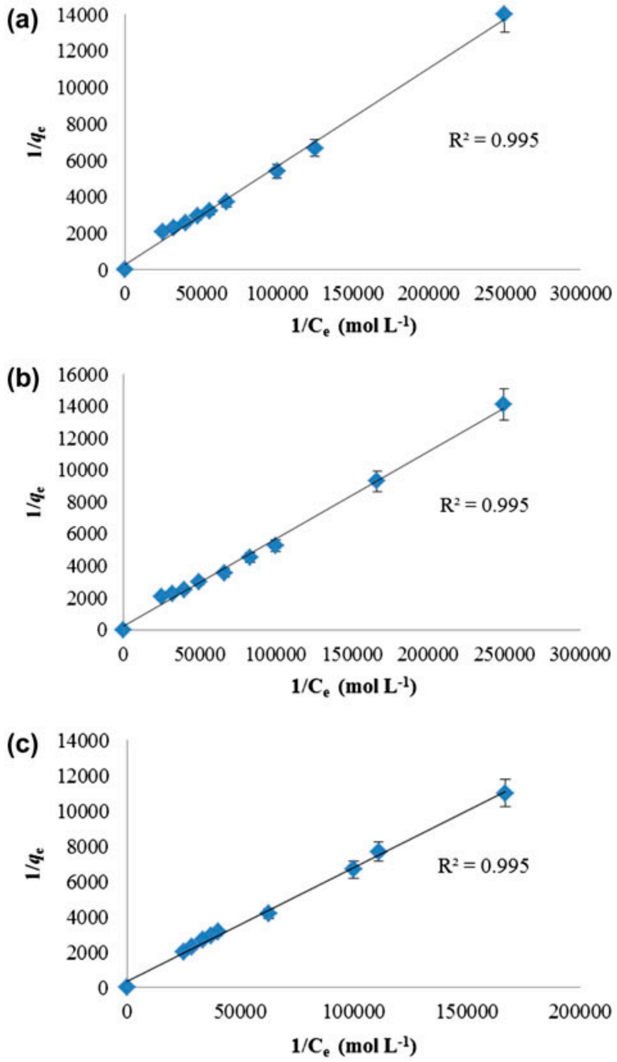

Fig. 5. Plotting $1/q_e$ vs. $1/C_e$ for m and n calculations: (a) 2,4-DCP, (b) 2,4,6-TCP, and (c) 4-NP.

A plot of $1/q_e$ vs. $1/C_e$ gives a straight line with the slope $1/mn$ and intercepts $1/m$ from Eq. (3).

The slope and intercept of the linear form of the Langmuir model are used to determine the values of m and n. The values of m and n for the three phenol species were calculated by plotting $1/q_e$ vs. $1/C_e$ as shown in Fig. 5(a)–(c). The values of m and n for the three phenol species at constant temperature (i.e. 50°C) were tabulated in Table 1.

The adsorption ability of micelle is presented by the adsorption capacity (m) and the energy of adsorption (n). The values of m and n vary with the temperature, which is a characteristic of both the surfactant and solute. However, when a CPE system is separated into two phases at a fixed temperature, the adsorption capacity (m) and the energy of adsorption (n) are constant. Values of m and n can be calculated from the slope and intercept of the linear form of Langmuir equation. As the values of m and n are taken into a developed Langmuir equation, the amount of surfactant required for the removal of solute up to a desired level can be calculated [26]. The equilibrium data for the sorption of 2,4-DCP, 2,4,6-TCP, and 4-NP over the entire concentration range were fitted to the Langmuir sorption. A linear plot was obtained when $1/q_e$ was plotted against C_e over the entire concentration range. The Langmuir model parameters and the statistical fits of the sorption data to this equation are given in Table 1. According to the Rawajfih and Nsour [4], the adsorption conforms to the Langmuir model when the

Table 1
The values of m and n with correlation coefficient (R^2) for the three phenol species are given below

	2,4-DCP	2,4,6-TCP	4-NP
m (mol mol^{-1})	3.33×10^{-3}	4.75×10^{-3}	2.27×10^{-3}
n (L mol^{-1})	5.67×10^{3}	3.90×10^{3}	7.00×10^{3}
Correlation coefficient (R^2)	0.995	0.995	0.995

value of the correlation coefficient (R^2) is greater than 0.89. The R^2 values obtained are shown in Table 1, which were greater than 0.89 for the three phenol species, indicating that the isotherms were consistent with the Langmuir model [4].

The adsorption isotherms of the three phenol species exhibited Langmuir behavior which indicates monolayer coverage. The adsorption capacity, m (mol mol^{-1}), which is a measure of the capacity of the adsorbent to retain the adsorbed solute, suggests that phenols-DC193C surfactant would be effective as an adsorbent of the phenol species. The adsorption capacity (m) increased on the increasing molecule hydrophobicity according to the following order; 4-NP (2.27×10^{-3}) < 2,4-DCP (3.33×10^{-3}) < 2,4,6-TCP (4.75×10^{-3}) mol mol^{-1}. Due to the different phenols, the monolayer adsorption capacity was greater for chlorinated phenols than nitrophenol. Tri-chlorinated phenol is more hydrophobic than di-chloronated phenol due to the increasing numbers of chlorine atoms in the molecular structure. According to Purkait et al. [24], for the non-ionic surfactant, the core is surrounded by a mantle of aqueous hydrophilic chains, and the solubilization may occur in both core and the mantle. The relative amount of solubilization in these two regions of non-ionic micelles depends on the ionic character of the solubilizate. Non-ionic surfactant appears relatively more hydrophobic at higher temperature, due to an equilibrium shift that favors dehydration of the ether oxygens. As the cloud point is approached, the solubilization of non-polar solubilizates increases, which may be due to an increase in the aggregation number of the micelles. For polar solubilizates, solubilization decreases owing to dehydration of the polyethylene chains accompanied by even tighter coiling. These observations demonstrate that non-polar species are solubilized in the core of micelles, while polar solubilizates are located on the mantle [45]. In concentrated aqueous surfactant solution, the loci of solubilization for a particular type of solubilizate with high polarity (i.e. 4-NP) are solubilized mainly in the outer region of the micellar structures, whereas non-polar solubilizates (i.e. 2,4-DCP and 2,4,6-TCP) are contained in the inner portions. Meanwhile, the values of energy of adsorption (n) were reversible to the values of adsorption capacity (m) for the three phenol species. The least hydrophobic species 4-NP has the highest energy of adsorption compared to 2,4-DCP and 2,4,6-TCP which are more hydrophobic species due to the fact that more energy was required for the former to solubilize into hydrophobic surfactant micelle.

3.5. Determination of thermodynamic parameters

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). Above the CPT, in the aqueous solution of non-ionic surfactant, the solute molecules are distributed between the two phases. Thus, the influence of temperature in the range 298–353 K was studied under optimum experimental conditions [41]. The effect of the temperature on the extraction of phenol species using the non-ionic DC193C surfactant has been discussed in the previous study [31]. It is observed that the solubilization capacity increased significantly with the temperature. The thermodynamic parameters of ΔG°, ΔH°, and ΔS° for this extraction process are determined using the following equations;

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{4}$$

$$\log(q_e/C_e) = \frac{\Delta S^{\circ}}{2.303\text{R}} + \frac{\Delta H^{\circ}}{2.303\text{R}} \tag{5}$$

$$q_e = \frac{\text{Moles of phenol solubilized}}{\text{Moles of DC193C used}} = \frac{A}{X} \tag{6}$$

Moles of phenols solubilized can be obtained from the mass balance,

$$A = V_o C_o - V_d C_e \tag{7}$$

$$X = C_s V_o \tag{8}$$

where q_e is the mole of phenol species solubilized per mole of non-ionic DC193C surfactant. C_e is the equilibrium concentration of phenol species (mol L^{-1}) after the completion of two phases, and T is the temperature in Kelvin. q_e/C_e is called the solubilization affinity. A is the moles of phenols solubilized onto the non-ionic surfactant of DC193C. V_o and V_d are the volumes of the feed solution and that of the aqueous phase after the CPE. C_o and, respectively; C_s are the concentrations of the surfactant in feed. The thermodynamic parameters ΔG°, ΔH°, and ΔS° are in the linear range of q_e vs. the C_e plot that can be calculated by experimental data. Referring to the Eq. (4), the values of Gibbs free energy can be calculated (ΔG°) by knowing the enthalpy of solubilization (ΔH°) and the entropy of solubilization (ΔS°). Eq. (5) has been used to calculate ΔH° and ΔS° that are obtained from a plot of log (q_e/C_e) vs. $1/T$ [45]. The values of ΔG°, ΔH°, and ΔS° for the three phenol species were calculated at different temperatures and reported systematically.

3.6. Variation of Gibbs free energy (ΔG°) during CPE of phenol species

Fig. 6 shows the variation of ΔG° with different temperatures at constant surfactant concentration and the three phenol species concentration. It has been noted from the figure that the adsorption increases linearly with the temperature. This increase in adsorption with a rise in temperature can be explained on the basis of thermodynamic parameters such as the change in standard free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). The thermodynamic parameters are shown in Table 2. The negative values of ΔG° for the three phenol species indicate that the phenol species solubilization process is spontaneous and thermodynamically favorable. The increase in the negative values of ΔG° with temperature implies the greater driving force of solubilization which is confirmed by the greater extent of the phenol species extraction with the increase in temperature. The positive values of ΔH° indicate that the solubilizations of phenols are endothermic in nature for the three phenol species. The endothermic nature is also indicated by the increase in the amount of solubilization with temperature [45]. It is already discussed in previous studies [31] that when the operating temperature increases, the extraction efficiency of the three phenol species increased because of high solubilization of phenol species with rising temperature. The effect of temperature can be explained on the basis of hydrogen bonding. In aqueous solutions of phenols, there exists extensive hydrogen bonding between the phenol molecules and the water resulting in appreciable solubility. These hydrogen bonds get broken at higher temperature, and this would cause phenols to be less soluble and therefore exhibit higher tendency to surfactant surface and get adsorbed rather than remaining in the solution. This would result in higher adsorption at higher temperature [46]. Meanwhile, the positive ΔS° corresponds to a decrease in the degree of freedom of the adsorbed species and that reflects good affinity of phenol species towards surfactant for the three phenol species. The values of ΔH° and ΔS° increase with the increased hydrophobicity of phenol species in the order; 4-NP< 2,4-DCP< 2,4,6-TCP.

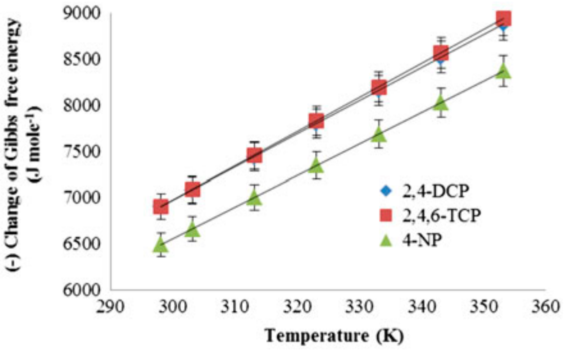

Fig. 6. Variation of Gibbs free energy change (ΔG°) with temperature at constant phenol species concentration for the three phenol compounds.

3.7. Determination of surfactant concentration required and the solute amount to a desired level

A calculation procedure is outlined using Eq. (3) to determine the amount of the concentration of surfactant required for the extraction efficiency up to the desired level. The derivation of Eqs. (9–15), as according to Purkait et al. [43], is as follows [43];

The amount of adsorption is defined as;

$$q_e = \frac{Q_d}{G_s} \tag{9}$$

where Q_d and G_s are the amount of solute and surfactant in the surfactant-rich phase, respectively.

$$E = \frac{Q_d}{Q_o} \tag{10}$$

where E is the extraction efficiency and Q_o is the feed amount of solute.

Table 2
Thermodynamic parameters for the CPE of the three phenol species at different temperatures

Phenol species	Temperature (K)	$-\Delta G^\circ$ (J mol^{-1}) (×10^3)	ΔH° (J mol^{-1}) (×10^3)	ΔS° (J mol^{-1} K^{-1}) (×10^1)
2,4-DCP	298	6.90	3.83	3.60
	303	7.08		
	313	7.44		
	323	7.80		
	333	8.16		
	343	8.52		
	353	8.88		
2,4,6-TCP	298	6.90	4.14	3.70
	303	7.08		
	313	7.45		
	323	7.82		
	333	8.19		
	343	8.56		
	353	8.93		
4-NP	298	6.49	3.69	3.41
	303	6.66		
	313	7.00		
	323	7.34		
	333	7.68		
	343	8.02		
	353	8.37		

$$C_e = \frac{Q_d(1-E)}{V_d} \tag{11}$$

where V_d is the volume of the dilute phase.

There are some assumptions that have been made for determining the amount concentration of the DC193C non-ionic silicone surfactant required up to the extraction efficiency of 90%. Here, the assumptions; the surfactant concentration (CMC) in the aqueous phase can be neglected in material balance due to it is too small compared to in coacervate phase is thousand times. Thus, G_s can represent the amount of the surfactant used in the feed (G_o) [25,26]; and V_d (volume of the dilute phase) can approximate the volume of the initial solution before CPE (V_o) because it is very large. Based on these assumptions, combining Eqs. (9–11) leads to:

$$\frac{G_o}{EQ_o} = \frac{1}{m} + \frac{V_o}{mnQ_o(1-E)} \tag{12}$$

$$\frac{G_o}{V_o} = C_{os} \tag{13}$$

$$\frac{Q_o}{V_o} = C_o \tag{14}$$

where C_{os} and C_o are the concentrations of the surfactant and solute in the feed, respectively. Combining Eqs. (12–14), in turn, leads to:

$$C_{os} = \frac{EC_o}{m} + \frac{E}{mn(1-E)} \tag{15}$$

C_{os} is the function of C_o. The values of m and n were calculated for the three aforementioned phenol species. Therefore, using the concentration of the phenol species in the feed and a desired level of extraction efficiency (E), Eq. (15) can be solved to obtain DC193C surfactant concentration required (C_{os}). Fig. 5 shows the required DC193C surfactant concentrations for the three phenol species at 50℃ in the CPE processes with the desired extraction efficiency of 90%.

As shown in Fig. 7, the required surfactant concentration increased with the increasing concentration of feed for the three phenol compounds to achieve the desired extraction efficiency of 90%. The different concentrations of DC193C were required in order to achieve extraction efficiency up to 90% for the three phenol compounds at varying initial concentrations of the phenol species. Generally, the adsorption behavior of organic compounds on non-polar and moderately polar polymeric adsorbent in aqueous solution is related to the hydrophobic properties of solute; whereby the more hydrophobic the solute, the more

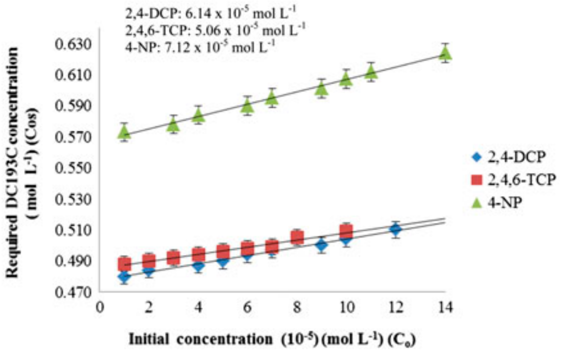

Fig. 7. Variation of required surfactant concentration for different feed concentrations of phenol compounds with the desired extraction efficiency of 90%.

readily it can be adsorbed [47]. It can be related to Fig. 7, where the amount of DC193C non-ionic surfactant was required more for polar compound (4-NP) compared to both non-polar compounds (2,4-DCP and 2,4,6-TCP).

4. Conclusions

The CPE technique combined with spectrophotometry offers several advantages such as the fact that its cost is low, it is sensitive, selective, and it provides safety with good extraction efficiency. Experimental results show that high recoveries can be obtained at the optimized parameters: DC193C, 0.5 mL of 0.5 v/v %; for Na_2SO_4, 1.5 mol L^{-1}, equilibration temperature, 50°C, and incubation time, 15 min for the three phenols at pH 7 as reported in previous works [31]. It is found that the experimental data of the adsorption amounts and concentration solute have fitted the Langmuir-type isotherm for the three phenol species. In this study, the straight line obtained for the Langmuir isotherm model which obeys the experimental equilibrium data, indicates the disclosing homogeneous distribution in the active sites of non-ionic DC193C silicone surfactant for the three phenol species. The monolayer adsorption capacity of non-ionic DC193C silicone surfactant was found to be 3.33×10^{-3} mol mol^{-1} (2,4-DCP); 4.75×10^{-3} mol mol^{-1} (2,4,6-TCP), and 2.27×10^{-3} mol mol^{-1} (4-NP) from Langmuir model equations. Our results further indicate that the adsorption of the phenol species from aqueous solution was in proportion to their hydrophobicities, according to the following order; 4-NP < 2,4-DCP < 2,4,6-TCP. Thermodynamic parameters such as the change in Gibbs free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) of the CPE of DC193C-phenol species were also studied. It is found that the process is feasible from thermodynamic studies. The spontaneity of the above phenol species extraction is governed by the negative value of ΔG°. The positive values of ΔS° dictate that the solubilized phenol species molecules are organized in a more random fashion on the mantle of an aqueous hydrophilic chain. The extraction processes are endothermic in nature, the fact also proven by the positive value of ΔH°. The non-ionic DC193C silicone 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. Furthermore, a non-ionic silicone surfactant of DC193C used in the CPE makes the micellar extraction procedure simple, greener, and economical and explains its high desirability for adsorption studies. In addition, it is compatible with UV–vis due to its structure without any aromatic structure that could not influence UV and fluorescence signals.

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