CLOUD POINT EXTRACTION METHOD FOR THE REMOVAL OF PHENOLIC COMPOUNDS FROM WATER SAMPLES USING DC193C NON–IONIC SURFACTANT

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ORIGINAL LITERARY WORK DECLARATION

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Field of Study: **Analytical Chemistry**

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ABSTRACT

A greener method based on cloud point extraction was optimized in three systems namely as cloud point extraction (CPE); CPE with β−cyclodextrin (CPE−βCD) and CPE with β−cyclodextrin functionalized with ionic liquids (CPE−βCD−IL) for removing phenolic compounds including 2,4−dichlorophenol (2,4−DCP), 2,4,6−trichlorophenol (2,4,6−TCP) and 4−nitrophenol (4−NP) in aqueous samples by using UV−Vis spectrophotometric technique. The DC193C surfactant was chosen as an extraction solvent due to its low water content in a surfactant rich phase. The parameters affecting the extraction efficiency such as pH, equilibration temperature and incubation time, concentration of surfactant, modifier, salt and analyte, volume of surfactant and modifier and water content were evaluated and optimized. In the three CPE systems, the solubilization were in proportion of the hydrophobicity of the target compounds, according to the following order; 4−NP < 2,4−DCP < 2,4,6−TCP. Langmuir model was found to fit well with the solubilization of the phenolic compounds into DC193C surfactant. The thermodynamic results indicated that the solubilization of the phenolic compounds solubilized into DC193C surfactant were feasible, spontaneous and endothermic. Finally, the inclusion complex formation, hydrogen bonding and $\pi-\pi$ interaction between the DC193C surfactant, β−CD, βCD−IL and the phenolic compounds were proven using the ^{1}H NMR and 2D NOESY spectroscopy.

ABSTRAK

Satu kaedah yang lebih hijau berdasarkan pengekstrakan titik awan telah dibangunkan dalam tiga sistem iaitu pengekstrakan titik awan (CPE); CPE dengan β−cyclodextrin (CPE−βCD) dan CPE dengan β−cyclodextrin difungsikan dengan cecair ionik (CPE−βCD−IL) bagi menyingkirkan kumpulan fenolik termasuk 2,4−dichlorophenol (2,4−DCP), 2,4,6−trichlorophenol (2,4,6−TCP) dan 4−nitrophenol (4−NP) dalam sampel akueus dengan menggunakan teknik spektrofotometri UV−Vis. Surfaktan DC193C dipilih sebagai pelarut pengekstrakan kerana kandungan air yang rendah dalam fasa kaya surfaktan. Parameter yang mempengaruhi kecekapan pengekstrakan seperti pH, keseimbangan suhu dan masa, kepekatan surfaktan, pengubahsuai, garam dan analit, jumlah surfaktan dan pengubahsuai dan kandungan air telah dinilai dan dioptimumkan. Di dalam tiga sistem CPE, kelarutan itu adalah berkadaran dengan hidrofobik kumpulan sasaran, mengikut urutan seperti berikut; 4−NP <2,4−DCP <2,4,6−TCP. Model Langmuir di dapati sesuai dengan kelarutan kumpulan fenolik ke dalam surfaktan DC193C. Keputusan termodinamik menunjukkan bahawa kelarutan kumpulan fenolik ke dalam surfactant DC193C adalah dilaksanakan, spontan dan endotermik. Akhirnya, pembentukan kemasukan kompleks, ikatan hidrogen dan interaksi π-π antara surfaktan DC193C, β−CD, βCD−IL dan kumpulan fenol telah terbukti menggunakan ^{1}H NMR dan 2D NOESY spektroskopi.

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NOMENCLATURE

C_e	equilibrium dilute phase phenol concentration (mol L^{-1})
C_s	surfactant concentration (mol L^{-1})
C_0	initial phenol concentration (mol L^{-1})
C_w	phenol concentration in aqueous phase (mol L^{-1})
Cos	surfactant concentration required
DCP	2,4−dichlorophenol
$\Delta G°$	delta Gibbs free energy
$\Delta H°$	delta enthalpy of solubilization
$\Delta S°$	delta entropy of solubilization
E	extraction efficiency
$\mathrm{G_o}$	amount of the surfactant used in the feed
$\mathrm{G_s}$	amount of the surfactant in the surfactant rich phase
K	Kelvin
m	Langmuir isotherm constant
n	Langmuir isotherm constant (L mol^{-1})
NP	4−nitrophenol
$\mathrm{Q_d}$	amount of solute
q_e	moles of phenol solubilized per mole of surfactant (mol mol^{-1})
$\mathrm{Q_o}$	feed amount of solute
R	constant in Eq. (4)
T	Temperature (°C)
TCP	2,4,6−trichlorophenol
V_s	volume of phenol concentration in surfactant rich phase (L)
V_w	volume of phenol concentration in aqueous phase (L)
V_o	volume of solution (L)

V_d	volume of dilute phase (L)
X	moles of DC193C used (mol)

CHAPTER 1

INTRODUCTION

1.1 Background of study.

As a result of rapid development of chemical and petrochemical industries, the surface and ground waters are polluted by various organic and inorganic chemicals such as phenolic compounds, dyes and heavy metals. There has been a large increase in the use of phenol and phenolic derivatives in recent times. This high demand for phenol and its derivatives has led to a production rate of about 6 million ton/year worldwide, with significantly increasing trend (Ofomaja *et al*., 2013). Phenol and its derivatives such as 2,4–dichlorophenol (2,4–DCP), 2,4,6–trichlorophenol (2,4,6–TCP) and 4–nitrophenol (4–NP) are found in aquatic environment as a result of the common availability of the by−products of many industrial processes (Martínez *et al*., 1996; Shen *et al*., 2006).

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 odour of water at low concentration. The utilization of phenol−contaminated waters causes protein degeneration, tissue erosion, and paralysis of the central nervous system and also damages the kidney, liver and pancreas in human bodies. Nowadays, phenol and its derivatives become particularly of interest and concern in accordance to the US Environmental Protection Agency (US EPA) and European Union (EU) which are included in their lists of aquatic environment (Cha and Qiang, 2012; Kavitha and Palanivelu, 2005; Rodrı́guez *et al*., 2000). Additionally, these compounds can persist under environmental condition, at ppm levels in waters for a number of days or weeks depending on the temperature and pH (Martínez *et al*., 1996). According to the recommendation of World Health

Organization (WHO), the permissible concentration of phenolic contents in potable waters is 1 µg L^{-1} and the regulations by the Environmental Protection Agency (EPA), call for lowering phenol content in wastewaters less than 1 mg L^{-1}. Therefore, removal of phenolic compounds from waters and wastewaters is an important issue in order to protect public health and environment (Senturk *et al.*,2009).

The most common methods that have been used in research work for removing the phenolic compounds in water samples are membrane separation process (Erhan *et al.*, 2002; Park *et al.*,2006), oxidation (Alcántara *et al.*, 2004; Wagner and Nicell, 2001), ozonation (Amin *et al.*,2010; Buffle *et al.*, 2006) as well as the adsorption (Abay *et al.*, 2005; Ku and Lee, 2000; Lin *et al.*, 2008) on different adsorbents. In contrast, simple, fast, economical and greener analytical methods are required for removing the phenolic compounds from the water samples. On this premise, few researchers have discovered about the principles and advantages of the cloud point extraction (CPE) as an alternative method to the conventional liquid−liquid extraction. Previous studies have found that CPE method is simple, cheap, highly efficient, and has lower toxicity which offers an alternative to more conventional extraction systems that can be classified as a “green chemistry” principle (Manzoori and Karim-Nezhad, 2003; Nazar *et al.*, 2011; Purkait *et al.*, 2005).

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 (Arunagiria *et al.*, 2012; Paleologos *et al.*, 2005). The hydrophobic tails can entrap and thus isolated hydrophobic substances. This ability has been extensively used in cloud point extraction (Paleologos *et al.*, 2003a). At certain temperature, an aqueous solution of the non−ionic surfactant micellar system becomes turbid. This temperature is known as cloud point temperature (CPT) (Kulichenko *et al*., 2003; Safavi *et al*., 2004; Sirimanne *et al*., 1996). Above the cloud point temperature, the solution separates into two phases: first off, the surfactant rich phase, which has small volume compared to the solution and it is also called coacervate phase while the other phase is the aqueous phase containing surfactant concentration which is slightly above the critical micelle concentration (CMC) (Bai *et al*.,2001; Luconi *et al*., 2000; Paleologos *et al*., 2003b).

There are many potential advantages to replace the volatile organic compounds (VOCs) with water or other types of aqueous solution as a surfactant. The most obvious advantages for the replacement of VOCs 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 copolyols, silicone glycols, and silicone surfactants) are class of amphiphilic materials having water soluble and a silicone soluble portion in one molecule. DC193C fluid is an example which is non–ionic surfactant based on silicone PEGs copolymer (Chen *et al*., 2005).

PEGs have been recognized as an alternative material to replace VOCs due to a number of advantages, e.g. non–toxic, odourless, colourless, and 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 most organic solvents. PEGs play an important role and well−known as 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. As reported by Chen *et al*. (2005), even if the PEGs are discharged to the environment; the environment would suffer from no significant effect. Moreover, the US FDA (Food and Drug Administration, United State) has permitted this surfactant for internal consumption. Therefore, in this study, the phenolic compounds are more concerned in removing them from the water samples rather than to recover the non–ionic surfactant of DC193C from water samples.

Nowadays, there are several types of surfactant that had been used as an extractant solvent 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 (Bai *et al.*, 2001). Therefore, DC193C fluid non−ionic surfactant was used to overcome this problem because it has more flexible polysiloxane chains without any aromatic structure. Furthermore, it can form more compact micelle structures which offer low water content in the surfactant rich phases; thus, enhancing the extraction efficiency (Yao and Yang, 2008a). Green chemistry can be defined as those procedures for decreasing or eliminating the use or generation of toxic substance for the following reasons: (a) DC193C surfactant uses as an extractor media diluted solutions of the surfactants that are inexpensive, resulting in the economy of reagents and generation of few laboratory residues; and (b) DC193C surfactants are not toxic, non−volatile, and non−flammable, unlike organic solvents used in the liquid–liquid extraction (Bezerra *et al.*, 2005).

Cyclodextrins (CDs) are cyclic glucose oligosaccharides that are classified as α−CD, β−CD, or γ−CD, corresponding to 6,7 or 8 glucose units, respectively (Ehsan *et al.*, 2007; Flaherty *et al.*, 2013). Recently, much attention has been devoted to CDs as cyclic component for the construction of supramolecular architecture due to their well−defined ring structure and has an affinity to form inclusion complex for different class of compounds with varying size and shape for a variety of applications, including pharmaceutical delivery, agricultural use, food and flavor protection, cosmetics formulations, and complexation with hydrophobic molecules (Flaherty *et al.*, 2013). The unique property of these lampshade−shaped molecules is that they have hydrophilic exterior and substantially more hydrophobic cavity capable hosting a wide range of organic guest molecules. They are known to solubilize many low−polarity organic compounds through the formation of water−soluble inclusion complexes (Hanna *et al*., 2003). Therefore, CDs allow their removal from aqueous solutions by encapsulating organic pollutants in their cavities. CDs can be tailored to match particular guests and meet the specific requirement of their host−guest interaction. Thus far, β−cyclodextrins (β−CD) have been used more frequently than other CDs because of the appropriate cavity size for a range of organic compounds (Ehsan *et al*., 2007; Harada, 1997). The β−CD is the most accessible, the lowest−priced, less toxicity and generally the most useful (Chadha *et al*., 2011; Singh *et al*., 2002). Thus, in this work, β−CD was chosen as modifier for removal phenolic compounds using CPE technique.

Ionic liquids (ILs), sometimes known as molten salt, are gaining wide recognition in analytical chemistry including extraction in gas chromatography (GC), in liquid chromatography (LC) and in capillary electrophoresis (CE) because they possess several unique properties (Delmonte *et al*., 2011; Fernández-Navarro *et al*., 2011; Han *et al*., 2011; Poole and Poole, 2011; Su *et al*., 2010; Vaher *et al*., 2011). ILs that consist of organic cations (i.e. imidazolium, pyridinium, pyrrolidinium, phosphonium and ammonium) paired with a variety of anions (i.e. Cl^-, PF_6^-, BF_4^-, NO_3^- and OTs^-) have most of the properties of conventional organic solvents. Their unique properties such as wide liquid temperature range, low melting points, and negligible vapor pressure have triggered researchers to explore their use as a replacement of the traditionally more toxic, flammable and volatile organic solvents. In addition, they have two characteristics of non−volatility and high electrical conductivities that conventional organic solvents have not. ILs provide an alternative media for “Green Chemistry” due to their negligible vapor pressure (Harada, 1997; Qi *et al*., 2004). The overall physicochemical properties of ILs result from the composite properties of both cation and anion. In general, the anion is used to control the water miscibility of the IL, but the cation can also influence the hydrophobicity or hydrogen−bonding ability of the solvent.

Owing to the unique properties of ILs and β−CD, β−CD functionalized with ILs may demonstrate an interesting phenomenon for extraction and separation study of organic compounds. In recent years, β−CD functionalized with ionic liquid was widely used as chiral selectors in capillary electrophoresis and stationary phase in HPLC (Huang *et al*., 2010;Yujiao *et al*., 2013; Zhou *et al*., 2010). Our research group has developed the research works related to the use of functionalized β−CD with ionic liquids such as macroporous material in removing 2,4−dichlorophenol from aqueous solution (Raoov *et al*., 2013) and βCD−IL as a modifier in CPE technique for extraction of paraben compounds (Noorashikin *et al*., 2013). Due to the fact, β−CD was found to be great of importance as a highly organized host media. By functionalized β−CD with ionic liquid, the hydrophobic cavity of β−CD can serve more as a selective container for polar organic molecules of proper size, and the hydrophobicity is really very convenient for the need of carrying out research works in aqueous solution compared to the native of β−CD. On the other hand, the ionic liquids (ILs) have good interaction between anionic or polar species for extraction from aqueous solution. Therefore, ionic liquids were selected to be used in this study to improve the extraction of the phenolic compounds performance from aqueous solution.

1.2 Significant of study.

In the present work, the feasibility of employing the CPE as a simple and effective method has been adopted in removing the phenolic compounds from water samples using the DC193C as a non−ionic surfactant. This is the first attempt of the DC193C surfactant used in the CPE for removal the phenolic compounds from water samples by spectrophotometric method. The three CPE systems have been optimized namely cloud point extraction (CPE), cloud point extraction with β−cyclodextrin (CPE−βCD) and cloud point extraction with functionalized β−cyclodextrin with ionic liquids (CPE−βCD−IL). The functionalized β−cyclodextrin with ionic liquids (βCD−IL) was prepared by reacting o−p−toluenesulfonyl−β−cyclodextrin (βCD−OTs) with 1−benzylimidazole (BIM) to be used as modifier in the CPE−βCD−IL system. Meanwhile, native of β−CD was used as modifier in the CPE−βCD system. The purpose of adding a modifier in the CPE system is to enhance the performance of the phenolic compounds extraction and also to study their behavior towards the modifiers in CPE system. In this work, several parameters used in the three CPE systems have been optimized for the extraction phenolic compounds such as effect of concentration and volume of DC193C surfactant, pH, concentration and volume of the modifiers, equilibrium temperature and time, concentration of salt and analyte, and water content. From the experimental data, a solubilization isotherm was developed to quantify the amount solubilization of the phenolic compounds in the three CPE systems. The solubilization behavior of the phenolic compounds on the non−ionic surfactant of DC193C in the three CPE systems was studied at fix surfactant concentration. Thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated to know the nature of solubilization. This fundamental study will be helpful for further application for removal pollutant in aqueous solution by using non−ionic surfactant of DC193C in the CPE method.

1.3 Objectives.

The objectives of the present study are as follow:

1) To optimize parameters affecting extraction efficiency in the cloud point extraction (CPE) for extraction of the phenolic compounds.
2) To optimize parameters affecting extraction efficiency in the cloud point extraction with β−cyclodextrin modifier (CPE−βCD) for extraction of the phenolic compounds.
3) To optimize parameters affecting extraction efficiency in the cloud point extraction with β−cyclodextrin functionalized with ionic liquid modifier (CPE−βCD−IL) for extraction of the phenolic compounds.
4) To compare the difference in the CPE systems towards the extraction of the phenolic compounds.

CHAPTER 2

LITERATURE REVIEW

2.1 Phenolic compounds in environment.

Polar compounds are the most problematic one among various organic pollutants in aquatic media, having high tendency to stay in water−based samples. Phenol and phenolic derivatives are examples of the most important contaminants present in the environment as a result of various industrial activities such as chemical, pharmaceutical, petroleum, paper, wood, rubber, dye and pesticide industries (Calace *et al*., 2002; Mousavi *et al*., 2007; Saraji and Bakhshi, 2005). Industrial sources of contaminants such as oil refineries, coal gasification sites and petrochemical units generate large quantities of phenol and phenolic derivatives. Besides, phenolic derivatives are widely used as intermediates in synthesis of plastics, colours, pesticides, and insecticides. These substances which present in industrial effluents lead to the appearance of phenol and its derivatives in the environment by degradation process. Phenolic compounds are classified as priority pollutants due to their toxicity to humans and aquatic life; create an oxygen demand in receiving waters. Most of these compounds are recognized as toxic carcinogens (Aygün *et al*., 2003; Ersöz *et al*., 2004). Concentration of phenolic compounds in wastes varies in a wide range from several to 2 – 3 mg/L. In view of the high toxicity, wide prevalence and poor biodegradability of phenolic compounds, it is necessary to remove them from aqueous solution before used by human being. The presence of their even low concentrations can be an obstacle to the use (and/or) reuse of water. Phenolic compounds caused unpleasant taste and odour of drinking water and can exert negative effects on different biological processes.

Several methods designed to remove phenolic compounds have been proposed. One of the most widely used methods for removing phenolic compounds from aqueous solution is solvent extraction using polar organic solvents (Palma *et al*., 2007). The disadvantage of this method is emulsion formation that may increase the organic loading of the treated stream, requiring additional cleanup. Attention has been given to the removal of phenolic compounds from the aqueous system by many researchers in the world, for example, the removal of phenolic compounds by adsorption, microbial degradation, and peroxidase−catalyzed oxidation processes. Previous studies proved that, adsorption is an effective technique for the removal of phenolic compounds from water to a lower level. The solubilization of phenolic compounds by different sorbent has been investigated to find the relation between solubilization capacity and solubilization characteristics such as surface area, and pore size distribution for separation applications in the drinking water (Farajzadeh and Fallahi, 2005; Roostaei and Tezel, 2004). However, only a few articles have been reported on solubilization studied of the phenolic compounds using micellar or surfactant from aqueous solution (Chen et al., 2009; Goswami et al., 2011; Purkait *et al*., 2006a, 2006b, 2009).

2.1.1 Physical and chemical properties of phenolic compounds.

Chlorophenols and nitrophenols are long−lived pollutants frequently found in industry effluents. The solubility of these compounds in water is low and decreases with increasing number of hydrophobic chlorine or nitro groups. Indeed, physical and chemical properties of chlorophenols and nitrophenols are strongly influenced by the ability of the compound to form hydrogen bonds and the ionic character in aqueous solution (Jaoui *et al*., 2002).

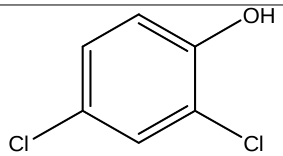
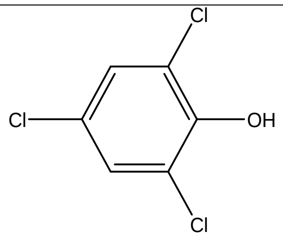
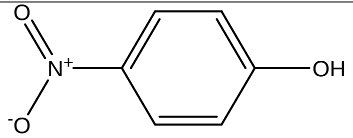
Chlorophenols are chlorinated aromatic ring structures consisting of the benzene ring, −OH group and atom (s) of chlorine. Chlorophenols are group of chemicals in which chlorines (between one and five) have been added to phenol. They include mono−, di−, tri−, tetra−, and pentra−chlorinated phenols (CP, DCP, TCP, TTCP, and PCP, respectively). They are mostly found in wastewater, sludge products, surface waters and groundwater. Other sources of contamination are accidental spills, hazardous waste disposal sites, storage tanks, or municipal landfills. They are also used in great diversity of application, such as herbicides, insecticides, bactericides and wood preservatives especially for 2−CP, 4−CP, 2,4−DCP and 2,4,6−TCP. In addition, 2−CP, 4−CP, 2,4−DCP and 2,4,6−TCP are the most significant chlorophenols which formed as by−products of water chlorination. Besides, chlorophenols are major group of pollutants of environmental concern because of their toxicity and widespread uses (Jung *et al*., 2001).

All chlorophenols are solids at room temperature except 2−chlorophenol (2−CP), which is liquid. The aqueous solubility of chlorophenols is low, but the sodium or potassium salts of chlorophenols are up to four orders of magnitude more soluble in water than the parent compounds. They are weak acids, which permeate human skin by in vitro and are readily absorbed by gastro−intestinal tract. The acidity of chlorophenols increases as the number of chlorine substitutions increases (Jaoui *et al*., 2002). The n−octanol/water partition coefficients (K_{ow}) of chlorophenols increase with chlorination, indicating a propensity for the higher chlorophenols to bio−accumulate. The partition of an organic pollutant between the water and organic phases is generally correlated with various properties, such as the water solubility (S) and the octanol/water partition coefficient (K_{ow}) (Olaniran and Igbinosa, 2011). Cholorophenols are toxic, mutagenic and carcinogenic pollutant. They have been also reported to cause adverse effects on human nervous system and respiratory problem such as chronic bronchitis, cough, and altered pulmonary function. The stable C−Cl bond and the position of chlorine atoms relative to the hydroxyl group are responsible for their toxicity and persistence in the biological environment (Hameed *et al*., 2008).

Nitophenols compounds are among the largest and most important groups of industrial chemicals in use today. These compounds are organic molecules that consist of at least one nitro group (−NO_2) attached to an aromatic ring. The strong electronegativity of the nitro group stems from the combined action of the two electron−deficient oxygen atoms bonded to the partially positive nitrogen atom. The nitro group is able to delocalize π−electrons of the ring to satisfy its own charge deficiency, when attached to a benzene ring. This not only provides charge to the molecule but also imparts unique properties that make the nitro group an important functional group in chemical syntheses (Ju and Parales, 2010). Nitophenols are used as intermediates in the synthesis of pesticides and dyes or are directly applied as herbicides and insecticides. Moreover, nitophenols act as uncoupling agents in oxidative phosphorylation, and they are known to affect cell metabolism at concentration lower than 10 µM. While some nitro−aromatic compounds are produced by incomplete combustion of fossil fuels, resulting large numbers of the pollutants are released into the environment. Besides, nitration is an important chemical reaction for the commercial production and use of several amino−aromatic intermediates as a feedstock for the production of explosives, pesticides, herbicides, polymers, dye, and pharmaceuticals. Furthermore, nitrophenols has been widely used by the weapon in industry for the production of bombs and grenades (Crini, 2005). Therefore, large areas of ground water and soil have been highly contaminated by these xenobiotic. Compounds which are recalcitrant, toxic and mutagenic to various organisms (Kulkarni and Chaudhari, 2007).

In this respect, the European Union (EU) has included the phenols cited below in its Directive 76/464/EEC concerning dangerous substances discharged into the aquatic environment: 2−amino−4−chlorophenol, 4−chloro−3−methylphenol, 2−chlorophenol, 3−chlorophenol, 4−chlorophenol, pentachlorophenol and 2,4,6−chlorophenols. The US Environmental Protection Agency (EPA) list of priority pollutants also includes 11 phenolic compounds. Some of them are included in the EU directive, but others are not, such as 2−nitrophenol, 4−nitrophenol, 2,4−dinitrophenol, 4,6−dinitro−2−methylphenol, 2,4−dichlorophenol, 2,4−dimethylphenol and 2,4,6−trichlorophenol (Bagheri *et al.*, 2004; Castillo and Puig, 1997; Gonzalez-Toledo *et al.*, 2001). Therefore, in this work three phenolic compounds namely 2,4−dichlorophenol, 2,4,6−trichlorophenol and 4−nitrophenol has been studied in detail due to their priority pollutants present in aqueous solution. The basic information concerning these three phenolic compounds are included in Table 2.1 (Dąbrowski *et al.*, 2005). The removal of phenolic compounds from the environment is crucial due to its high toxicity, carcinogenic properties, structural stabilization and persistence in the environment.

Table 2.1 :
Basic information concerning the three phenolic compounds of interest (Dąbrowski, *et al.*, 2005).

Phenolic compounds	IUPAC name	Boiling Point (˚C)	pK_a at 25˚C	Aqueous solubility at 25˚C (g l^{-1})
	2,4−dichlorophenol (2,4−DCP)	210	7.70	4.5
	2,4,6−trichlorophenol (2,4,6−TCP)	246	7.40	28.6
	4−nitrophenol (4−NP)	279	7.20	1.69

2.2 Cloud point extraction.

There are various methods that can be used to extract phenol compounds in aqueous samples. Extraction is a well−known techniques used to recover and separate various substances including undesirable organic pollutants. Commonly used methods for extraction are liquid−liquid extraction (LLE), solid phase extraction (SPE) and solid phase micro−extraction (SPME). However, these methods have several disadvantages as shown in Table 2.2 (Sosa Ferrera *et al*., 2004).

LLE is one of the most frequent methods for sample extraction and pretreatment which based on the partitioning of the target compound between two immiscible phases. The major disadvantages of LLE are the use of large volumes of high purity organic solvents, which will lead to costs for the analysis and their toxicity. Moreover, other drawbacks include the length of the analysis time and the difficulties regarding automating the procedures. The recoveries of this method are generally acceptable and vary from one component to another and are lower for the more volatile ones. A further serious limitation is the problems associated with the formation of emulsion or foam when surface or waste waters are extracted (Sun and Armstrong, 2010). Therefore, SPE has been proposed, to solve emulsion problem.

SPE is based on differential migration processes, during which compounds are adsorbed and eluted as they are swept through a porous medium by a mobile phase flow, which is dependent on the differential affinities between the sorbent material and the mobile phase. The choice of sorbent is a limitation in SPE. Several sorbents are required to be tested for extraction phenolic compounds. Besides, designs of the cartridge have certain disadvantages for water analysis: the cross−sectional area is small; sample processing rates are slow, the tolerance to blockage by particles and adsorbed matrix components is low, and channeling reduces the capacity to retain analytes. Another drawback in SPE, which is the same for LLE, is the considerable amount of time needed and manual operations involved. Sample throughput is low and the economic expense is high. Laborious operations such as conditioning, washing, elution and solvent evaporation are needed in SPE. In addition, clotting channeling and percolation are typical problems of SPE encountered in everyday laboratory work (Santana *et al.*, 2002). Other methodologies have been developed with a view to eliminate or, at least, to minimize the use of organic solvents. Solid phase micro−extraction (SPME) is a most recent method used for the extraction of organic compounds from environmental samples. SPME is based on the partition equilibrium of analytes between a polymeric stationary phase and the sample matrix. Desorption step is usually carried out by placing the fibre in a hot injector of a GC system or it can be performed in an HPLC system by introducing an interface. An inherent disadvantage of SPME is that quantitative work is still rather laborious because severe carry over may occur between samples. Moreover, a relatively long equilibration time (up to 1 h) is needed for the adsorption of analytes (Sosa Ferrera *et al.*, 2004).

Table 2.2:
A summary of several extraction methods for liquid sample matrices (Sosa Ferrera *et al.*, 2004).

	LLE	**SPE**	**SPME**	**CPE**
Brief description	Analyte is partitioned between two immicible solvents.	Analyte retained on a solid adsorbent.	Partition equilibrium of analytes between a polymeric stationary phase and the sample matrix.	Analyte is partitioned between two isotropic phase "surfactant−rich phase" and "aqueous phase".
Extraction time	Up to 24 h	20 – 30 min	Up to 60 min	20 min
Solvent usage	Organic solvent	Organic solvent	None	Surfactant solution
Cost	Relatively low cost	Relatively low cost	Relatively low cost	Low cost
Ease of operation	Relatively easy	Relatively easy	Relatively easy	Easy
Disadvantages	Large consumption of solvent and concentration of sample required after extraction.	Insufficient retention of very polar compounds and limited selectivity.	Choice of fiber and optimization of procedure required.	Optimization of operating conditions.

In 1978, cloud point extraction (CPE) was first exploited for analytical purposes by pre−concentration of zinc(II) after formation of a hydrophobic complex with 1− (2−pyridylazo)−2−naphthol (Calace *et al.*, 2002). Since then the approach has been widely explored as a green alternative to the conventional liquid–liquid extraction. The use of surfactant−mediated phase separations, also known as CPE, offers an alternative environmentally benign separation approach to more conventional extraction systems. Recently, CPE attracted the attention of analytical chemists for these reasons; (a) good capacity to solubilize solutes with different types and nature; (b) ability to concentrate solutes with high recoveries; (c) safety and cost benefits (surfactant based on water, avoiding organic toxic solvent in large amount); (d) very small amounts of the relatively non−flammable and non−volatile surfactant are required; (e) easy disposal of the surfactant; and (g) the inhibition by the surfactants of adsorption of nonpolar analytes to glass surface (Nazar *et al*., 2011; Sirimanne *et al*., 1996; Tabrizi, 2006).

The CPE is a new promising environmentally benign extraction technique which is based upon phase separation behavior exhibited by aqueous solutions of certain surfactant micelles. In the CPE, the role of extraction solvent is played by a micellar (surfactant rich) phase originating from a homogenous surfactant solution that is added to the sample. A surfactant aggregate (a micelle) orientates its hydrocarbon tails towards the center to create a nonpolar core. Isolated hydrophobic compounds (a large number of bioactive compounds) present in the aqueous solution are favorably partitioned in the hydrophobic core of micelles (Madej, 2009).

Aqueous solutions of certain surfactants display the so−called cloud point phenomenon in which the aqueous surfactant solution (surfactant above the critical micelle concentration) suddenly becomes turbid because of a decrease in the solubility of the surfactant in water. The clouding phenomenon is usually induced by an increase in temperature. The result is the formation of the single isotropic micellar phase separation into two isotropic phases: the small volume “surfactant rich phase” is separated from the bulk aqueous solution; and the “aqueous phase” which contains the surfactant concentration is slightly above the critical micelle concentration (CMC) (Afkhami *et al*., 2006). Depending upon the density of this surfactant rich phase in relation to that of the aqueous phase, it can be either the bottom or top layer. By addition of salt to the system, the density of the aqueous phase can be adjusted to some degree (Quina and Hinze, 1999).

It has been demonstrated that the surfactant rich phase, thus, separated under the cloud point condition, is able to extract and pre−concentrated a wide range of inorganic and organic compounds from the aqueous phase. The solute present in aqueous solution of surfactant is distributed between the two phases above the cloud point temperature. This phenomenon is known as CPE process. This process is schematically described in Figure 2.1.

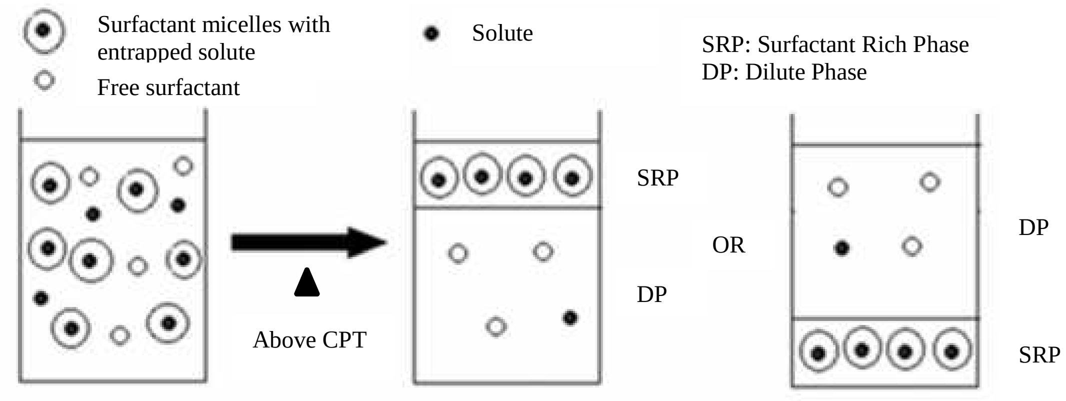


Figure 2.1: Schematic of basic cloud point extraction process (Zain *et al*., 2014).

The extraction process of the CPE system is very simple as shown in Fig. 2.1. First, the surfactant or a concentrated surfactant solution is added to the aqueous solution containing the analytes to be extracted or pre−concentrated. In order to ensure formation of micelle aggregates, the final surfactant concentration must exceed its CMC value. Hydrophobic analytes can be incorporated into the surfactant rich phase formed by the phase separation of the micellar solution due to the hydrophobic interaction between analytes and surfactant assemblies, while hydrophilic components remain in the residual aqueous solution. The distribution of analytes between two phases is already equilibrated when the surfactant micelles are homogenously dispersing in the aqueous solution. Hence, the extraction of analytes occurs along with the phase separation (Saitoh *et al*., 1999). Analytes may remain referentially in the hydrophobic domain of the micelles in a surfactant rich phase, thus, being extracted and pre−concentrated. Then, by raising or lowering the temperature and adding the additives (analyte, salt) the conditions are altered to obtain phase separation. After de−mixing of the biphasic system, the analytes are extracted and pre−concentrated in a small volume of surfactant rich phase, either by gravity settling or centrifugation. Depending on the density of the surfactant, the surfactant rich phase can be either at the bottom or the top. Finally, the surfactant rich phase need to be diluted with aqueous or organic solvent due to the surfactant rich phase is so viscous before proceed to instrumental analysis (Xie *et al*., 2010).

2.2.1 Surfactants / Micelles.

Surfactant aggregates, or micelles, can form in a number of different types of solvents. Micelles represent so−called colloidal dispersions that belong to a large family of dispersed systems consisting of particulate matter or dispersed phase, distributed within a continuous phase or dispersion medium. The colloidal dispersions occupy a position between molecular dispersions with particle size under 1 nm and coarse dispersions with particle size greater than 0.5 µm in terms of size. More specifically, surfactant aggregates or micelles normally have particle size within 50 − 100 nm range. They are divided into three principle groups among colloidal dispersions; lyophilic, lyophobic, and association colloids (Torchilin, 2001).

The distinct structural feature of a surfactant originates from its ‘duality’: the hydrophilic region or the tail group that usually consists of one or few hydrocarbon chains (Vaisman *et al*., 2006). Their molecules present a long hydrocarbon chain and a small charged group or polar hydrophilic. A typical surfactant has a R−X structure, where R is a hydrocarbon chain, which can have between 8 and 18 atoms of carbon, and X is the polar or ionic head group (Bezerra *et al*., 2005). Normal micelles that spontaneously form surfactant aggregates (with the hydrophobic tails toward the center and the hydrophilic head groups at the outer surface) in water. Reverse or inverse micelles or surfactant aggregates also can form in non−polar organic solvents. At low concentration of surfactant, aggregates are present in aquatic solution, mainly as a monomer although dimers and trimers may also be detected (Paleologos *et al*., 2005).

Monomer surfactants form a layer at the liquid−air surface, as surfactant molecules added to aqueous solution. However, micelles are formed in bulk solution when the surface becomes saturated with surfactant monomers (i.e., a monolayer is formed) when concentration above a certain threshold, called the critical micellar concentration (CMC) (Anderson *et al*., 2003; Paleologos *et al*., 2005). The micelles can adopt a variety of shapes, ranging from roughly spherical to ellipsoidal (oblate or prolate) depends on their specific surfactant and solution conditions. In either case, the interior region of the micelle contains the hydrophobic moieties of the surfactant molecules and the outer surface consists of the hydrated hydrophilic groups along with any bound water molecules (Quina and Hinze, 1999). Since the micelles in water have both hydrophobic and hydrophilic parts, and the hydrophilic part surrounding the hydrophilic core, the micelles have the ability to solubilize the hydrophobic compounds into their interior. This type of interaction can be expressed by Langmuir isotherm (Zhou *et al*., 2009).

Surfactants belong to a group of association or amphiphilic organic substances. Amphiphilic molecules consist of an ionic or nonionic polar head group and a hydrophobic portion. The ambivalence of amphiphiles for an aqueous environment is creditworthy for the phenomenon of self−association of single amphiphile molecules leading in a variety of micellar aggregate structures above CMC. The formation of micelles or surfactant aggregates is primarily operated by three forces: the hydrophobic repulsion between the hydrocarbon chains and aqueous solution, the charge repulsion of ionic head groups, and the van der Waals attraction between the hydrocarbon tails (Rub *et al*., 2012). It has been demonstrated that surfactant solutions provide a reaction medium, able to modify reaction rate, equilibrium position, products obtained and spectral or analytical parameters (Silva *et al*., 1997). There are four types of general surfactants that are classified based on their charge on head group; non−ionic, cationic, anionic, and amphoteric (or zwitterions). Table 2.3 presents some characteristics and examples of each of the four groups (Bezerra *et al*., 2005; Vaisman *et al*., 2006).

Table 2.3:
Classification and characteristics of surfactants (Bezerra *et al*., 2005).

Classification	**Characteristic**	**Example**
Anionic	The hydrophilic group carrying a negative charge such as carboxyl ($RCOO^-$), sulfonate (RSO_3^-)	$CH_3(CH_2)_{11}SO_4^-Na^+$ Sodium dodecyl sulfate (SDS)
Cationic	The hydrophilic group carrying a positive charge as, for example, the quaternary ammonium halides ($R_4N^+Cl^-$)	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ Cetyl trimethyl ammonium bromide (CTAB)
Non–ionic	The hydrophilic group has no charge but derives its water solubility from highly polar groups such as polyoxyethylene ($–OCH_2CH_2O–$) or polyol groups	$CH_3(CH_2)_{11}(OCH_2CH_2)_{23}OH$ Polyoxyethylene (23) Dodecanol (Brij 35)
Amphoteric or zwiterrionic	Its molecules present both the anionic and cationic groups and, depending of pH, its prevalence the anionic, cationic, or neutral species	$CH_3(CH_2)_{11}N^+(CH_3)_2$ (CH3)COO^- 4–(Dodecyldimethyl ammonium) butirate (DAB)

Surfactants or micelles are reported to possess unique solubilization properties. This is attributed to their formation consisting of a hydrophilic surface and a hydrocarbon core. The hydrophobic core can entrap and thus isolate hydrophobic substances as illustrated in Figure 2.2. This ability has been extensively used in the past few years under the term cloud point extraction for pre−concentration of organic molecules and metal chelates. On the other hand, the outer sphere as well as the interface of the micelle has been overlooked with regard to their binding capacity. These areas can interact electrostatically with amphoteric or even charge substances, like metal ions under certain conditions (Paleologos *et al.*, 2003).

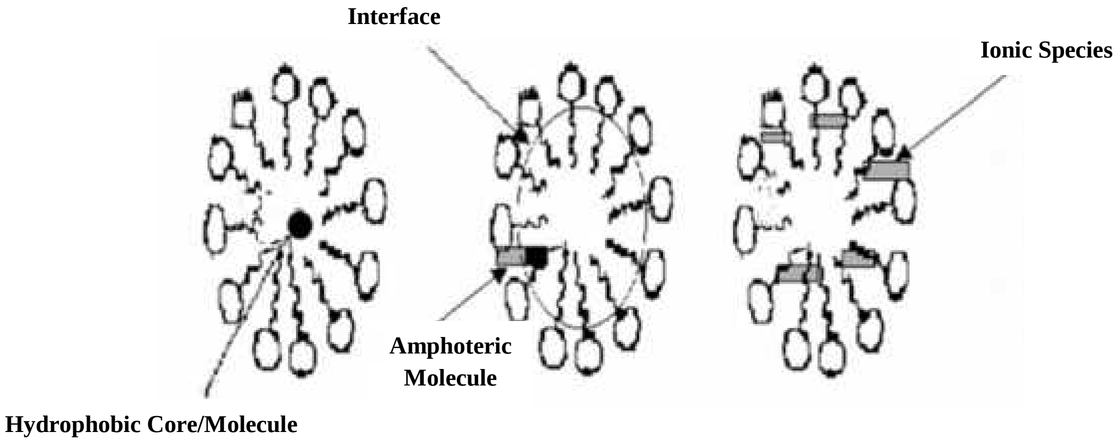


Figure 2.2: Binding sites of a micelle for hydrophobic, amphoteric and ionic species (Paleologos *et al.*, 2003).

Among the class of surfactants, the non−ionic surfactant such as Triton X−114 is well known for micelle formation. However, its aromatic chromophore has strong UV absorbance or fluorescence signals detected, resulting in measuring of the phenolic compounds signal in spectrophotometric method. Moreover, its harm to the environment also made it forbidden to be used in many places, including Europe (B. Yao & Yang, 2008a, 2008b). Table 2.4 shows the previous studies on the application of CPE technique for extracting organic pollutant from water samples using several types of surfactant.

Table 2.4:
Some applications of CPE for selected organic pollutant in water samples.

Type of surfactant	**Analyte**	**References**
Non−ionic surfactant		
Poly(oxyethylene)−7,5−(*p*−tert−octylphenyl)ether (Triton X−114)	Polycyclic aromatic hydrocarbons (PAHs)	(Ferrer *et al*., 1996)
Oligoethylene glycol monoalkyl ether (Genapol X−080) Polyoxyethylene−10−cetyl ether (Brij 56)	Polychlorinated dibenzofurans (PCDF)	(Fernández *et al.*,1999)
Poly(oxyethylene)−7,5−(*p*−tert−octylphenyl)ether (Triton X−114)	Chlorophenols (2−chlorophenol, 4−chloro−3−methyl phenol, 2,4−dichlorophenol, 2,4,6−trichlorophenol, pentachlorophenol	(Calvo Seronero *et al*., 2000)
Poly(oxyethylene)−7,5−(*p*−tert−octylphenyl)ether (Triton X−114)	Polybrominated diphenyl ethers (PBDEs)	(Fontana *et al*., 2009)
Oxyethylated methyl dodecannoates (Denoted OMD) *t*−octylphenol polyethoxylate (Triton X−100)	Phenol,4−nitrophenol 4−methylphenol Aromatic contaminants (Benzene, toluene, ethylbenzene)	(Materna *et al*., 2001) (Trakultamupatam *et al*., 2002)

Dow Corning 193 (DC193) Dow Corning 190 (DC190)	PAHs (anthracene, phenanthrene, pyrene)	(Yao *et al*., 2007)
Ethoxylated	Phenol	(Taechangam *et al*., 2009)
Anionic surfactant		
Sodium dodecyl sulfate (SDS) Sodium dodecylbenzenesulfonic acid (SDBSA) Sodium dodecanesulfonic acid (SDSA) Sodium dioctylsulfosuccinatem (Aerosol OT)	Polycyclic aromatic hydrocarbons (Pyrene and various PAHs)	(Casero *et al*., 1999)
Cationic surfactant		
Tricaprylmethylammonium chloride (Aliquat 336)	Bisphenol−A (BPA)	(Yu *et al*., 2009)
Amphoteric or zwiterrionic surfactant		
Dodecyltrimethylammonium bromide (DTAB) Alkyldiphenyloxide disulfonaate (DPDS)	Benzene	(Weschayanwiwat *et al*., 2008)

‘**Table 2.4**, continued’

2.2.1.1 Silicone surfactant / DC193C.

Silicone surfactants (also called PEG/PPG dimethicone) are one class of amphilic materials having water soluble and a silicone soluble portion in one molecule. DC193C fluid which is non−ionic surfactant based on silicone PEGs copolymers. Silicone−based surfactants are used in a wide variety of applications in the industry, such as foam stabilizers, wetting agents, emulsifiers or lubricants. The polysiloxane backbone is highly flexible and carries methyl groups from which the cohesive energy is very low, giving rise to a low surface tension. Most commercial silicone surfactant consists of a linear backbone with pendant polyalkylene oxide groups grafted within the chain (Laubie *et al*., 2013).

Silicone surfactant are of novel and specialty agents and consist poly(dimethylsiloxane)s as the hydrophobic part alongside a hydrophilic moiety, and the latter can be non−ionic, ionic, and zwiterrionic in nature. The non−ionic hydrophilic groups are made of oxyethylene or grids of oxyethylene and oxypropylene units. Silicone surfactants are available in different molecular architectures such as graft (rake or comb) like, trisiloxane, linear, or branched. Silicone surfactants with non−ionic hydrophilic moieties not only share many common features with conventional low molar mass non−ionic surfactants but also possess the following properties unique only to them (Soni *et al*., 2003).

Silicone surfactants are (i) equally surface active in water as well as in non−aqueous solvents such as mineral oils and polyols, (ii) lower surface tension of water to as low as 20 mN m^{-1}, and (iii) remain as liquids even with very high molecular weights. Silicone surfactants have been widely used as foam stabilizers for polyurethanes, foam controlling agents for diesel fuel, and better wetting agents in ink, paint and coating, and formulations for effective spreading and penetration of herbicides on plant leafs. Despite their extensive use, only a few investigations are available in the literature on the surface active, phase, and association behavior of these interesting amphiphilic copolymeric surfactants (Soni *et al*., 2003).

2.2.2 Influential factor.

The performance of a CPE process is influenced by many factors, such as surfactant type and its concentration, ionic strength, pH and equilibration temperature and time.

2.2.2.1 Type and concentration of surfactant.

Explicitly, surfactant plays a vital role in the CPE process. Thus, proper selection of surfactant could leads to satisfactory performance of the CPE process. There are several types of surfactants used in the CPE processes include Triton series, Igepal series and PONPE series (polyethyleneglycol mono−4−nonylphenyl ethers).

However, these surfactants contain alkyl phenyl groups in their hydrophobic moiety, leading to some environmental concerns. To overcome this problem, biodegradable surfactant, mainly polyethylene glycol or silicone surfactant without phenyl group is proposed (Hung *et al*., 2007).

The main requirements for a surfactant to be selected as suitable for the CPE experiments are associated mainly with its physicochemical characteristics: high density, which facilitates phase separation; low cloud−point temperature, below or near room temperature in a narrow concentration range, for thermolabile molecules; balanced hydrophobicity; commercial availability; and, low cost (Stalikas, 2002).

Depending on the nature of the hydrophilic group, surfactants are classified as non−ionic, zwiterrionic, cationic, and anionic. Nowadays, non−ionic, zwiterrionic and anionic surfactants are most widely used in the CPE process for organic compounds, drugs, biomaterials and inorganic metal ions. However, the application of the cationic surfactants in the CPE is scarce. Since, it can directly affect the extraction and pre−concentration, and accuracy of the final analytical results, it is very important to select an appropriate surfactant for a successful CPE analysis (Xie *et al*., 2010).

2.2.2.2 Effect of ionic strength.

Generally, clouding is a phenomenon detected in non−ionic surfactants when the solution is heated to a threshold temperature which is known as clouding point temperature (CPT). Occurrence of the clouding phenomenon is uncommon with the ionic surfactants, presumably because of the large electrostatic repulsion between the aggregates prevents phase separation in most cases. The phase separation occurs within a narrow temperature range into surfactant rich phase and aqueous phase, because of density difference due to sharp increase in aggregation number of the micelles and the decrease in intermicellar repulsion. The CPT has been found extremely dependent on the presence of additives (Rub *et al*., 2012). Usually, the CPT of a non−ionic surfactant can be altered in the addition of additives, such as inorganic salt and organic compounds, into an aqueous solution. This phenomena is known as salting−out effect where the addition of neutral salts depresses the CPT of a non−ionic surfactant aqueous solution in proportion to their concentration (Wang and Dai, 2010).

Several factors have been considered to be responsible for the CPT phenomenon such as surfactant molecule and its concentration, temperature and additives in the system of CPE. However, CPT is very sensitive to the presence of additives used in the CPE system, even at a very low concentration. The additives modify the surfactant−solvent interactions, change the CMC, size of micelles and phase behavior in the surfactant solutions. Many efforts has been made to investigate the effect of various additives e.g. inorganic electrolytes, organic compounds, ionic surfactant, cationic surfactant and zwitterionic surfactants on the cloud point of a non−ionic surfactant (Sharma *et al*., 2003).

2.2.2.3 Effect of pH.

pH is one of the parameters to be considered in the CPE systems. Generally, the pH effect on the CPE system depends on the characteristics of both surfactants and analytes. In most studies the influence of pH on extraction efficiency is not crucial for those neutral or non−ionized compounds such as organic pollutant. However, a few notable exceptions have been reported that the pH plays an important role in the CPE for analytes possessing an acidic or a basic moiety. Normally, the ionic form of a molecule formed upon deprotonation of a weak acid or protonation of a weak base does not interact or bind as strongly as its neutral form of an analyte is extracted (Xie *et al*., 2010).

2.2.2.4 Equilibration temperature and time.

Phase separation and efficient pre−concentration can be influenced by optimal equilibration temperature and time. Theoretically, the phase separation can be achieved once the optimal equilibration temperature of the CPE is higher than the CPT of the surfactant. If the temperature is lower than the CPT, two phases cannot be formed. However, too high temperature may lead to the decomposition of analytes. It has also been demonstrated that the analyte extraction efficiency and preconcentration in the CPE increase as the equilibration temperature for phase separation is progressively increased to above the CPT. Similarly, as the equilibration temperature increases; the volume of surfactant rich phase decrease because the hydrogen bonds are disrupted and dehydration occurs. Based on a physical point of view, the increase of temperature provokes the dehydration of the hydrophilic groups of the surfactant molecules, an increase of the aggregation number and the swelling of the micelles until the micellar solution become turbid and the separation of the surfactant rich phase takes place (Materna *et al.*, 2001). Since longer equilibration times (> 30 min) do not have any significant effect on the extraction, the equilibration time of 10 – 20 min is sufficient to obtain good extraction in most work (Xie *et al.*, 2010).

2.3 Cyclodextrins.

Cyclodextrins (CDs) have been known for nearly 100 years. In 1881, Villiers first produced them by digesting the starch with *Bacillus amylobacter* and in 1903; Schardinger demonstrated the cyclic structure of these compounds. CDs are cyclic oligosaccharides derived from starch containing six (α−CD), seven (β−CD) and eight (γ−CD) as shown in Figure 2.3 (Davis and Brewster, 2004).

In general, CDs are fairly soluble in water. They are produced as a result of intramolecular trans glycosylation reaction from degradation of starch by cyclodextrin glucanotransferase enzyme (CGTase) (Singh *et al*., 2002). Supramolecular chemistry is intriguing and potential for future functional molecular devices and nanoscience (Zhang *et al*., 2011). Supramolecule is a system of two or more molecular entities held together and organized by means of inter−molecular non−covalent binding interaction.

CDs are a class of supramolecules in the shape of a truncated cone or torus with a hydrophilic exterior and a less polar cavity in the center that are ideally suitable to accommodate various kinds of guest molecules into their cavities (Li *et al*., 2009; Xu *et al*., 2012). The hydroxyl functions are oriented to the cone and the secondary hydroxyl groups at the wide edge. The geometry of CDs gives a hydrophobic inner cavity having a depth of ca. 7.0 Å, and an internal diameter of ca. 4.5, 7.0, and 8.5 Å for α−, β−, and γ−CD, respectively. Various molecules can be fitted into the cavities of CDs to form supramolecular inclusion complexes, which have been extensively studied as models for understanding the mechanism of molecular recognition (Brewster *et al*., 2007; Li *et al*., 2008).

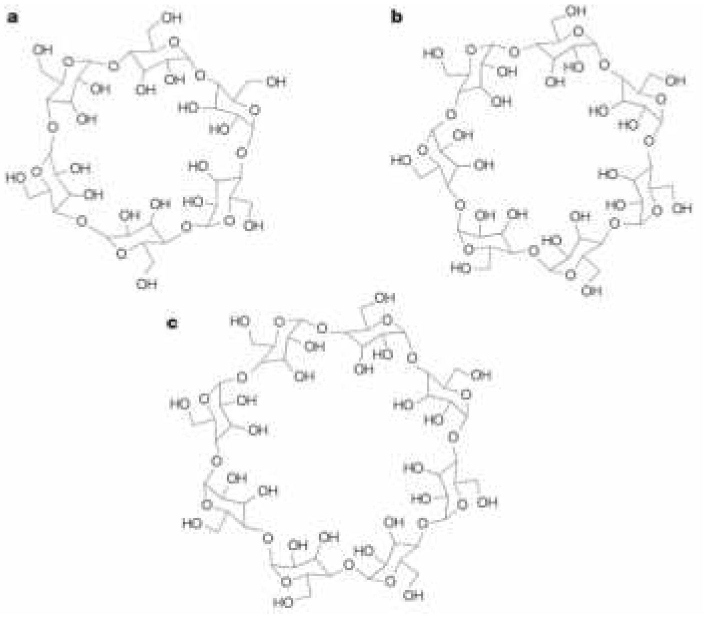


Figure 2.3: Structural formulae of **(a)** alpha (α−CD), **(b)** beta (β−CD) and **(c)** gamma (γ−CD) cyclodextrins (Davis and Brewster, 2004).

β–Cyclodextrin (β–CD) is the most studied and most frequently used owing to its cavity with an internal diameter of 6.5Å and a depth of 8Å. As shown in Figure 2.4, the most characteristic feature of the β–CD molecule is its ability to form inclusion compounds with various molecules, ions, polymers (including aromatic hydrocarbons, volatile organic compounds, and metal), through host−guest interactions (Li *et al.*, 2012). Each substance which presents a steric complementary, even partial, with β−CD cavity might be included. In general, β–CD constitutes a good compromise as its hydrophobicity cavity and its rather flexible macrocycle present an intermediate size between α−CD and γ–CD. Besides that, it is most accessible, the lowest−priced and generally the most useful. The main properties of those cyclodextrins are given in Table 2.5 (Del Valle, 2004; Morin-Crini & Crini, 2013).

Table 2.5:
The properties of cyclodextrins (Del Valle, 2004; Morin-Crini & Crini, 2013).

Property	**α–Cyclodextrin**	**β–Cyclodextrin**	**γ–Cyclodextrin**
Number of glucopyranose	6	7	8
Molecular weight (g/mol)	972	1135	1297
Solubility in water at 25˚C (%, w/v)	14.5	1.85	23.2
Outer diameter (Å)	14.6	15.4	17.5
Cavity diameter (Å)	4.7-5.3	6.0-6.5	7.5-8.3
Height of torus (Å)	7.9	7.9	7.9
Cavity volume (Å^3)	174	262	427

2.3.1 Inclusion complex.

The formation of inclusion complexes is the basis for applications of cyclodextrins (CDs) in several fields, including spectrophotometric analysis and chromatographic separation, as well as in the pharmaceutical, cosmetic, and food industries. The most notable feature of CDs is their ability to form solid inclusion complexes (host−guest complexes) with various molecules, ions and polymers (including aromatic derivatives, dyes, polycyclic aromatic hydrocarbons, volatile organic compounds and metal), the stability of the complex depends on how the guest molecule fits into the cavity of the CDs (Abay *et al.*, 2005). Furthermore, the influence of CDs on the aggregation of surfactants in aqueous solution has attracted increasing attention in colloid science. CDs are able to form host−guest complexes with most surfactants that have high binding constants by including the surfactants' hydrophobic tails into the CDs' cavities. The CD−surfactant complexes are usually believed to be soluble in water and unable to form aggregates because of the hydrophilic outer surface. However, all the above examples are based on the well−known observation that CD inclusion complexes have stronger hydrophilicity, and the studies were carried out at the premicellar region or around the critical micelle concentration (CMC). This is especially true for the investigation of complexation between CDs and surfactants, but may not be true for aqueous surfactant solutions of higher concentration (Xu *et al.*, 2012).

Due to the CDs have a high density of hydroxyl groups which can interact with functional groups of the encapsulated substrates giving additional stability to the inclusion complex. In these complexes, a guest molecule is held within the cavity of the CDs host molecule (Singh *et al.*, 2002). Complex formation is a dimensional fits between host cavity and guest molecule. The stability of the inclusion complexes depends primarily on hydrophobic interactions and on size and shape considerations (Leyva *et al.*, 2001). Despite a hydrophilic surface, CDs contain a hydrophobic cavity. It is the presence of this cavity that enables CDs to entrap hydrophobic molecules. Entrapment or inclusion occurs without the formation of formal chemical bonds. The main driving force of complex formation is the release of enthalpy−rich water molecules from the cavity. Water molecules are displaced by more hydrophobic guest molecules present in the solution attain an a polar − a polar association and decrease of cyclodextrin ring strain resulting in a more stable lower energy state (Del Valle, 2004).

The formation of an inclusion complex between β−CD molecule and aromatic solute are shown in Figure 2.4.

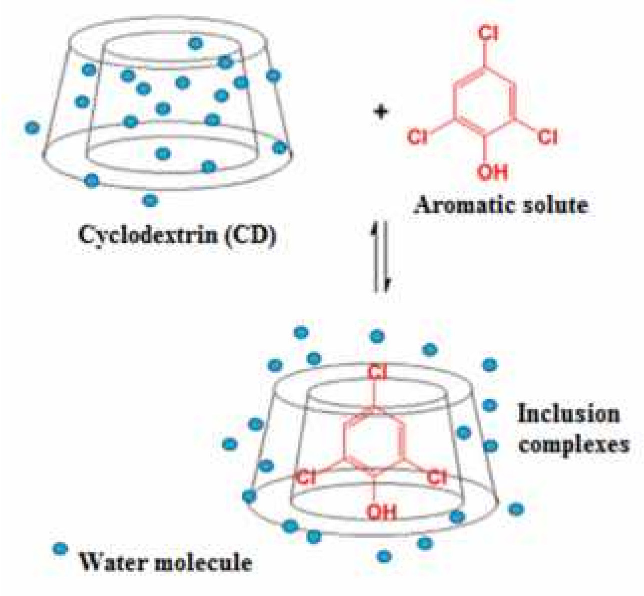


Figure 2.4: A schematic representation showing the formation of an inclusion complex between β−cyclodextrin molecule and aromatic solute (Li *et al*., 2012).

2.3.2 Application of β−cyclodextrin in extraction and separation techniques.

More recently, β−cyclodextrin (β−CD) has been proposed as an alternative agent in order to enhance water solubility of hydrophobic compounds. The β−CD is a cyclic oligosaccharide with seven glucose units, with is cavity structure, and can form an inclusion complex with certain molecules through a host−guest interaction. It has a low−polarity cavity within which organic compounds of appropriate shape and size can form inclusion complexes. This property provides β−CD a capacity to increase the apparent solubility of several hydrophobic pollutants such as chlorinated phenols, nitro−aromatic compounds, PAHs, pesticides and thus their availability for biodegradation. This intriguing property of β−CD has inspired considerable basic research, applied science, and also use in a variety of products. Separations represent a large area of analytical chemistry. It has found wide application as HPLC stationary phases for separation of various compounds (Guo *et al*., 2009; Mitchell and Armstrong, 2004; Panda *et al*., 2006; Zhang *et al*., 2008). Masqué *et al*. (2000) have utilized β−cyclodextrin bonded silica as a selective sorbent for on−line solid phase extraction of 4−nitrophenol. Also, Hu *et al*. (2005) have applied β−cyclodextrin bonded silica as a coating material for solid phase microextraction of some phenolic compounds.

2.4 Ionic liquids.

The field of ionic liquids (ILs) has received an increasing amount of attention in the past decade largely due to their unique and tunable physicochemical properties and their versatility in various applications. The increased interest in ionic liquids by chemists and technologists clearly is due to the utility of ILs as solvents for reaction chemistry, including catalytic reactions. ILs is very simple molten salts. As salts they are by essence made of cations and anions. They are composed of ions comprising a relatively large asymmetric organic cation (i.e. alkyl pyridinium, dialkyl imidazolium ions) and an inorganic or organic anion (i.e. halide, hexafluorophosphate, tetraflurophosphate and ions based on fluorinated amides) (Mizuuchi *et al*., 2008).

ILs has been recognized as a possible environmentally benign alternative to classical organic solvents, mainly due to their thermal stability and ability to solubilize a large range of organic molecules and transition metal complexes. The desire for “green” solvents for industrial processes is partially responsible for this, but also many chemists now realize that ILs offer some unique properties as solvents (Kohoutová *et al*., 2009). Furthermore, ILs solvents have the prospect for custom design of the solvent to meet specific requirements for a particular reaction type (Wilkes, 2004).

2.4.1 Physicochemical properties of ionic liquids.

Although the first room temperature ionic liquids (RTILs) were first observed in the middle of the 19th Century, only since the 1980s the room temperature ILs attracted a significant and growing interest. Now, ILs which is green solvents, have been studied extensively due to their tempting properties such as negligible vapor pressure, wide liquid range, high thermal stability, and ability to solvate compounds of widely varying polarity (Yao and Anderson, 2009). Utilizing ILs is one of the goals of green chemistry because they create a cleaner and more sustainable chemistry and are receiving increasing interest as environmental friendly solvents for many synthetic and catalytic processes. An intriguing characteristic is to fine tune the physical−chemical properties by suitable choice of cations and anions. Therefore, ILs have been recognized as “designer−solvents (Zhang *et al.*, 2006).

ILs are generally, defined as a class of non−molecular ionic solvents with low melting points. Compared to traditional metallic molten salts, such as sodium chloride which possesses a melting point of 801°C, ILs exists as liquid below 100°C (Anderson *et al.*, 2006). ILs possesses their melting point equal to or lowers than room temperature which is referred to as RTILs. The use of a solvent in industrial processes depends on its price and on its physical properties, such as viscosity, density, and thermal stability. In fact, it is convenient to have solvents with low viscosities to facilitate mixing and with a large density difference in comparison with the other fluids used in the process to facilitate the phase separation (Vidal *et al.*, 2005).

Selected properties, such as thermal stability and miscibility, mainly depend on the anion, while others, such as viscosity, surface tension and density, depend on the length of the alkyl chain in the cation and/or shape or symmetry. Beside their low melting point, they have a wide range of solubility, viscosity or density. The extremely low vapour pressure of most ILs is the main reason that renders them useful in green chemistry. In chemical processes, they are easily recyclable and produce minimum pollution. ILs vapour pressure is most often non−measurable at room temperature (Berthod *et al*., 2008). The viscosities of ILs are governed largely by hydrogen bonding and van der Waals−type interactions between the cation and anion. For imidazolium−based ILs, there is often an increase in viscosity with increasing length of the alkyl chain substituents on the cation. The viscosity of an ILs can be additionally tuned by functionalized of the substituents on the cation. ILs derived from the imidazolium cation tends to be more thermally stable than ammonium−based ILs. The thermal stability of ILs can usually be improved by increasing the length of the alkyl substituent on the cation. ILs are able to solubilize inorganic as well as organic compounds (Berthod and Carda-Broch, 2004).

2.4.2 Application ionic liquids in separation and extraction techniques.

Recently, several researchers have reported the uses for RTILs in chemical analysis. RTILs have been used as stationary phase in gas chromatography (Anderson & Armstrong, 2005; Armstrong *et al*., 1999; Ding *et al*., 2004) and mobile phase in liquid chromatography (He *et al*., 2003; Polyakova *et al*., 2006; Xiaohua *et al*., 2004). RTILs were able to dissolve chiral selectors to make chiral stationary phases and they were used as unique running electrolytes in the separation of the phenolic compounds by capillary electrophoresis (Qin *et al*., 2003; Vaher *et al*., 2001; Vaher *et al*., 2002; Vaher *et al*., 2011). Another direction for the use of RTILs as a solvent is extraction, where non volatility could be an advantage in cases of large−scale processes, and RTILs thus may be suitable candidates for replacement of volatile organic solvents in liquid−liquid extraction processes (Koel, 2005; Visser *et al*., 2001; Wei *et al*., 2003).

The interaction mechanisms between ILs and micelles have been investigated. It was found that the properties of micellar solution such as critical micellization concentration (CMC), aggregation number, aggregate size, and dipolarity of micellar pseudo−phase can be altered by the addition of ILs. Although the modifications of these properties are significant, their practical applications are very few. Besides, ILs has received increasing attention in liquid−liquid extraction of metal ions because of their unique chemical and physical properties which improves the extraction efficiency (Gao *et al*., 2013). A possible strategy is to introduce ILs in CPE to improve the extraction of organic pollutant in environment.

2.5 Synthesis of mono−functionalized β−cyclodextrin with ionic liquids.

In recent years, much attention has been paid to chemical separation techniques and the design and synthesis of new extraction reagents for ions and molecules. This attention results in part from environmental concern, efforts to save energy and recycling at the industrial level. In this respect, the supramolecular chemistry has provided a much better solution to the search for molecular structures that can serve as building blocks for the production of sophisticated molecules by anchoring functional groups oriented in such a way that they delineate a suitable binding site.

Native of β−CD and their hydrophilic, hydrophobic or ionic derivatives can be used in the decontamination of wastewater, aquifers, air and soil to increase the stabilization, encapsulation, separation and sorption of contaminants. This is mainly due to the fact that the hydrophobic cavity in their structure can take up aromatics and other hydrophobic organic molecules, providing ideal binding sites (Morin-Crini et al., 2013). Although native β−CD are able to encapsulate many organic pollutants, this ability can be enhanced in many cases by their derivatization. Each glucose unit that is part of the macrocyclic ring of native cyclodextrins has two secondary hydroxyl groups on C2 and

C3 position and one primary hydroxyl group on C6 position. However, the primary and secondary hydroxyl groups may be functionalized with hydrophobic (i.e. methyl, propyl) or hydrophilic groups (sulphate, phosphate, quaternary amine). Additional interactions, such as $\pi - \pi$ staking, dipole−dipole, ion−pairing, electrostatic and steric repulsive effects can be introduced between the associated analytes and the appropriately functionalized β−CD. In this way, the solubility, complex−forming capacity and selectivity of β−CD towards certain analyte can be improved (Zhong *et al.*, 2006).

Modification of β−CD has important effects on separation and extraction efficiency. The unique structures of β−CD, which have a cavity possessing a hydrophilic external surface and a hydrophobic internal surface, make them useful in extraction and separation processes. It is well known that a chemical modification of the hydroxyl groups bring about changes in the shapes and sizes of their cavities, in their hydrogen−bonding abilities and in other physical properties, as well as affecting their molecular−recognition abilities (Araki *et al.*, 2000). Currently, substituent group−modified β−CDs can be divided into three types: the hydrophobic, the hydrophilic and the charge groups. Introduction of substituent groups onto the rim of β−CD can change the size of the cavity and form $\pi - \pi$ interactions, dipole−dipole interactions and electrostatic interactions, and it can increase hydrogen bonding between hosts and guests (Zhou *et al.*, 2010). Through modification, the applications of β−CD are expanded. The β−CD are modified through substituting various functional compounds on the primary and/or secondary face of the molecule. Modified β−CD are useful as enzyme mimics because the substituted functional groups act in molecular recognition. The same property is used for targeted drug delivery and analytical chemistry as modified β−CD show increased enantiomer selectivity over native β−CD (Del Valle, 2004).

Due to many derivatized and all non−derivatized β−CD are soluble in water, they are often used in aqueous environments as solubilizers of hydrophobic compounds via inclusion complex formation. Under appropriate conditions, this ability also makes them potentially useful agents for various type extractions and separations (Li *et al.*, 2008).

2.5.1 Application mono−functionalized β−cyclodextrin with ionic liquids in extraction and separation techniques.

ILs, a kind of organic salts, are liquids at or near room temperature. They have been widely used in many fields because of their negligible vapour pressure, non−flammability, high thermal and chemical stability, high polarity, and wide electrochemical. Besides, they can also be designed to be environmentally benign, with large potential benefit for sustainable chemistry. Among their various applications, separation is important and intriguing. Owing to the interaction of ILs with CDs, separation processes of CDs and ILs have been applied in separation and extraction methods as shown in Table 2.6.

Table 2.6:
Application β−cyclodextrin functionalized with ionic liquids (βCD−IL) in extraction and separation technique.

βCD−IL	**Extraction and separation techniques**	**References**
3−alkylimidazolium and pyridinium based β−cyclodextrin−ionic liquid (βCD−IL polymers).	Preparation of βCD−IL polymers was achieved by an initial tosylation or iodination of the primary hydroxyl group at the C−6 position. These polymers were tested to remove both organic and inorganic pollutants from water.	(Mahlambi *et al.*, 2010)
β−Cyclodextrin with Molecular imprinted polymer (β−CD−MIPs) and cooperative effect of ILs.	βCD−MIPs have been applied for separation of small molecules, nanometer−scaled molecules and larger bioactive molecules in non−aqueous and aqueous media. ILs and CDs together are being studied to apply into	(Zhang *et al.*, 2011)

	separation methods, e.g., CE and GC. When CDs are running electrolytes of CE, the addition of ILs can take synergic or reverse effects on the separation processes.	
6−tosyl−β−cyclodextrin with 1,2−dimethylimidazole or 1−amino−1,2,3−triazole	Chiral stationary phases was obtained by 6−tosyl−β−cyclodextrin with 1,2−dimethylimidazole or 1−amino−1,2,3−triazole, and bonded to silica gel to be used in high−performance liquid chromatography. The separation performances of these stationary phases were examined with 16 chiral aromatic alcohol derivatives and 2 racemic drugs.	(Zhou *et al*., 2010)
Permethylated mono−6−(butylimidazolium)−cyclodextrin (BIM-BPM) and permethylated mono−6−(tripropylphosphonium)−cyclodextrin (TPP−BPM)	Ionic liquids are used to dissolve ionic cyclodextrin derivatives to produce new type of gas chromatographic chiral stationary phase. The new ionic liquid−based stationary phase exhibits broader enantioselectivities, up to seven time's higher efficiencies, and greater thermal stabilities. The most profound separation enhancements are usually found for more polar analytes.	(Huang *et al*., 2010)
6−O−monotosyl−6−deoxy−β−cyclodextrin with 1−benzylimidazole (βCD−BIMOTs−TDI)	βCD−BIMOTs−TDI is a macroporous material. This material was used as SPE sorbent for extraction of phenols in river water samples by using Gas Chromatography−Flame Ionization Detector (GC−FID).	(Raoov *et al*., 2014)

'**Table 2.6**, continued'

CHAPTER 3

METHODOLOGY

3.1 Chemicals and materials.

Dow Corning DC193C, also known as polyethyleneglycol (PEG) silicone, was supplied by Dow Corning (Shanghai, China). Figure 3.1 shows the chemical structure of the PEGs. The values of x, y and molecular weight of these compounds were available from the manufactures. 2,4−dichlorophenol, 2,4,6−trichlorophenol and 4−nitrophenol were purchased from Sigma−Aldrich, Malaysia. Figure 3.2 shows the absorption of the UV−Vis spectra for 2,4−dichlorophenol (molecular weight: 163 g mol^{-1}, λ_{max}: 285 nm), 2,4,6−trichlorophenol (molecular weight: 197.45 g mol^{-1}, λ_{max}: 295 nm) and 4−nitrophenol (molecular weight: 139.11g mol^{-1}, λ_{max}: 318 nm).

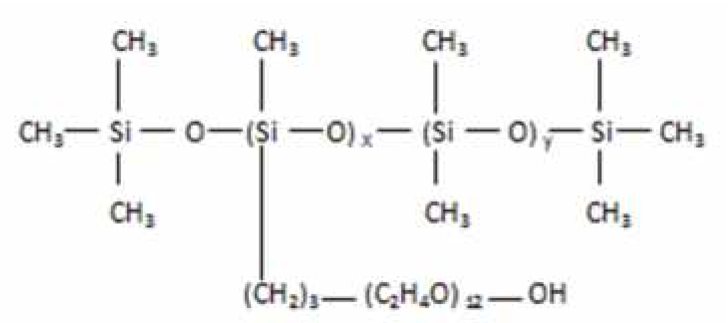


Figure 3.1: Structural formulae of silicone surfactant (DC193C) (Zain *et al*., 2014).

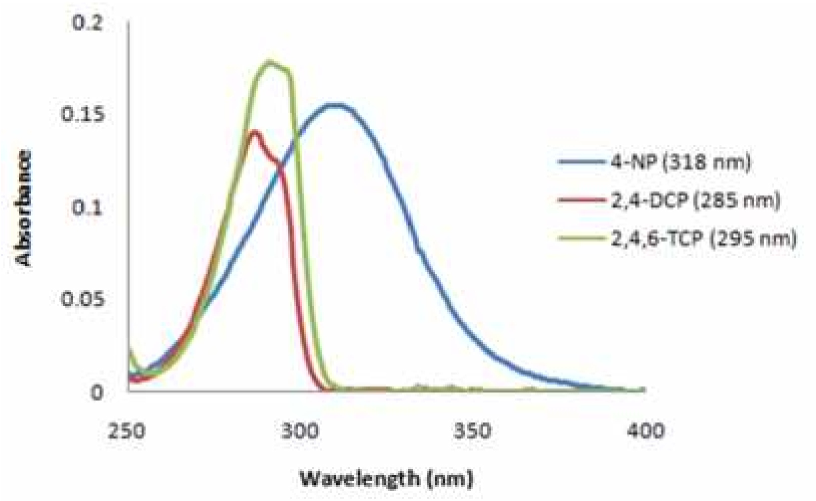


Figure 3.2: The absorption of the UV−Vis spectra for individual phenolic compounds at the respective λ_{max} in the surfactant rich phase after the CPE.

Standard stock solutions of chlorophenols (1000 mg L^{-1}) were prepared in methanol and 4−nitrophenol (1000 mg L^{-1}) in distilled water. The working solutions were freshly prepared daily by an appropriate dilution of the stock solutions. For all experiments, the surfactant and phenolic compounds were used without further purification. HCl and NaOH were used for pH adjustment. Na_2SO_4 was prepared by dissolving an appropriate amount in distilled water.

β−CD is commercially available and was purchased from Acros (Acros, Geel, Belgium) (99%). 1−benzylimidazole was supplied from Sigma Aldrich (Aldrich, Buches SG, Switzerland). The absorption of the UV−Vis spectra imidazolium−based of 1−benzylimidazole (molecular weight: 158.20, λ_{max}: 210 nm). Other reagents and chemicals were of the analytical reagent grade and were used and received without further purification. Double distilled water was used throughout the experiments. *N*,*N*−Dimethylformamide (DMF) and hexane anhydrous were purchased form Merck (Merck, New York, USA). *p*−Toluene sulfonic anhydride was prepared according to a literature procedure (Zhong *et al.*, 1998) and was used without further purification. The synthesis of β−cyclodextrin functionalized with ionic liquid will be discussed in Section 3.1.1.

3.1.1 Synthesis of β−cyclodextrin functionalized with ionic liquids (βCD−IL).

βCD−IL was prepared by reacting 6−O−Monotosyl−6−deoxy−β−cyclodextrin (βCD−OTs) with 1−benzylimidazole (BIM). βCD−OTs was prepared according to (Zhong *et al*., 1998). Since tosyl is a good leaving group, imidazole can easily undergo nucleophilic substitution. The reaction was carried out in DMF solvent since βCD−OTs and BIM form a homogeneous solution. The preparation of mono−functionalized β−CD with BIM (βCD−IL) was done according to the following procedure (Ong *et al.*, 2005), as shown in Figure 3.3: Freshly dried βCD−OTs (1.00 g, 78 mmol) and appropriate amount of BIM (10 mole equivalent) in excess amount were dissolved in anhydrous DMF (40 mL) and the solution was stirred at 90ºC in an inert atmosphere. After two days, the resultant solution was cooled to room temperature and slowly added into acetone. Then the mixture was stirred for 30 min and thereafter filtered and washed in excess acetone.

The obtained product was recrystallized three times from hot water to get the final product, as a white precipitate. Figure 3.3 shows the reaction to form of compound, βCD−IL in D_6−DMSO solvent. The formed product was soluble in water and several organic solvents (DMF, DMSO and ethanol). Protons of imidazole ring (Hf, He, Hd) appeared in the downfield region since the protons are de−shielded upon functionalization. New peak is observed in proton (H6*, 3.95 ppm) and carbon signal (C6*, 45.2 ppm), belongs to the substituted of β−CD.

IR/KBr, cm^{-1} 3297 (OH), 2922 (C−H), 1652 (C=C), 1152 (C−N). **^{1}H NMR/ppm**, DMSO−d_6 H_f (9.3, s), H_e (7.94, s), H_d (8.20, s), H_c (7.49, s), H_b (7.74, t), H_a (7.46,s), Hg (5.18, s), H_8 (7.4, d), H_9 (7.1, d), OH_2−OH_3 (5.5−5.9, m), H_1 (4,81, s), OH_6 (4.4−4.6, m), H_6* (3.95), H_3, H_5, H_6 (3.4−3.60), H_2−H_4 (3.2−3.4, m), H_{11} (2.07, s). **^{13}C NMR/ppm**, DMSO−D_6 C_a (127), C_b (123.4), C_c (128.3), C_d (128), C_e (119), C_f (136.9),

C_g (52), C_h (137.8), C_7 (145.26), C_{10} (137.3), C_9 (128.7), C_8 (125.6), C_1 (101.8), C_4 (81.16), C_2 (73.27), C_3 (71.6), C_5 (69.37), C_6 (60.03), C_6* (45.2), C_{11} (21.97). **CHNS (%)** C (38.2), H (6.67), S (0.47), N (1.0). Percentage yield (90%).

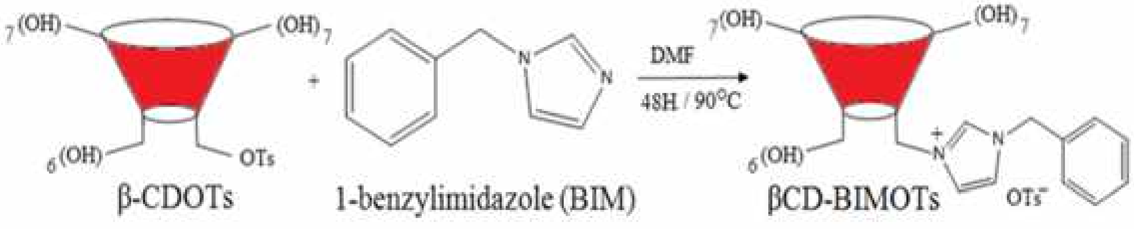


Figure 3.3: Preparation of mono−functionalized β−cyclodextrin (βCD−BIMOTs).

3.2 Instrumentation.

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 maintain CPE system at the desired temperature. The pH value of the sample solution was determined by pH meter (Hanna instrument). A 15 ml calibrated centrifuge tube was used (Copen, Malaysia). Fourier transform infrared (FT−IR) spectra for characterization of the βCD−IL monomers were recorded on a Perkin Elmer RX1 FT−IR (Perkin Elmer, Waltham, MA, USA) between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1} in KBr pellets. ^1H NMR, ^{13}C NMR and 2D NOESY spectra were performed on an AVN 600 MHz (Bruker, Fallanden, Switzerland) for characterization of the βCD−IL monomers and analysis of inclusion complex. An elemental analysis of the βCD−IL monomers was determined with a Perkin Elmer CHNS−2400 analyzer (Perkin Elmer, Waltham, MA, USA).

3.3 Cloud point extraction (CPE) system.

3.3.1 Procedure of CPE system.

An aliquot of 1.0 mL of a sample or standard solution containing the analyte (10 mg L^{-1}), surfactant of DC193C (0.5 v/v%) and 1.5 mol L^{-1} of Na_2SO_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 minutes. The separation of the phases was achieved by centrifugation for 2 minutes at 1500 rpm. On cooling in an ice−bath for 5 minutes, the surfactant rich phases became viscous. Then, the surfactant rich phase at the top layer was separated using a syringe to minimize the possibility of cross−contamination of analyte 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 phenolic compound spectrophotometrically at the respective maximum absorption against a reagent blank prepared under similar conditions.

3.4 Cloud point extraction with β−cyclodextrin as a modifier (CPE−βCD) system.

3.4.1 Procedure of CPE−βCD system.

The same procedure as in Section 3.3.1 was applied in the CPE−βCD system but in the presence of β−CD modifier for the phenolic compounds. The modifier of β−CD (10 mg L^{-1}, 100 µL) was added in the CPE−βCD system.

3.5 Cloud point extraction with β−cyclodextrin functionalized with ionic liquids as modifier system (CPE−βCD−IL).

3.5.1 Procedure of CPE−βCD−IL system.

In the CPE−βCD−IL system, the same procedure was applied as the CPE system (Section 3.1.1.). The modifier of βCD−IL (10 mg L^{-1}, 100 µL) was added in the CPE−βCD−IL system.

3.6 Optimization of parameters study.

The classical optimization (one−factor−at−a−time) was carried out by the several parameters which affect the extraction efficiency of the phenolic compounds in the three systems of CPE. In this method, the experimental responses have been observed by this approach. The effect of one factor at time (OFAT) means that only one factor is changed, whereas the others parameters are remained constant. Although, this approach does not ensure at all the real optimum will be conformed, but it would be valid only if the variables to be optimized would be totally independent from each other (i.e. no interactive effects among the variables). Nevertheless, the classical optimization certainly leads at least to an improvement of the analytical method. In as much as the extraction efficiency of the CPE depends on dual factors, some of regarding the prior formation of a complex with sufficient hydrophobicity and the other for the formation of micelles to obtain the desired extraction. Consequently, the effects of pH, concentration of surfactant, modifier, salt and analyte, volume of surfactant and modifier, temperature and incubation time and water content were selected in this study. In the optimization procedure of impact parameters, each data point was obtained from the mean value of triplicate extractions.

3.6.1 Effect of DC193C surfactant concentration.

The effect of DC193C concentration was evaluated in the range 0.1 − 0.8 (v/v %). Then, the mixture solution containing DC193C surfactant, 10 mg L^{-1} of each phenolic compounds and 1.5 mol L^{-1} of Na_2SO_4 was induced by heating the content in a water bath at 50ºC for 15 minutes. The same procedure was carried out for each analyte in both CPE−βCD and CPE−βCD−IL systems but in the presence of 100 µL of β−CD and βCD−IL modifier at 10 mg L^{-1} concentration, respectively.

3.6.2 Effect of DC193C surfactant volume.

Different volumes of DC193C (0.5 v/v %) ranging from 0.1 − 1.0 mL were used in the CPE system at previously optimum condition for the phenolic compounds. The same procedure was carried out for each analyte in the CPE−βCD and CPE−βCD−IL systems but in the presence of 100 µL of β−CD and βCD−IL modifiers at 10 mg L^{-1} concentration, respectively.

3.6.3 Effect of pH.

In the CPE system, to study the effect of pH, 10 mg L^{-1} of each phenolic compound was investigated by varying the initial pH of the solutions from pH 2 to 9 and mixed with 0.5 v/v% of DC193C and 1.5 mol L^{-1} of Na_2SO_4. The phase separation of solutions was induced by heating the content in a water bath at 50ºC for 15 minutes. The pH was adjusted by adding HCl and NaOH. The same procedure was carried out for each analyte in the CPE−βCD and CPE−βCD−IL systems but in the presence of 100 µL of βCD and βCD−IL modifiers at 10 mg L^{-1} concentration, respectively.

3.6.4 Effect of equilibration temperature and incubation time.

The solution containing the analyte (10 mg L^{-1}), surfactant of DC193C (0.5 v/v %), and 1.5 mol L^{-1} of Na_2SO_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 by varying the temperature from 25ºC to 80ºC for 15 min in the CPE system for each phenolic compounds. The same steps were taken in the CPE−βCD and CPE−βCD−IL systems in the presence of 100 µL of βCD and βCD−IL modifiers at 10 mg L^{-1} concentration, respectively.

The effect of incubation time also was investigated in the range 5 to 30 minutes at the previous optimum condition in the different systems for phenolic compounds.

3.6.5 Effect of salt concentration.

In this CPE work, different concentrations of Na_2SO_4 salt, ranging from 0.5 to 2.0 mol L^{-1} were added to the solution that containing 10 mg L^{-1} of each phenolic compounds at pH 7 and 0.5 v/v % of DC193C. Then, the mixture was heated at 50ºC for 15 minutes to induce the phase separation. The same process was carried out in the CPE−βCD and CPE−βCD−IL systems in the presence of 100 µL of β−CD and βCD−IL modifiers at 10 mg L^{-1} concentration, respectively.

3.6.6 Effect of modifier concentration.

The effect of the β−CD and βCD−IL modifier concentration on extraction of phenolic compounds was studied in the concentration range of 2 − 10 mg L^{-1}. The others parameters were kept constant as the previous optimum condition for each phenolic compounds in the CPE−βCD and CPE− βCD−IL systems.

3.6.7 Effect of modifier volume.

The optimum concentration of the β−CD and βCD−IL modifiers was used in the CPE−βCD and CPE−βCD−IL systems, respectively, by different volumes of modifier (β−CD or βCD−IL; 10 mg L^{-1}) ranging from 50 – 500 µL were used in this study at the previous optimum conditions for each phenolic compounds.

3.6.8 Effect of analyte concentration.

Each phenolic compound was studied on the effect of analyte concentration in the range of 2 to 20 mg L^{-1} at pH 7 in the three CPE systems. The other optimized parameters were kept constant.

3.6.9 Water content.

The water content of the surfactant rich phase after the extraction was measured by drying surfactant rich phase at 353 K until no mass was observed in the three CPE systems for the phenolic compounds. 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.

3.7 Isotherm study.

To study the effect of initial concentrations on the phenolic compounds uptake in the three CPE systems, the initial concentrations were varied from 2 to 20 mg L^{-1}.

The initial pH of the solution was adjusted by adding either 1.0 M HCl or 1.0 M NaOH to pH 7 for each analyte in the three CPE systems whereas the other parameters such as the concentration of DC193C surfactant, salt and modifier, equilibration temperature and incubation time were remained constant.

3.8 Thermodynamic study.

The effect of solution temperature on the adsorption process was studied by varying the adsorption temperature at 25, 30, 40, 50, 60, 70 and 80ºC by adjusting the temperature controller of the water bath for each phenolic compounds in the three CPE systems, while other parameters such as concentration of DC193C surfactant, salt, modifier and analyte; incubation time were remained constant while the each analyte solution pH was adjusted to pH 7 by adding either 1.0 M HCl or 1.0 M NaOH.

3.9 Preparation and characterization of inclusion complex.

3.9.1 Inclusion complexes of β−CD, non−ionic surfactant DC193C and 4−NP.

The amount of non−ionic surfactant DC193C, β−CD and 4−NP (pH 7) at room temperature was prepared in equimolar; 1.00 g (β−CD), 0.12 g (4−NP) and 2.73 g (DC193C) were blended together in a mortar with sufficient in ethanol to produce a paste by physical mixing, kneading method. The kneading operation was kept for at least 40 minutes at room temperature. At the end of the reaction, a great deal of milky liquid, inclusion complex of the 4−NP, DC193C and β−CD was obtained. Then, the product was stored in a glass vial in vacuum desiccators. After drying, the milky solution of complex was obtained. ^{1}H NMR and 2D NOESY spectra were recorded on AVN 600 MHz and DMSO−d_6 was used as a solvent.

3.9.2 Inclusion complexes of βCD−IL, non−ionic surfactant DC193C and 4−NP.

The inclusion complexes of βCD−IL−DC193C−NP were prepared in equimolar; 1.00 g (βCD−IL), 0.10 g (4−NP, pH 7) and 2.73 g (DC193C) at room temperature. These substances were blended together and next procedure applied was similar to the procedure in Section 3.9.1.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Optimization of parameters in the three CPE systems for the phenolic compounds.

The main variables affecting the extraction process, such as pH, concentration of DC193C surfactant, modifier, salt and analyte, equilibration temperature and time, volume of DC193C surfactant and modifier and water content were optimized. All the data given in this study were the average of triple measurement. The extraction efficiency of the phenolic compounds by DC193C surfactant from sample was calculated using an equation as shown in Eq. (1) (Chadha *et al*., 2011);

$$\text{Extraction efficiency (\%)} = \frac{C_sV_s}{C_oV_o} \times 100 \qquad (1)$$

$$= \frac{C_oV_o - C_wV_w}{C_oV_o} \times 100$$

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

4.1.1 Effect of DC193C surfactant concentration.

It is desirable to use a minimum amount of DC193C surfactant for a maximum extraction of the phenolic compounds. A successful of the CPE should be maximized the extraction efficiency by minimizing the phase volume ratio (V_s/V_o). The amount of DC193C surfactant not only affected the extraction efficiency, but also the volume of the surfactant rich phase. The effect of DC193C surfactant concentration on extraction efficiency in the three CPE systems was evaluated in the range 0.1 − 0.8 (v/v %) for the phenolic compounds.

As shown in Figure 4.1, the similar trend was observed for the phenolic compounds in the three CPE systems. These results indicated that the optimum extraction efficiency was obtained for the concentration of DC193C surfactant starting from 0.5 (v/v %) and remained constant up to 0.8 (v/v %) for the phenolic compounds in the three CPE systems. The extraction efficiency and the volume of the surfactant rich phase (V_s) increased on the increasing of DC193C surfactant concentration up to 0.5 (v/v %) and remained constant up to 0.8 (v/v %).

An increase in the surfactant concentration also increases the volume of the surfactant rich phase in order to maintain the material balance, as the concentration surfactant in the dilute phase remains almost constant. Therefore, by increasing of DC193C surfactant concentration, the number of hydrophobic micelles increased and caused responsive increase of extractability of DC193C surfactant (Purkait *et al.*, 2004). The extract was therefore more diluted when higher amount of surfactant were used, resulting in loss of sensitivity with the increase of DC193C surfactant concentration above 0.5 (v/v %) due to the increased viscosity of the surfactant rich phase (Ghaedi *et al.*, 2009). An excessive amount of DC193C surfactant increases the viscosity of the surfactant rich phase which lowers the diffusivity of the phenolic compounds and the extraction rate through the highly viscous phase (Balasubramanian and Venkatesan, 2012).

At concentration below this value (0.5 v/v %), the extraction efficiency of the phenolic compounds was low because there are few molecules of surfactant entrapping the phenolic compounds quantitatively. The same phenomena were observed in the addition of β−CD and βCD−IL modifiers. To fulfill the "environmentally benign" extraction, a low concentration of DC193C, 0.5 (v/v %), was selected for use in the three CPE systems in this work.

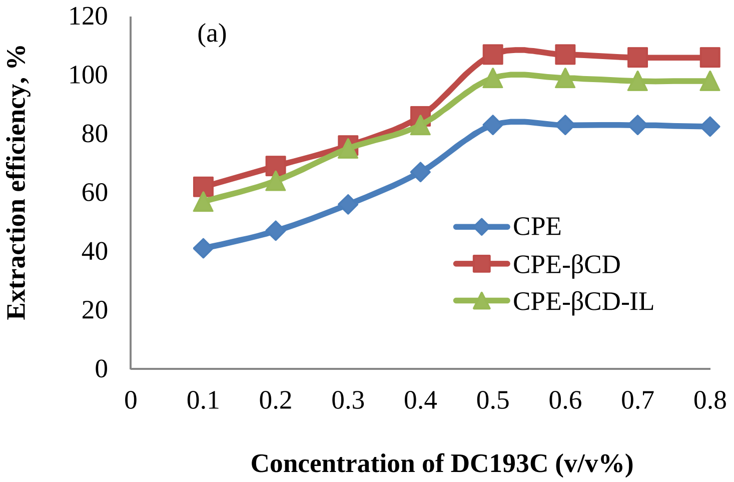
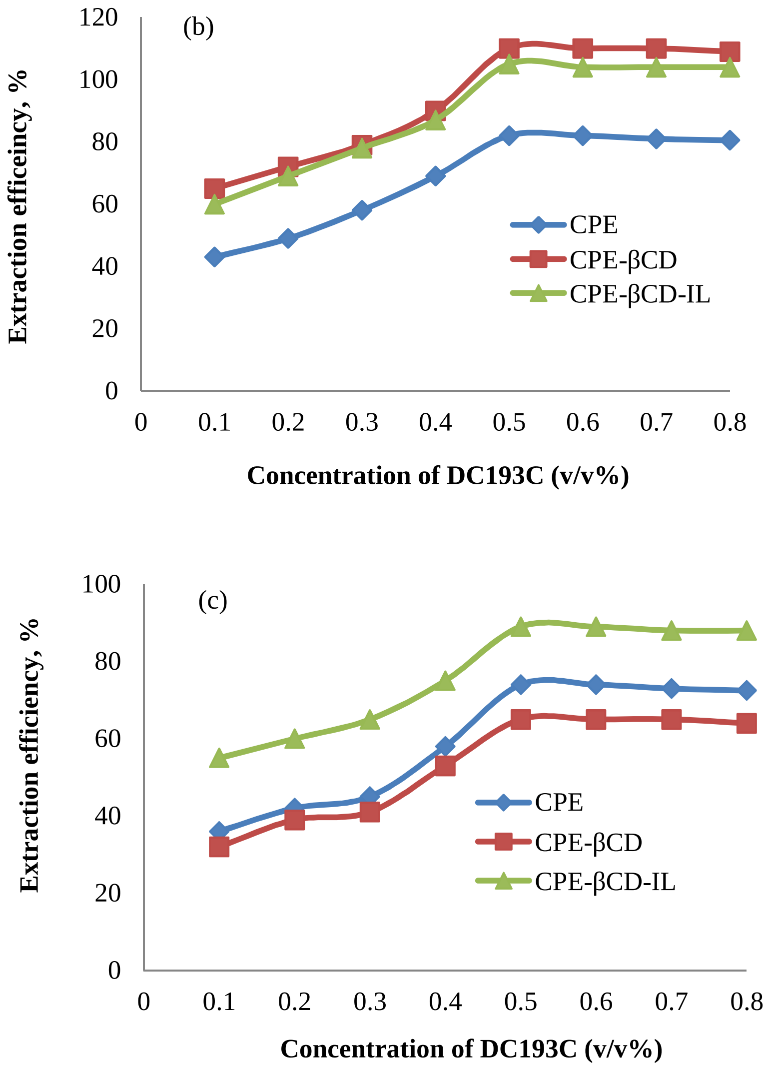


Figure 4.1: Effect of DC193C surfactant concentration on extraction efficiency in the three CPE systems for the phenolic compounds (a) 2,4−DCP; (b) 2,4,6−TCP; (c) 4−NP. Condition: 10.0 mg L^{-1} of analyte concentration, pH 7.0, 10.0 mg L^{-1} of modifier (β−CD; βCD−IL), 1.5 mol L^{-1} of Na_2SO_4 at 50ºC.

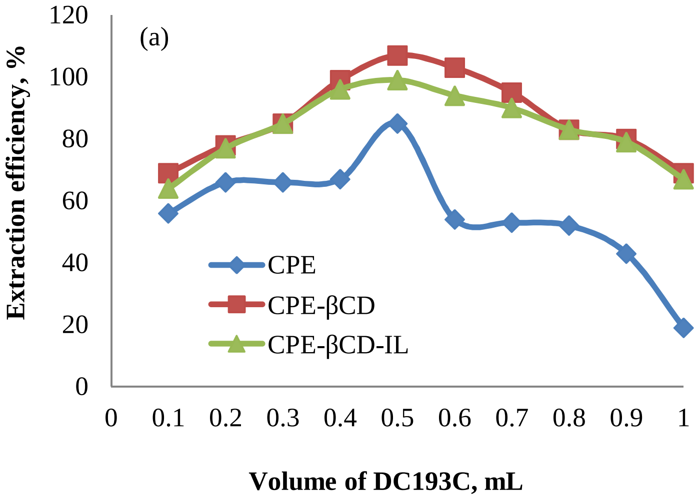


‘**Figure 4.1**, continued’.

4.1.2 Effect of DC193C surfactant volume.

Figure 4.2 depicts the effect of the variation DC193C surfactant volume on the percentage extractions of the phenolic compounds in the three CPE systems. Different volumes of DC193C surfactant (0.5 v/v %) ranging from 0.1 to 1.0 mL were used in this study. As shown in Figure 4.2 (a) and (b), the same trend was observed for 2,4−DCP and 2,4,6−TCP on the percentage of extraction in the three CPE systems. The percentage of extractions in the three CPE systems increased by increasing the volume of DC193C surfactant up to 0.5 mL and suddenly decreased at higher amounts than 0.5

mL. 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. Meanwhile, as shown in Figure 4.2 (c), the same trend was also observed but there was no significant effect in the CPE−βCD system by increasing the volume of DC193C compared to both CPE and CPE−βCD−IL systems. The results indicate that the native of β−CD modifier did not really affect the extraction performance of 4−NP compared to the functionalized of β−CD. Therefore, 0.5 mL of 0.5 v/v % DC193C surfactant was used as the optimum amount in the three CPE systems for the phenolic compounds in this work.



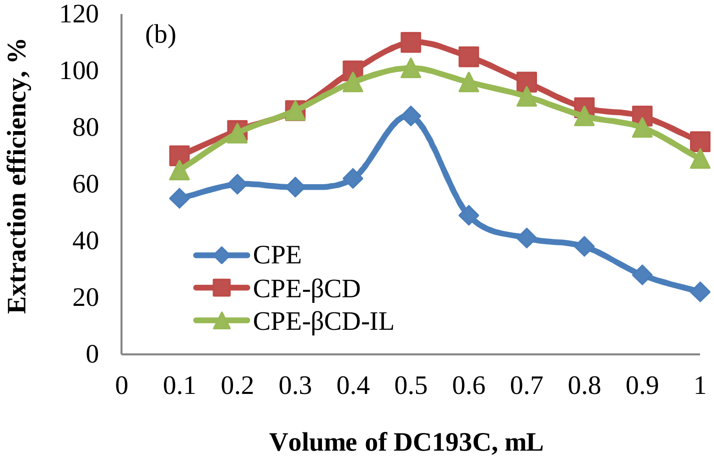
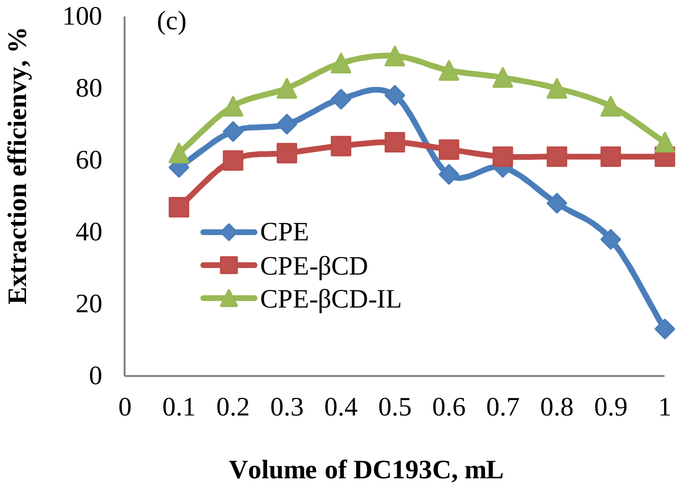


Figure 4.2: Effect of DC193C volume on extraction efficiency in the three CPE systems for the phenolic compounds (a) 2,4−DCP; (b) 2,4,6−TCP; (c) 4−NP. Condition: 10.0 mg L^{-1} of analyte concentration, pH 7.0, 0.5 (v/v %) DC193C, 10.0 mg L^{-1} of modifier (β−CD; βCD−IL), 1.5 mol L^{-1} of Na_2SO_4 at 50ºC.



‘**Figure 4.2**, continued’.

4.1.3 Effect of pH.

In the CPE system, pH plays an important role in the extraction of organic compounds in environmental water samples because the pH value of the solution determines the existing state of analyte. This behavior can be related to the charged characteristics of the phenolic compounds which determine the extraction efficiency of the analyte of interest. In this work, the effect of pH on extraction performance of phenolic compounds in the three CPE systems within the range 2 to 9 was investigated and the results were shown in Figure 4.3. This figure illustrates the dependence of extraction efficiency against pH in the three CPE systems for 2,4−DCP (pK_a 7.7), 2,4,6−TCP (pK_a 7.4) and 4−NP (pK_a 7.2). The acidity of sample solution can also influence the extraction efficiency of weak organic base or acid. The sample solution was often adjusted to appropriate acidity to de−ionize analytes for obtaining higher extraction efficiency (Peng *et al*., 2007).

Our results indicate that the maximum extraction of the three CPE systems were achieved at pH 7 for all phenolic compounds, where the uncharged form of target analyte prevails (Mashhadizadeh and Jafari, 2010). In the CPE system, all the phenolic compounds were protonated at lower pH (less than pKa value) and their ionic characteristics increased, leading to less solubilization of the phenolic compounds in the hydrophobic micelles due to the interaction of the protons with polyethylene oxide. At pH > 7 (above pKa value), the extraction efficiency of the phenolic compounds decreases, and this may be because of the formation of phenolate ion, which leaded to the disappearance of hydrogen bond (Zhou *et al*., 2014). The molecular forms of the phenolic compounds at different pH were shown in Table 4.1. 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.

Similar trend were observed in the CPE−βCD and CPE−βCD−IL systems. In the CPE−βCD system, all the phenolic compounds showed a decline at below pH 5 (protonated) and above pH 7 (deprotonated) as shown in Table 4.1. Some research findings have proved that the phenolic compounds could form inclusion complex with β−CD modifier. It was established that the hydrophilic guest molecules (protonated or deprotonated) were unfavorable to complex with β−CD. Thus, neutral forms of the phenolic compounds were favorable to form inclusion complex (Abdel Salam and Burk, 2008; Li *et al*., 2010; N. Li *et al*., 2012). Meanwhile, in the CPE−βCD−IL system, the extraction of phenolic compounds was low at below pH 5 due to electrostatic repulsion between imidazolium ring of IL and protonated of phenolic compounds (Pan *et al*., 2011). However, the low extraction at high pH (pH > 7) was due to the presence of high concentration of hydroxyl group competing with the negative phenolate ions on the positive charge of imidazole ring of IL (Wang *et al*., 2013). As reported by Barraza *et al*. (2004), the analytes of the phenolic compounds is found completely in the neutral form at pH 5, whereas, most of the phenolic compounds have been transformed to its phenoxide ion at pH 8.

The sorption mechanism was probably simultaneously dominated by hydrogen bonding, $\pi - \pi$ interaction, electrostatic attraction between phenolic compounds and imidazolium ring of IL and inclusion complex as discussed in Section 4.2. Therefore, pH 7 was chosen for the subsequent analysis for all the phenolic compounds in the three CPE systems.

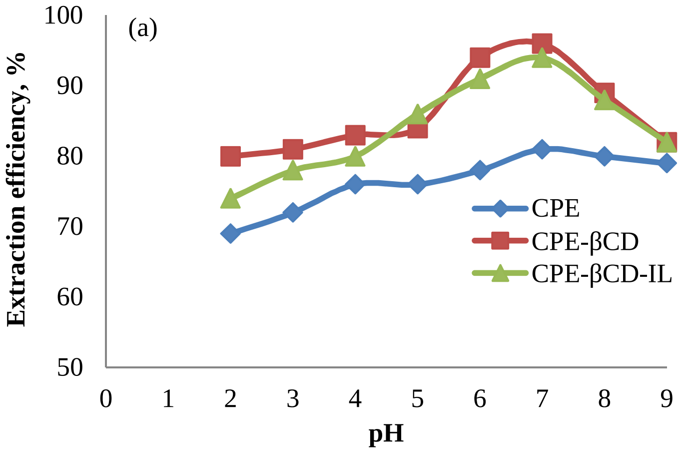
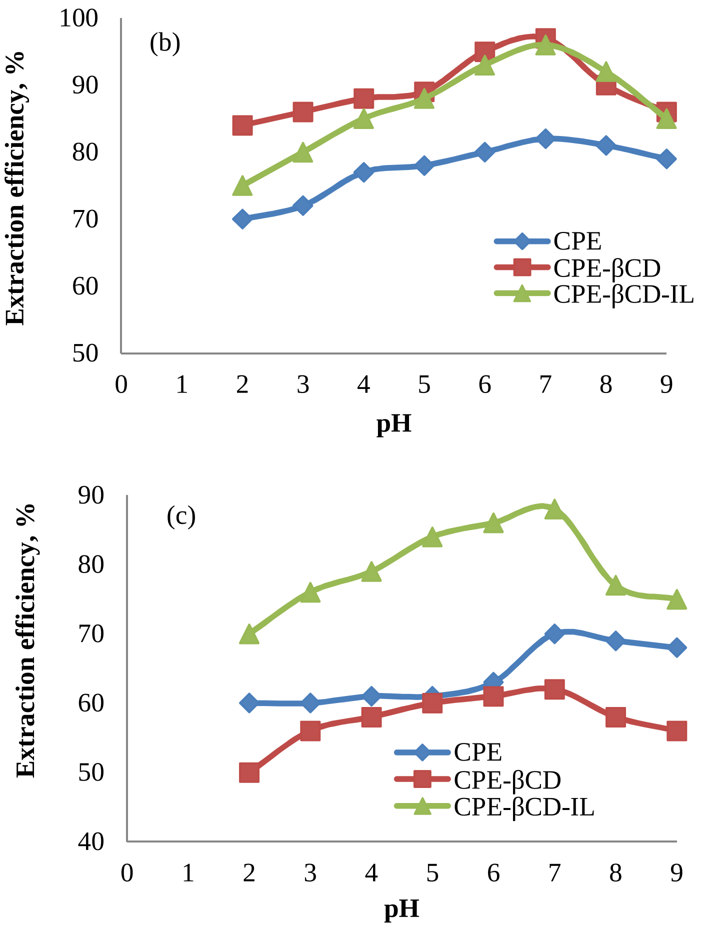
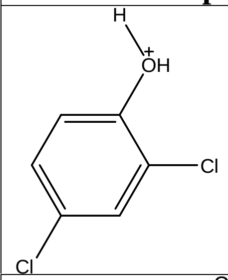
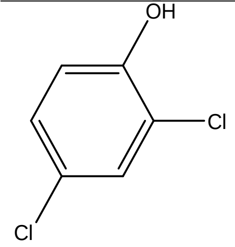
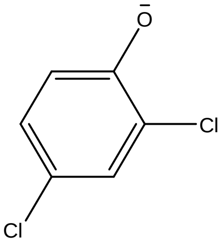
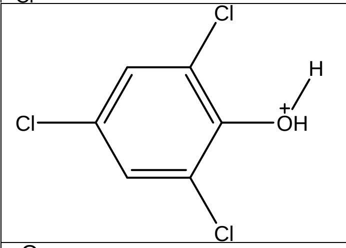
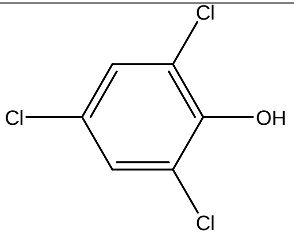
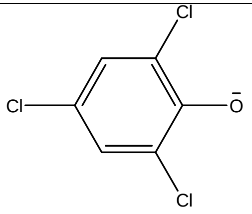
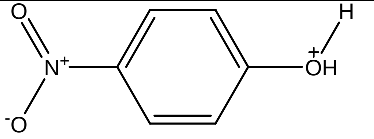
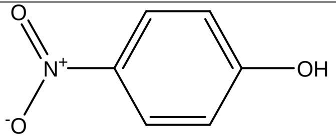
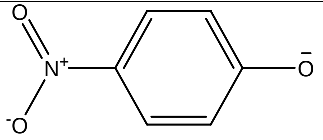


Figure 4.3: Effect of pH on extraction efficiency in the three CPE systems for the phenolic compounds (a) 2,4−DCP; (b) 2,4,6−TCP; (c) 4−NP. Condition: 10.0 mg L^{-1} of analyte concentration, 0.5 (v/v %) DC193C, 10.0 mg L^{-1} of modifier (β−CD; βCD−IL), 1.5 mol L^{-1} of Na_2SO_4 at 50ºC.



‘Figure 4.3, continued’.

Table 4.1: The molecular structure of the phenolic compounds at different pH.

Analyte	**pH**		
	5 < pH	**5 ≤ pH ≤ 7**	**pH > 7**
2,4−DCP			
2,4,6−TCP			
4−NP			

4.1.4 Effect of equilibrium temperature and time.

Temperature is the key factor and the driving force to make modifier and surfactant disperse into the sample solution. It is desirable to have the lowest possible equilibration temperature and the shortest incubation time, which compromise completion of the reaction and efficient separation of phase. The lowest possible equilibration temperature should be used to avoid unstable and decomposition of the compound at elevated temperature (Giokas *et al*., 2012). In the CPE process, the cloud point can be altered with increasing length of the hydrocarbon and sometimes dramatically, in the presence of acids or bases, salts and organic additives (Quina and Hinze, 1999). A series of experiments were designed from 25ºC to 80ºC for the optimization of temperature in the three CPE systems for the phenolic compounds.

The results were exhibited in Figure 4.4, the extraction efficiency increase when the temperature increases from 25ºC to 50ºC and almost constant up to 80ºC in the CPE system for all phenolic compounds. The temperature affects the interaction of analyte and surfactant in the both phases, decreasing the hydration of solutes i.e., the phenolic compounds and DC193C surfactant in the aqueous phase and surfactant rich phase. Due to that, depending upon experimental conditions, an increase in temperature can cause an increase or a decrease in the extraction of the phenolic compounds (Tatara *et al*., 2005). It is well known that, the critical micelle concentration (CMC) decreases at higher temperature. Above CMC, surfactant monomers accumulate to form micelles. Moreover, non−ionic DC193C surfactant becomes relatively more hydrophobic at higher temperature because of an equilibrium shift that favors dehydration of the ether oxygens (Purkait *et al*., 2006a).

Meanwhile, in CPE system with both modifiers, the extraction efficiency was found to gradually increase when the temperature increases from 25ºC to 40ºC and almost constant up to 70ºC. The extraction of the phenolic compounds decreased at above 70ºC. As shown in Figure 4.4, CPE−βCD and CPE−βCD−IL systems have higher percentage of extraction to CPE system without modifier between the range of 40ºC to 70ºC due to stability of complex between the phenolic compounds with β−CD or βCD−IL modifiers. However, above 70ºC, the decomposition of the complex occurs, thus, decreasing the extraction of the phenolic compounds. At below 40ºC, the extraction of the phenolic compounds was lower due to the performance of dispersing of β−CD and/or βCD−IL modifier was poor (Zhou *et al*., 2011).

As reported by Zhou *et al*., (2011), the rise temperature has bi−functions. One of the functions is the rise of temperature has enhanced the transferring rate of the phenolic compounds and β−CD and/or βCD−IL modifier into the surfactant rich phase. Another function is it also enhances the migrating rate of the phenolic compounds out from β−CD and/or βCD−IL's cavity as temperature reached 70ºC and above (Zhou *et al*., 2011). The fact that temperature gives more than one effect upon cyclodextrin complexes shows how important it is in the CPE system with β−CD and/or βCD−IL modifier. This can be supported by Del Valle (2004), heating can increase the solubility of the complex but it also destabilizes the complex. These effects often need to be balanced. The thermal stability of β−CD inclusion complexes varies with the different guest molecule; especially if the guest is strongly bound or the complex is highly insoluble (Del Valle, 2004; Ratnasooriya and Rupasinghe, 2012).

By adding of the modifier and salt into CPE process, the cloud point of DC193C surfactant can be altered to room temperature where the two phases can be formed even at room temperature. Therefore, equilibrium temperature at 50ºC was selected as an operating temperature in this study for the three CPE systems for all phenolic compounds.

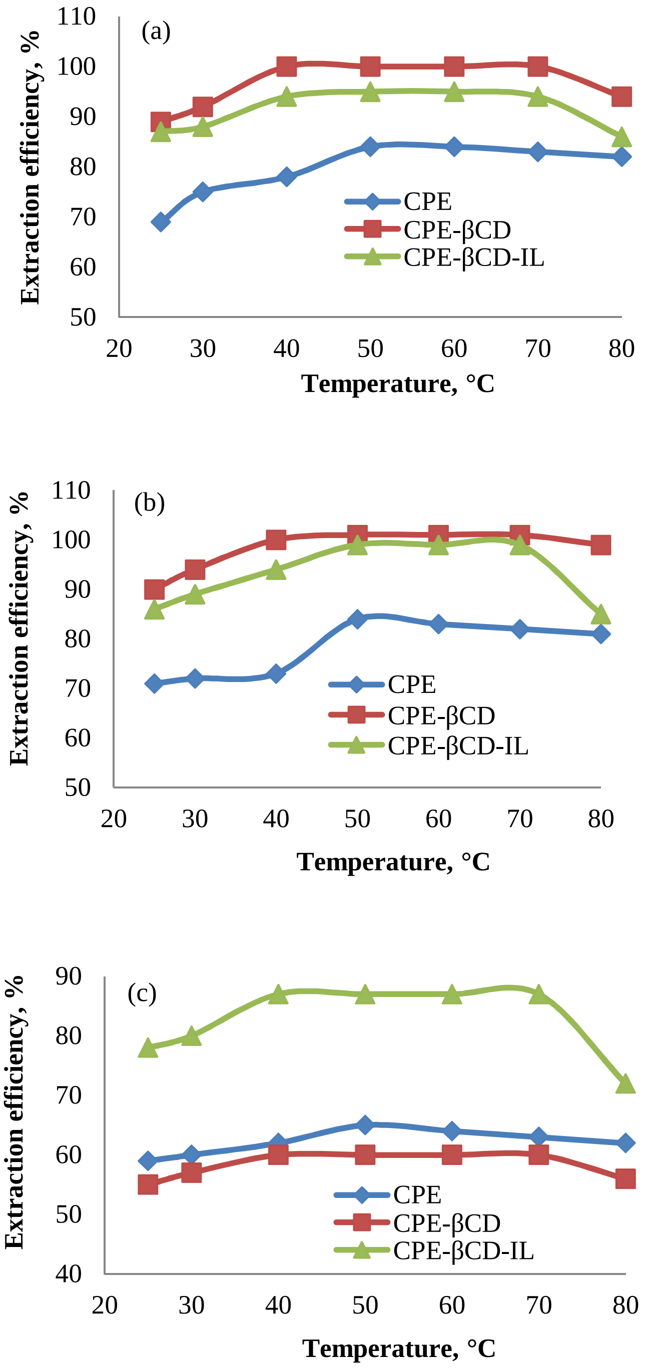


Figure 4.4: Effect of temperature on the extraction efficiency in the three CPE systems for the phenolic compounds (a) 2,4−DCP; (b) 2,4,6−TCP; (c) 4−NP. Condition: 10.0 mg L^{-1} of analyte concentration, pH 7.0, 0.5 (v/v %) DC193C, 10.0 mg L^{-1} of modifier (β−CD; βCD−IL), 1.5 mol L^{-1} of Na_2SO_4.

The dependence of extraction efficiency upon incubation time was also studied in the range 5 to 30 minutes at 50ºC. Figure 4.5 displays that the incubation time of 15 minutes was sufficient to complete the quantitative extraction of the phenolic compounds in the three CPE systems. The extraction efficiency declined for the phenolic compounds in the three systems as the incubation time exceeded 15 minutes, which was probably due to the stability of the phenolic compounds, DC193C surfactant and complex decreasing (Wen *et al.*, 2013). Hence, 15 minutes at 50ºC was chosen as an incubation time for the phenolic compounds in the three CPE systems.

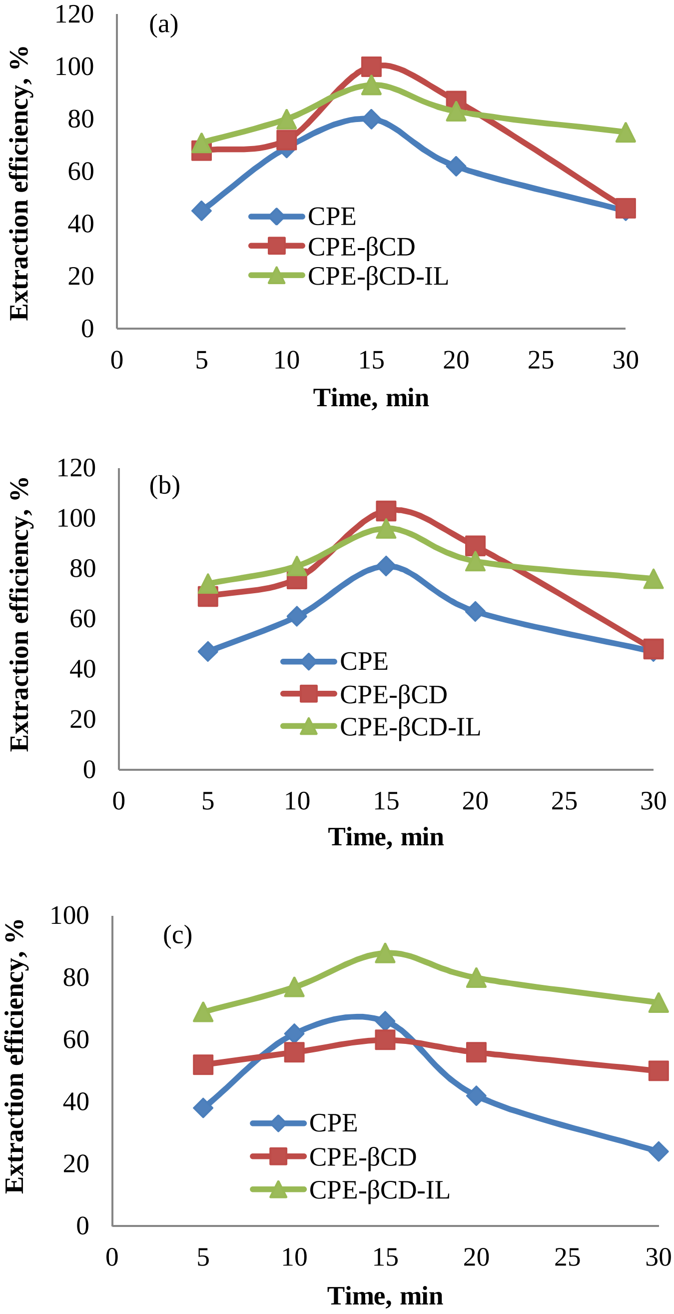


Figure 4.5: Effect of incubation time on the extraction efficiency in the three CPE systems for the phenolic compounds (a) 2,4−DCP; (b) 2,4,6−TCP; (c) 4−NP. Condition: 10.0 mg L^{-1} of analyte concentration, pH 7.0, 0.5 (v/v %) DC193C, 10.0 mg L^{-1} of modifier (β−CD; βCD−IL), 1.5 mol L^{-1} of Na_2SO_4 at 50ºC.

4.1.5 Effect of salt concentration.

In most sample pretreatment techniques, the addition of salt often increases the extraction performance due to the salting out effect. Previous works proved that the addition of salt can improve the extraction efficiency in the CPE (Wang *et al.*, 2007; Wei *et al.*, 2008). This is because salt acts as "drying agent", causing partial dehydration which occurs by the breaking the hydrogen bonds with water molecules for both surfactant and phenolic compounds. Furthermore, the addition of salt induces the phase separation in the CPE by heating the mixture containing the surfactant up to a temperature above the cloud point. The salting−out effect of salt was adopted as an alternative to induce phase separation in the aqueous solutions of DC193C surfactant.

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 PEGs chain by cation and increasing water molecule self−association by anions. However, the CPE systems had different behavior against the type of salt. Na_2SO_4 can form the two−phase system when the concentration of the salt is in the range of 0.5 − 2.0 mol L^{-1}. However, the other salts cannot form the two−phase system ≤ 2.0 mol 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-}, have stronger interactions with water molecule than water itself. Therefore, the ions are capable of breaking water−water hydrogen bonds and beneficial to the phase separation formation.

However, the chaotropic ions, e.g. Cl^-, K^+, 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 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^+ (Ferreira and Teixeira, 2010). In general sulphate ion (SO_4^{2-}); 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 interaction between PEO and sulphate ion in water can be explained as follows: The water surrounding the sulphate 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 sulphate ion approaches the PEO, the amount of the intervening water decreases, leading to a repulsive force between the sulphate 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 (Kadam *et al.*, 2010). Therefore, Na_2SO_4 has been chosen due to its ability to form the two phases of separation.

The effect of salting out in the three CPE systems was investigated over a sodium sulphate concentration in range of 0.5 to the 2.0 mol L^{-1} for the phenolic compounds. The experimental results were demonstrated in Figure 4.6. As can be seen, the extraction efficiency of the CPE system for the phenolic compounds increases with increasing in Na_2SO_4 concentration from 0.5 to 1.5 mol L^{-1} and almost constant above 1.5 mol L^{-1} due to the concentration of the salt becomes saturated, causing no changes on the extraction efficiency, compared to the concentration of salt at 1.5 mol L^{-1}. Meanwhile, in the CPE−βCD system, the extraction efficiency of phenolic compounds increases from 0.5 to 1.5 mol L^{-1} and then, slightly decrease above this range concentration of Na_2SO_4 up to the 2.0 mol L^{-1}. However, different trend was observed in the CPE−βCD−IL system, where, the extraction efficiency of phenolic compounds increases and was started to become constant from the 0.5 mol L^{-1} until 2.0 mol L^{-1} concentration of the Na_2SO_4.

Based on these observations, the concentration of Na_2SO_4 at 1.0 mol L^{-1} already shows a good enough to obtain satisfactory result for the extraction of phenolic compounds in the CPE−βCD and the CPE−βCD−IL systems. This is because of the phase separation was induced faster at equilibrium condition in the presence of modifier compared to the CPE system without modifier. The β−CD modifier also plays a role in terms of its ability to act as water structure maker (kosmotroph) as well as functionalized β−CD modifier. Kosmotrophs decrease the CMC by removing water molecules surrounding the micelles, hence increasing the hydrophobic interactions which affect the CPT by two ways: (a) decrease of hydration, and (b) making easy approach of micelles to each other, leading the formation of larger micelles (Rub *et al*., 2012).

In the presence of ILs, Parmar *et al*. (2012) reported that ILs is hydrophobic and relatively less soluble in water. They contributed this to the fact that βCD−IL modifier may align itself along with DC193C within the micelles through hydrophobic interactions. The micelle size of DC193C increases as the electrostatic repulsion between PEO groups of DC193C is increased due to the permeation of imidazolium cation and forms bigger aggregates. This may cause expulsion of water from the micelles causing contraction of size. The presence of βCD−IL modifier within the micelles results in enhanced dipolarity with significantly altering CPT, micelle size and aggregation number. This may turn out to be useful in faster induced phase separation (Parmar *et al*., 2012). In addition, the experiment results showed that, with increasing concentration of Na_2SO_4 (0.5 − 1.5 mol L^{-1}), the extraction efficiency increase due to more DC193C surfactant and modifier were enriched in the surfactant rich phase. This approach was compatible with the UV−visible detection even by adding salts under saturated conditions to the surfactant solution (Mahugo *et al*., 2009).

Therefore, 1.5 mol L^{-1} Na_2SO_4 was selected as an optimum concentration of the salt in the three CPE systems for the phenolic compounds. It is a fact that the addition of Na_2SO_4 electrolyte increased the size of the micelle and aggregation number, thus, enhancing the phenolic compounds to be more solubilize in the surfactant rich phase. Consequently, more water goes to the dilute phase due to the salting−out effect. The addition of sulphate 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 (El-Shahawi *et al*., 2013). It has been mentioned that adding too much Na_2SO_4 is not always favorable. The addition of excessive Na_2SO_4 to the micellar solution will lead to the very low cloud point temperature (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 Na_2SO_4 will contribute to the occurrence of the dehydration process, resulting less water content in the surfactant rich phase (Ulusoy *et al*., 2012).

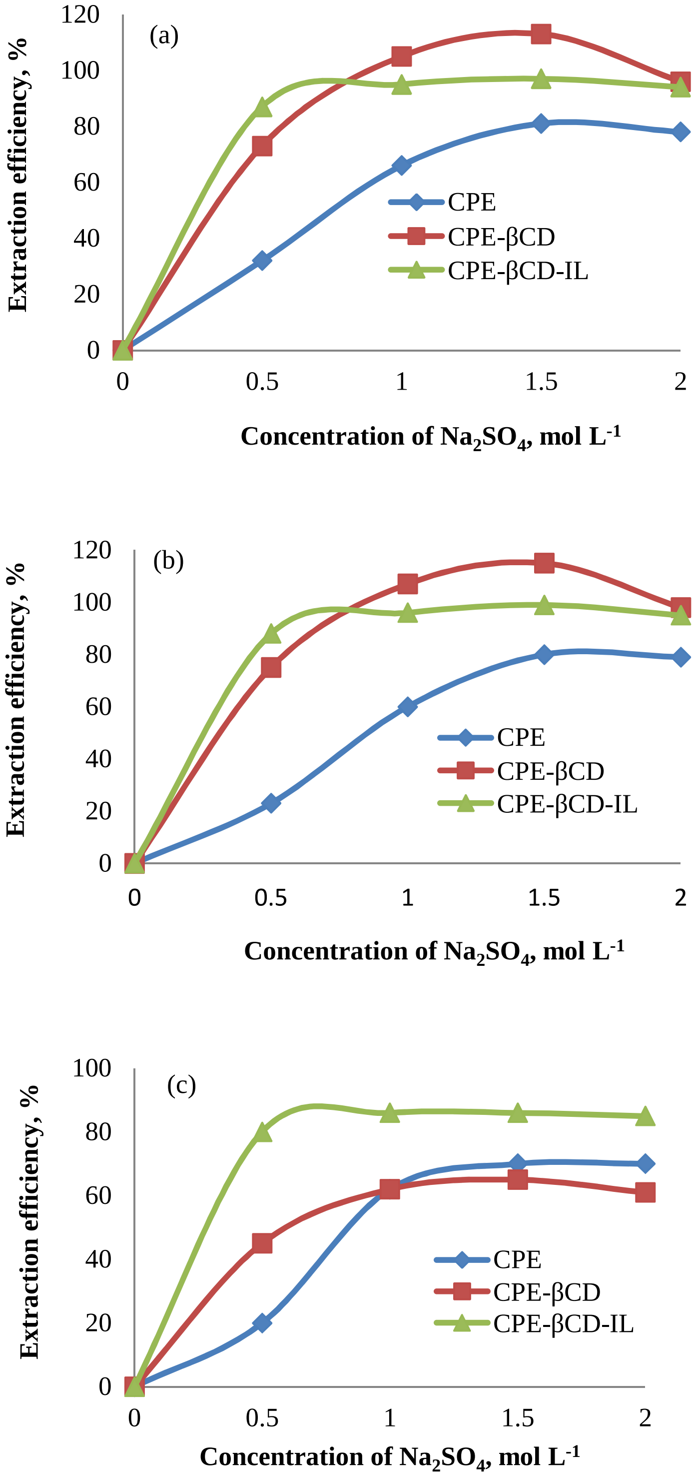


Figure 4.6: Effect of salt concentration on extraction efficiency in the three CPE systems for the phenolic compounds (a) 2,4−DCP; (b) 2,4,6−TCP; (c) 4−NP. Condition: 10.0 mg L^{-1} of analyte concentration, pH 7.0, 0.5 (v/v %) DC193C, 10.0 mg L^{-1} of modifier (β−CD; βCD−IL) at 50°C.

4.1.6 Effect of modifier concentration.

In this study, β−CD and βCD−IL have been used as a modifier to enhance the extraction efficiency of the phenolic compounds. The concentrations of both modifiers have been investigated in the range of 2.0 to 10.0 mg L^{-1} for the phenolic compounds. It was shown obviously that the extraction efficiency gradually increases with the increase of the both modifiers concentration in the both systems for the three phenolic compounds as shown in Figure 4.7. This studied has been further investigated for the concentration of modifier above 10 mg L^{-1} since the extraction efficiency increased with the increases of concentration modifier in both systems for the phenolic compounds. Nevertheless, the volume of surfactant rich phase obtained was too small for the modifier concentration above 10 mg L^{-1}. Hence, this study was carried within the concentration of 10 mg L^{-1} for both modifiers. Therefore, 10 mg L^{-1} was selected as the modifiers concentration for further experiment in this study.

The βCD−IL modifier shows that there was no significant effect compared to the native β−CD modifier for the 2,4−DCP and 2,4,6−TCP. However, the βCD−IL modifier shows obviously increment in the extraction efficiency of 4−NP. These results indicates that the βCD−IL modifier improve the extraction performance of the hydrophilic species of 4−NP. On contrary, β−CD modifier already sufficient to enhance the extraction of the hydrophobic species of 2,4−DCP and 2,4,6−TCP. These findings show that the influence of IL functionalized to β−CD which can improve the extraction performance for the hydrophilic of 4−NP.

The binding of the phenolic compounds within the hydrophobic host of β−CD is not fixed or permanent but rather is a dynamic equilibrium. Besides that, the binding strength depends on how well the ‘host−guest’ complex fits together and on specific local interactions between surface atoms (Singh *et al*., 2002). Based on these properties, the hydrophobic species of 2,4−DCP and 2,4,6−TCP are favorable to form inclusion complex with β−CD than hydrophilic species of 4−NP. As amply exemplified in the literature, the most probable binding mode of the native β−CD with various guest involves the insertion of the less hydrophilic part of the guest molecule into the β−CD's cavity, while the more hydrophilic species, often charged, group stays just outside the primary or secondary rim of the cavity. To force the charged group of the hydrophilic 4−NP to contribute appreciably to the overall complexation thermodynamics, it is a need to introduce an oppositely charged group into the β−CD. This is expected to enhance the binding through the attractive "long range" coulombic interaction. In fact, it has been reported that cationic mono−CD exhibit higher or lower affinities toward negatively or positively charged guests such as 4−NP than the corresponding of the native β−CD (Rekharsky and Inoue, 2002).

Therefore, by functionalized the native of β−CD with ionic liquids, the 'host−guest' complex with the hydrophilic 4−NP can be improved due to the interaction between imidazolium ring of ionic liquid and aromatic rings of 4−NP via electrostatic attraction and $\pi - \pi$ interaction. It is proposed that electron−withdrawing groups enhance the $\pi - \pi$ interactions by reducing the electron density of π electrons, diminishing the repulsive electrostatic interactions between the aromatic rings. As both nitro and chloro are electron−withdrawing groups, the $\pi - \pi$ interactions are enhanced with the increase in the number of these groups. However, the nitro group has stronger electron− withdrawing ability than the chloro group, hence the $\pi - \pi$ interactions are stronger for 4−NP than 2,4−DCP and 2,4,6−TCP (Tan *et al.*, 2009). These interactions have been supported by the results obtained in Section 4.2.

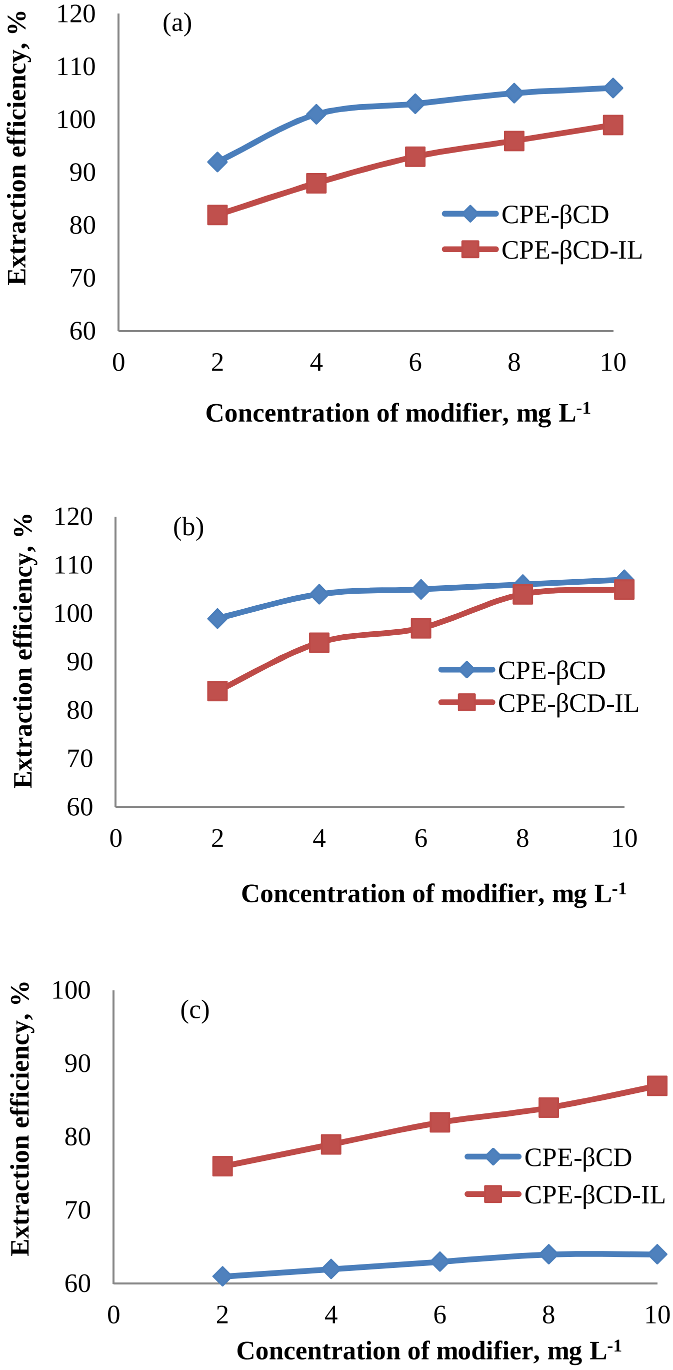


Figure 4.7: Effect of modifiers concentration on extraction efficiency in the three CPE systems for the phenolic compounds (a) 2,4−DCP; (b) 2,4,6−TCP; (c) 4−NP. Condition: 10.0 mg L^{-1} of analyte concentration, pH 7.0, 0.5 (v/v %) DC193C, 1.5 mol L^{-1} of Na_2SO_4 at 50ºC.

4.1.7 Effect of modifier volume.

The effect of volume modifier was a crucial parameter, which would have an important effect on the extraction performance. Large volume of modifier may lead longer time to dissolve modifier completely and mixed entirely. Figure 4.8 shows the volume of β−CD and βCD−IL modifier was examined within the range of 50 to 500 µL in the CPE−βCD and CPE−βCD−IL systems, respectively, for the phenolic compounds. The extraction efficiency of the phenolic compounds increases from 50 µL up to 100 µL, but suddenly decreases above the 100 µL for both modifiers in the three CPE systems for the phenolic compounds.

In the CPE−βCD system, the hydrophobic 2,4−DCP and 2,4,6−TCP interact with β−CD modifier to form inclusion complex. Hence, enhance the solubilization of 2,4−DCP and 2,4,6−TCP into the surfactant rich phase due to inclusion complexes occurred between solutes, surfactant and modifier. For hydrophilic 4−NP, the inclusion complex was unfavorable. By increasing β−CD modifier, the extraction of the phenolic compounds decreases. There was no two−phase when the volume exceeds 400 µL in the CPE−βCD system for the three phenolic compounds due to increasing the volume of β−CD modifier. In fact, β−CD contain water molecules in its cavity and exclude the water molecules once inclusion complex occur. The aqueous phases become too large while the surfactant rich phases become too small due to the increase of volume β−CD modifier that contributes to the aqueous phase volume due to its polarity. The host cyclodextrin molecules generally possessed a greater inclusion affinity for more hydrophobic guest molecules.

In the CPE−βCD−IL system, fine modifier of the βCD−IL droplets increased along with the increase of the volume and then more target analytes were transferred into the surfactant rich phase that contain of the βCD−IL modifier, but larger volume led to the increase of sediment phase volume, which resulted in low extraction efficiency for the phenolic compounds. However, in this system, the extraction of hydrophilic 4−NP enhanced compared to β−CD modifier due to the interaction between the ionic liquid and 4−NP. However, for the hydrophobic 2,4−DCP and 2,4,6−TCP, the βCD−IL modifier did not affect the extraction. This interaction between the βCD−IL modifiers with hydrophobic analyte has been discussed in detail in previous Section 4.1.6. Thus, 100 µL was selected as an optimum volume for both β−CD and βCD−IL to be added as a modifier in the CPE system for the phenolic compounds.

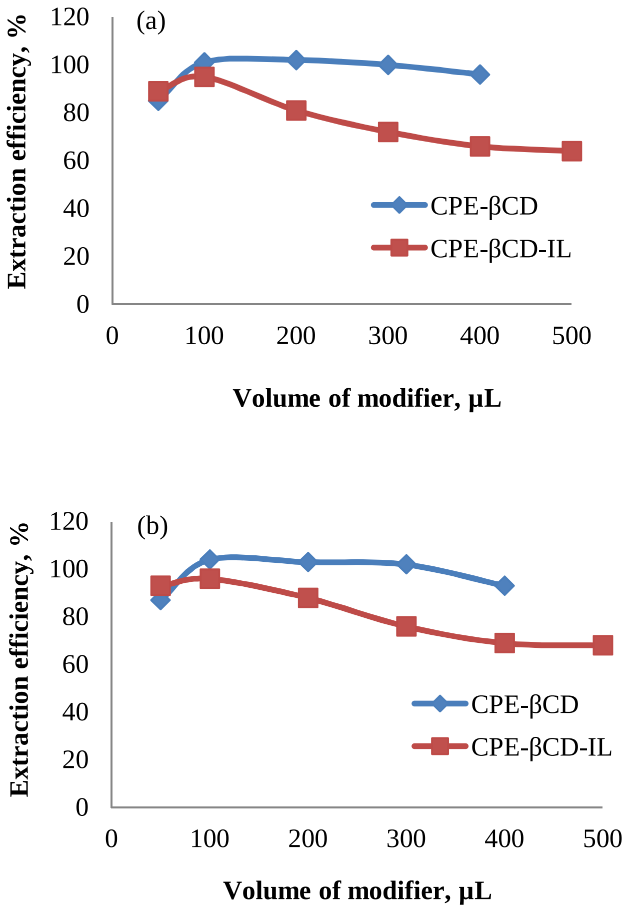
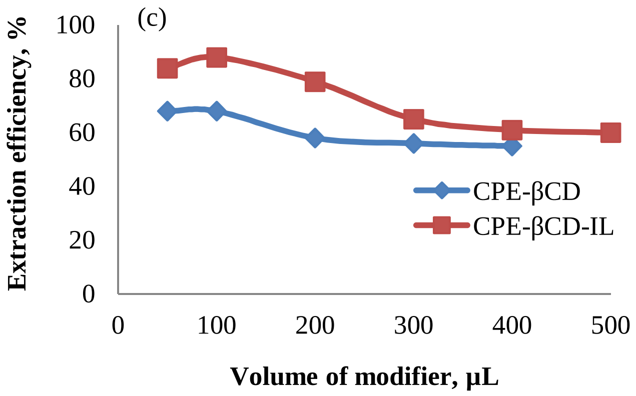


Figure 4.8: Effect of modifier volume on extraction efficiency in the three CPE systems for the phenolic compounds (a) 2,4−DCP; (b) 2,4,6−TCP; (c) 4−NP. Condition: 10.0 mg L^{-1} of analyte concentration, pH 7.0, 0.5 (v/v %) DC193C, 10.0 mg L^{-1} of modifier (β−CD; βCD−IL), 1.5 mol L^{-1} of Na_2SO_4 at 50°C.



‘**Figure 4.8**, continued’.

4.1.8 Effect of analyte concentration.

The influence of various initial concentrations of the phenolic compounds on extraction was investigated in the three CPE systems (Figure 4.9). The quantity of DC193C surfactant and both modifiers were kept constant while the concentrations of the phenolic compounds were varied between 2.0 and 20.0 mg L^{-1} in the three CPE systems. The initial concentration provides an important driving force between both solute molecule on the surfactant and bulk phase, in order to overcome all mass transfer resistance of the phenolic compounds. The results showed that the extraction efficiency decreases with the increment in concentration of the phenolic compounds and becomes constant from 16 mg L^{-1} to 20 mg L^{-1} in the three CPE systems for the phenolic compounds. This phenomenon was due to the a large number of vacant surface sites were available at lowest and moderate concentration of solute, and at a certain level of solute concentration, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the surfactant and bulk phase (Tan *et al*., 2009).

As shown in Figure 4.9 (a) and (b), the extraction of 2.4−DCP and 2,4,6−TCP were obtained more than 80 % in the range of 2 to 20 mg L^{-1} in the CPE−βCD and

CPE−βCD−IL systems. Meanwhile for 4−NP, the extraction of 4−NP was obtained more than 80 % at 2 to 10 mg L^{-1} in the CPE−βCD−IL system. However, about 60 to 77 % of extraction efficiency was achieved for the CPE−βCD systems in that range of concentration for 4−NP. The concentration of surfactant in the both aqueous and rich surfactant phase remains constant at a constant operating temperature (50ºC). Hence, the phenolic compounds solubilization capacity of the surfactant micelles remains almost invariant in the both phases. Therefore, with further increase in the phenolic compounds concentration led to excess the phenolic compounds insolubilized and were retained in aqueous phase which account for a decrease in extraction efficiencies of phenolic compounds in the three CPE systems (Arunagiria *et al*., 2012).

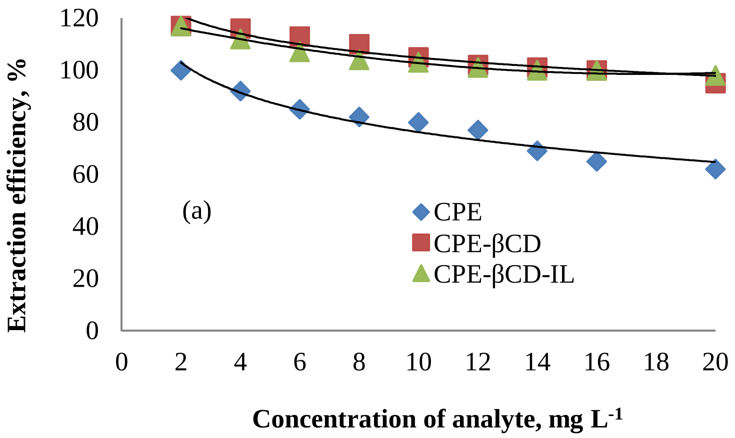
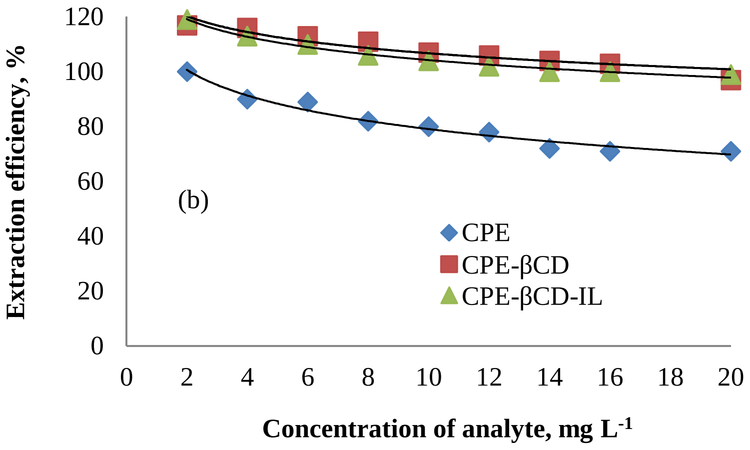
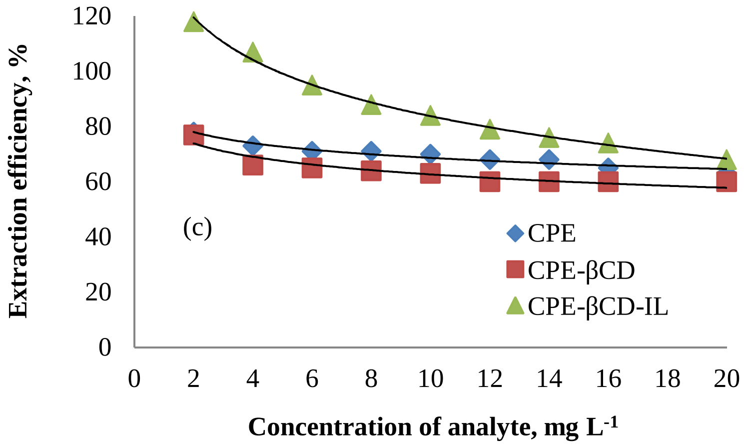


Figure 4.9: Effect of analyte concentration on extraction efficiency in the three CPE systems for the phenolic compounds (a) 2,4−DCP; (b) 2,4,6−TCP; (c) 4−NP. Condition: 0.5 (v/v %) DC193C, pH 7.0, 10.0 mg L^{-1} of modifier (β−CD; βCD−IL), 1.5 mol L^{-1} of Na_2SO_4 at 50ºC.





‘**Figure 4.9**, continued’.

4.1.9 Water content.

Water content in the surfactant rich phase is one of the factors that should be considered to improve the efficiency of extraction. 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 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 caused the difficulty in distribution coefficient and extraction efficiency (Yao and Yang, 2008a).

Therefore, in this study, the comparison of the percentage water content in the surfactant rich phase of the CPE process between DC193C surfactant and Triton X for the three phenolic compounds was investigated, Figure 4.10. Based on the results, Triton X obtained the higher percentage of water content in the surfactant rich phase compared to DC193C surfactant after the CPE process for the three phenolic compounds. The percentage of water content in the surfactant rich phase for DC193C surfactant 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 the three phenolic compounds in the CPE system.

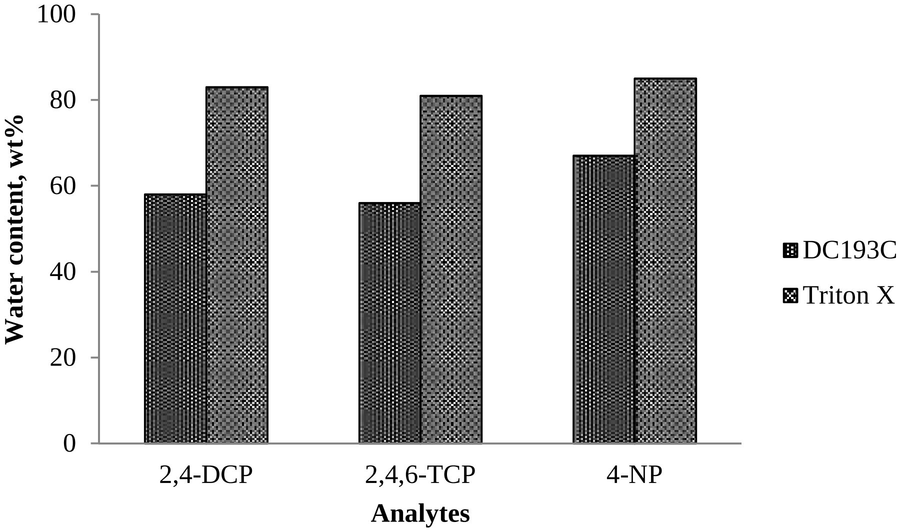


Figure 4.10: Water content in the surfactant rich phase obtained by the CPE process with DC193C and Triton X at 0.5 (v/v %) surfactant concentration.

Referring to the structure of DC193C surfactant (Figure 3.1), more conformation of the PEGs dimethicone molecules was present in the formation of surfactants in the 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 (Yao and Yang, 2008a). Therefore, DC193C surfactant was favorable for the excellent performance of the CPE process.

Another factor that contributes to the specificity of the interphase transfer in the surfactant extraction system was the influence of the analyte molecule structure and their hydrophobicity on its distribution between the aqueous and the surfactant rich phase (Doroschuk *et al*., 2005). As illustrated in Figure 4.10, the surfactant rich phase has the highest water content for the hydrophilic 4−NP compared to 2,4−DCP and 2,4,6−TCP which are hydrophobic. The hydrophilic molecule of 4−NP has the potential to solubilize in the aqueous phase that causes the spaces to remain for the water inside the surfactants were not efficiently compressed. Meanwhile, the surfactant rich phase becomes more hydrophobic when hydrophobic analytes for 2,4−DCP and 2,4,6−TCP were bound into the surfactants. Trichlorophenol is more hydrophobic than dichlorophenol due to the increasing numbers of chlorine atoms in the molecular structure (Li *et al*., 2012). Therefore, the solubilization increases in the hydrophobic surfactants 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−TCP > 2,4−DCP > 4−NP.

Figure 4.11 shows the percentage of water content in the surfactant rich phase in the three CPE systems for the phenolic compounds. The water content in the surfactant rich phase was studied for the concentration of DC193C surfactant in the range of 0.1 to 0.8 v/v% in the three CPE systems for the phenolic compounds. The percentage of water content decreases as concentration of DC193C surfactant increases in the range of 0.1 to 0.5 v/v % and almost constant up to 0.8 v/v % in the three CPE systems studied for the phenolic compounds. This is due to increasing in number of hydrophobic micelles which results in extraction efficiency of the three CPE systems (El-Shahawi *et al*., 2013). This finding has been supported by the results obtained as shown in Figure

4.1, in which it can be concluded that, the lowest percentage of water content in the surfactant rich phase, the higher extraction efficiency of the phenolic compounds.

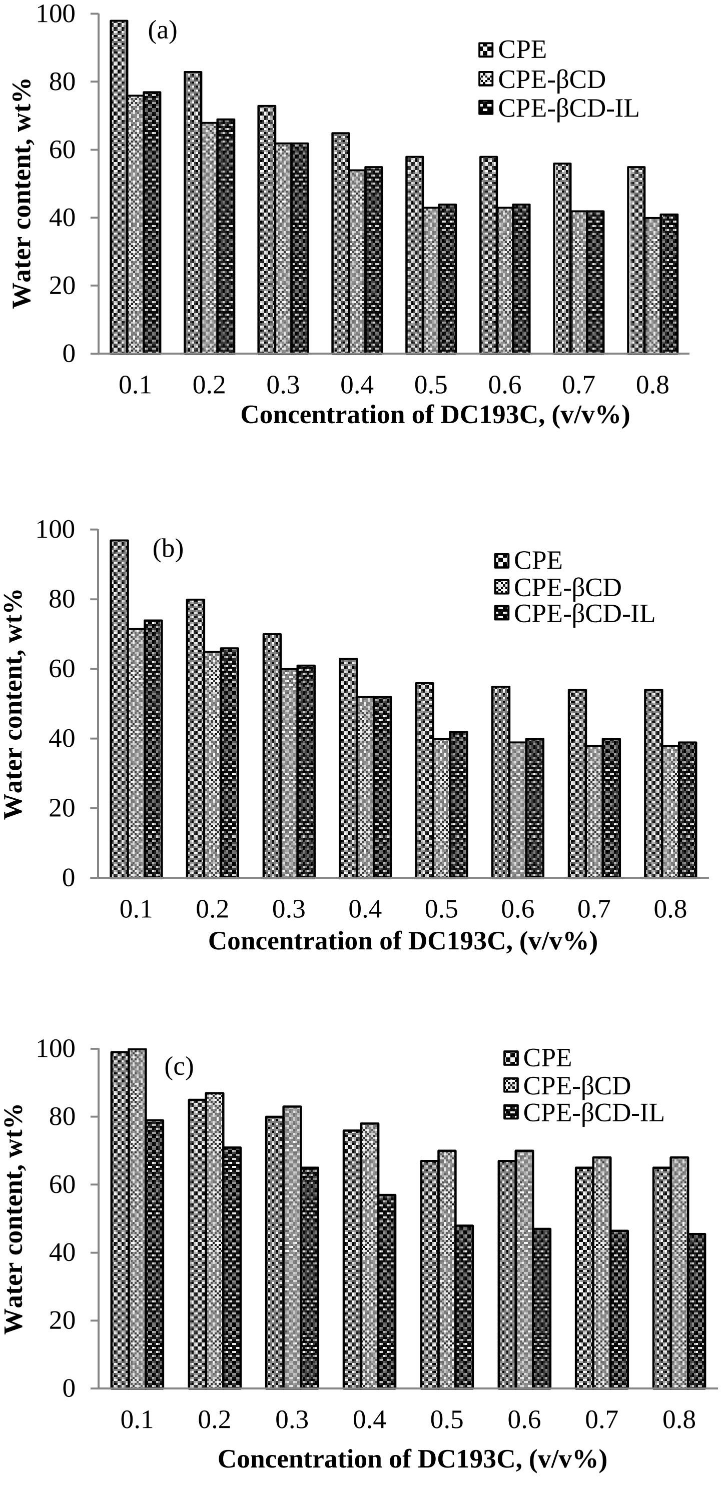


Figure 4.11: Water content in the surfactant rich phase in the three CPE systems for the phenolic compounds (a) 2,4−DCP; (b) 2,4,6−TCP; (c) 4−NP. Condition: 10.0 mg L^{-1} of analyte concentration, pH 7.0, 0.5 (v/v %) DC193C, 10.0 mg L^{-1} of modifier (β−CD; βCD−IL), 1.5 mol L^{-1} of Na_2SO_4 at 50ºC.

Based on these results, the lowest percentage of water content in the surfactant rich phase was obtained in the CPE−βCD system compared to the CPE system for the hydrophobic 2,4−DCP and 2,4,6−TCP. However, in the CPE−βCD−IL system, the percentage of water content in the surfactant rich phase slightly higher and almost similar to the CPE−βCD system for 2,4−DCP and 2,4,6−TCP. In contrast to 4−NP, the lowest percentage of water content in the surfactant rich phase was obtained in the CPE−βCD−IL system than that of CPE and CPE−βCD systems. Meanwhile, the percentage of water content in the surfactant rich phase in the CPE−βCD system was higher than the CPE system for 4−NP. Once inclusion complex formed, the water molecules exclude from the cavity of β−CD, and then the spaces remain for the water molecules efficiently compressed in the surfactant rich phase.

The inclusion complex is favorable for hydrophobic 2,4−DCP and 2,4,6−TCP and opposite to hydrophilic 4−NP. The lowest water content in the surfactant rich phase was obtained in the CPE−βCD−IL system for 4−NP where IL improves the inclusion complex between the hydrophilic species of 4−NP with β−CD. The water content in the surfactant rich phase is correlated to the interaction mechanism as discussed in detail in Section 4.1.6. According to Li *et al*. (2012), the different extraction capability might be explained mainly from the inclusion effect and hydrogen bonding between solutes, surfactant and modifier. The hydrophobicity of analytes also affect the extraction and distribution between aqueous and surfactant rich phases in the three CPE systems for the phenolic compounds. Aforementioned, the extraction of analyte increases with the increases of analyte hydrophobicity as well as low the percentage of water content obtained in the surfactant rich phase.

4.2 Extraction behavior of 4−NP with DC193C surfactant and modifiers.

The cavity of β−CD was maintained even in the functionalized of β−CD with the ionic liquid. Due to these, inclusion complex is a vital work to analyse the complexes between the native and functionalized of β−CD, 4−NP and DC193C surfactant. The evidence of the formation of inclusion complex can directly be obtained from ^{1}H NMR spectra. In addition, from ^{1}H NMR, the information of the stoichiometry, stability, and structure of the β−CD complexes can be obtained (Chen *et al.*, 2006). In this study, the inclusion complex between the native and functionalized of β−CD, DC193C surfactant and 4−NP were investigated.

2D NOESY and 2D ROESY NMR spectroscopic technique can provide supporting evidence for specific structures in cyclodextrin complexes. 2D NMR spectroscopy has become a powerful method to study the conformation of β−CD and derivatives and their complexes because one can conclude that two protons are closely located in space (*ca.* 5Å) if an NOE correlation is detected between the relevant proton signals in the NOESY or ROESY spectrum. Therefore, it is possible to estimate the orientation of substituent or guest molecule in the β−CD cavity with the aid of the assigned NOE correlations.

On the basis, 2D NOESY was performed to obtain further information about the conformation of the host β−CD and their complexes (Chen *et al.*, 2010). These experiments give rise to the cross peaks between dipolar coupled spins (Neuhaus, 2000; Sanders, 1993) and they are used to indicate the close proximately between atoms in the two components of the complex. Therefore, the formation of an inclusion complex was further proven by the 2D NOESY analysis since 2D NMR is a powerful toll for investigating intermolecular interactions and to gain more information on the conformation of the inclusion complex (Li *et al.*, 2003). The main interactions of inclusion complex that take place between native or functionalized of β−CD, 4−NP and DC193C surfactant in the extraction process can be supported by these findings. In order to evaluate the geometry of inclusion complex of native or functionalized of β−CD, 4−NP and DC193C surfactant, ^{1}H NMR and 2D NOESY measurements (DMSO−D_6, 25ºC, 600 MHz) were performed on an AVN600 spectrometer. As for 2,4−DCP and 2,4,6−TCP, similar interaction was obtained, thus, only inclusion complexes for 4−NP was reported in this study.

4.2.1 Extraction behavior of 4−NP and DC193C surfactant with β−CD.

The ^{1}H NMR spectrum of native β−CD, 4−NP, DC193C and βCD−DC193C−NP inclusion complex were shown in Figure 4.12 (a) – (d). The ^{1}H NMR chemical shifts (δ) of β−CD, 4−NP, DC193C surfactant and βCD−DC193C−NP inclusion complex were listed in Table 4.2. Based on the result obtained in Table 4.2, the proton of DC193C surfactant and 4−NP has an interaction with the inner of the native of β−CD due to the changes of H5 proton signal. However, the proton of the DC193C surfactant shows the higher shift compared to the proton of 4−NP.

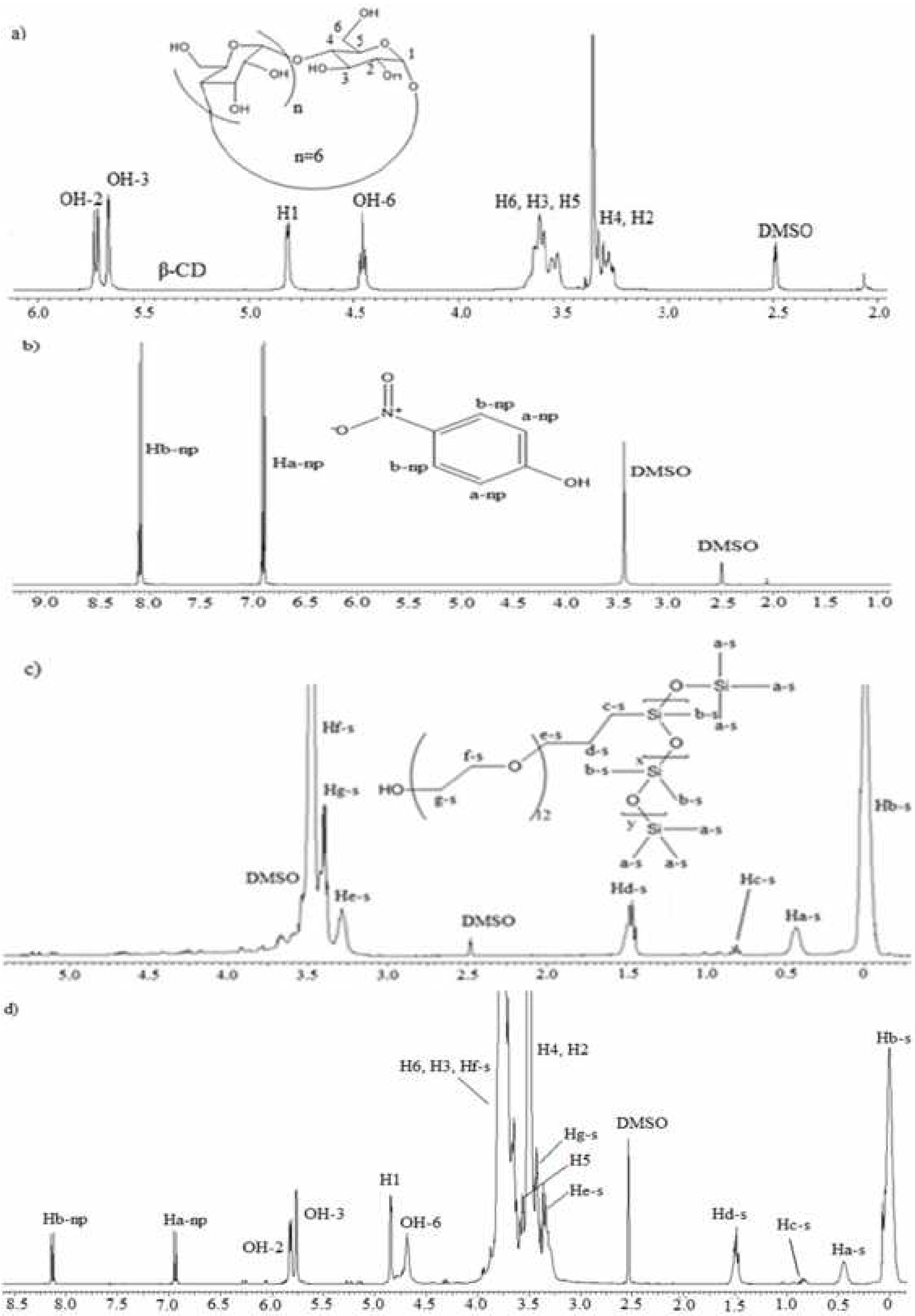


Figure 4.12: ^{1}H NMR spectrum of the (a) β−CD (b) 4−NP (c) DC193C and (d) βCD−DC193C−NP.

Table 4.2: ^{1}H NMR chemical shift (§) of β−CD, 4−NP, DC193C and βCD−DC 193C−NP.

Proton	**β−CD**	**4−NP**	**βCD−DC193C−NP**	
	§	**§**	**§**	**Δ§**
H1	4.8167		4.8430	+0.0263
H2	3.3121		3.3400	+0.0279
H3	3.5984		3.5880	−0.0104
H4	3.3572		3.3630	+0.0058
H5	3.5541		3.5790	**+0.0249**
H6	3.6144		3.6210	+0.0066
Proton		§	§	Δ§
Ha−np		6.9130	6.9270	+0.0140
Hb−np		8.1035	8.1190	+0.0155
Proton		**DC193C**	**βCD−DC193C−NP**	
		§	§	Δ§
Ha−s		0.4320	0.4400	+0.0080
Hb−s		0.0305	0.0430	+0.0125
Hc−s		0.8262	0.8008	**−0.0254**
Hd−s		1.4791	1.4900	+0.0109
He−s		3.3182	3.3860	**+0.0678**
Hf−s		3.5580	3.5160	**−0.0420**
Hg−s		3.4037	3.4170	+0.0133

Values in bold refer to the highest chemical shift of that particular proton.

Thus, in order to further prove which one has accommodated into the cavity, 2D NMR was carried out to indicate the interaction. It was found that the 2D NMR result shows the strong interaction between β−CD with DC193C surfactant compared to 4−NP (Figure 4.13). Therefore, we can conclude that may be because the binding of 4−NP within the host of β−CD is not fixed or permanent but rather dynamic equilibrium as reported by Singh et al. (Singh *et al.*, 2002). The binding of guest molecules within the host of β−CD is not fixed or permanent but rather is a dynamic equilibrium. Binding strength depends on how well the ‘host−guest’ complex fits together and on specific local interactions between surface atoms.

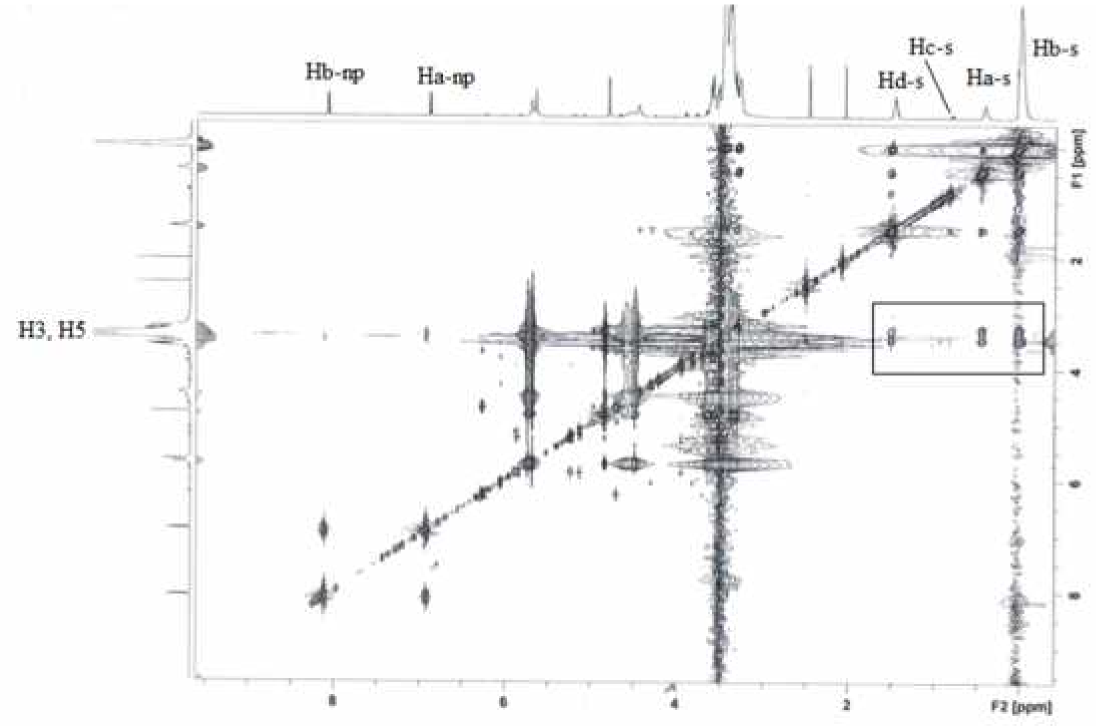


Figure 4.13: Two−dimensional NOESY spectrum of the βCD−DC193C−NP complex in DMSO−D_6.

As shown in Figure 4.14, we have proposed that only DC193C surfactant enters the β−CD's cavity. According to Valero and Carrillo (2004), β−CD modifier has found to form inclusion complexes with various polymers including PEGs with high specificity to give stoichiometric compounds in crystalline states. In these complexes, polymer chains were threaded into β−CD and recognized by the host. The formation of the complexes is thought to be promoted by hydrogen bond formation between β−CD (Valero and Carrillo, 2004).

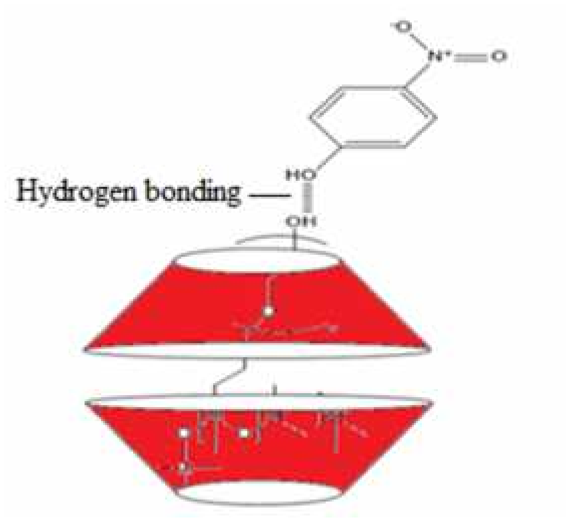


Figure 4.14: Schematic illustration of the complexation between molecular form of the 4−NP and DC193C with β−CD.

4.2.2 Extraction behavior of 4−NP and DC193C surfactant with βCD−IL.

In order to evaluate the geometry of inclusion formation of the βCD−IL, 4−NP and DC193C surfactant the ^{1}H NMR (Figure 4.15 (a) − (d)) measurement was carried out. The protons of DC193C surfactant and 4−NP were found to be shifted upon the formation of inclusion complex (βCD−IL−DC193C−NP) (Table 4.3). Besides, the obvious upfield shifts of the protons on the inner cavity of the βCD−IL (H3, H5) were observed and the results obtained indicate that DC193C surfactant or 4−NP has been entered into the cavity of βCD−IL. It could be observed that in the ^{1}H NMR spectrum of the βCD−IL−DC193C−NP (Figure 4.15 (d)), the presence of proton signals belonging to the βCD−IL, 4−NP and DC193C molecules which strongly suggests that the new inclusion complex has been formed. In this study there are two guest compounds (DC193C surfactant or 4−NP), thus, it is necessary to investigate further with the 2D NMR in order to predict which one enters into the cavity of βCD−IL.

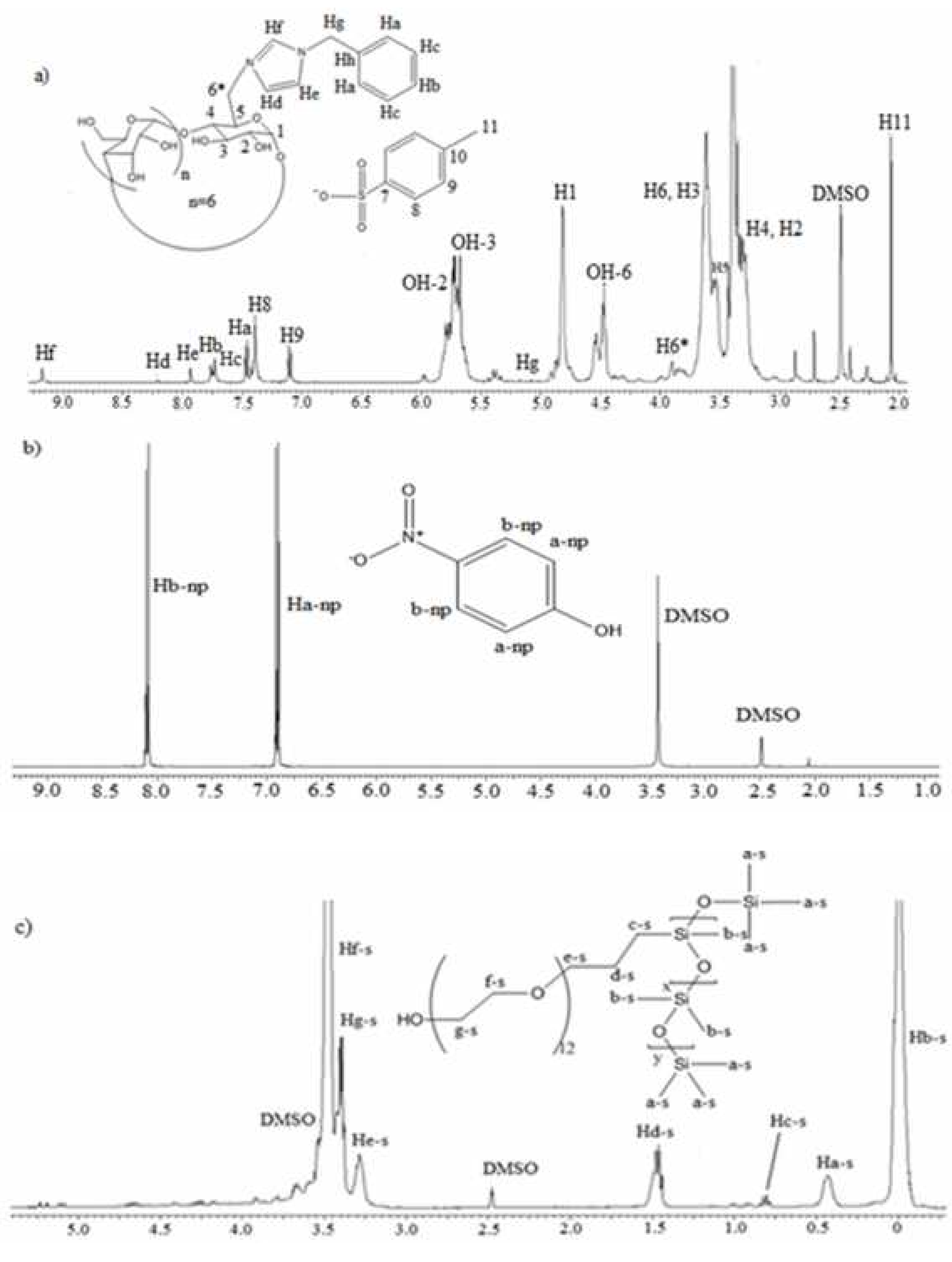
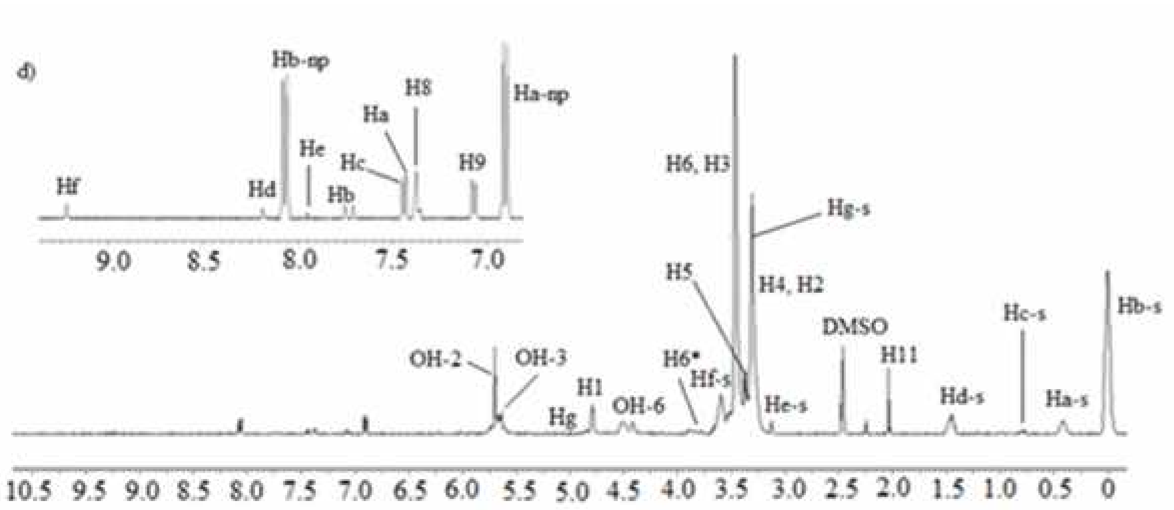


Figure 4.15: ^{1}H NMR spectrum of the (**a**) βCD−IL (**b**) 4−NP (**c**) DC193C and (**d**) βCD−IL−DC193C−NP.



Chemical shift (ppm)

‘**Figure 4.15,** continued’.

Table 4.3: ^{1}H NMR chemical shift (§) of βCD−IL, 4−NP, DC193C and βCD−IL−DC193C−NP.

Proton	**βCD−IL**	**4−NP**	**βCD−IL−DC193C−NP**	
	§	**§**	**§**	**Δ§**
H1	4.8167		4.8420	+0.0253
H2	3.3121		3.3046	−0.0075
H3	3.5984		**3.5362**	**−0.0622**
H4	3.3572		3.3791	+0.0219
H5	3.5541		**3.4635**	**−0.0906**
H6	3.6144		3.5941	−0.0170
H8	7.3930		7.3427	−0.0503
H9	7.0938		7.0808	−0.0130
H11	2.0694		2.0399	−0.0295
Ha	7.4556		7.4297	−0.0259
Hb	7.7251		7.7521	+0.0270
Hc	7.4755		7.4496	−0.0255
Hd	8.2060		8.1582	−0.0478
He	7.9312		7.9363	+0.0051
Hf	9.1747		9.2210	+0.0463
Hg	5.3365		5.3816	+0.0451
Proton				
Ha−p		6.9130	6.8933	–0.0197
Hb−p		8.1035	8.0678	–0.0357
Proton		**DC193C**	**βCD−IL−DC193C−NP**	
		§	**§**	**Δ§**
Ha−s		0.4320	0.4743	**+0.0423**
Hb−s		0.0305	0.1462	**+0.1157**
Hc−s		0.8262	0.8999	**+0.0737**
Hd−s		1.4791	1.4233	**−0.0558**
He−s		3.3182	3.3046	−0.0136
Hf−s		3.5580	3.5941	+0.0361
Hg−s		3.4037	3.3791	−0.0246

Values in bold refer to the highest chemical shift of that particular proton.

Therefore, the formation of an inclusion complex was further proven by the 2D−NOESY analysis (Figure 4.16). The cross peaks in the spectra, indicated in SD3 originate from the interaction of the protons of DC193C surfactant, 4−NP and βCD−IL. The cross peaks of the βCD−IL (H3, H5) and DC193C surfactant (Ha−s, Hb−s, Hc−s, Hd−s) demonstrate strong intensity. Based on these results (2D NOESY spectra), we can conclude that DC193C surfactant has been accommodated in the βCD−IL's cavity and may be within less than 5 Å apart from H3 and H5 of βCD−IL. Furthermore, 2D NOESY also shows interactions between the βCD−IL and 4−NP. The cross peak (Ha−p, Hb−p) shows an interaction with the βCD−IL (H3, H5) and it also supports that 4−NP has been accommodated in the cavity of βCD−IL. Apart from that, the cross peak around 6 − 8 ppm belonging to the βCD−IL and 4−NP shows that the present of the π – π interaction and electrostatic attraction between the imidazolium rings and 4−NP.

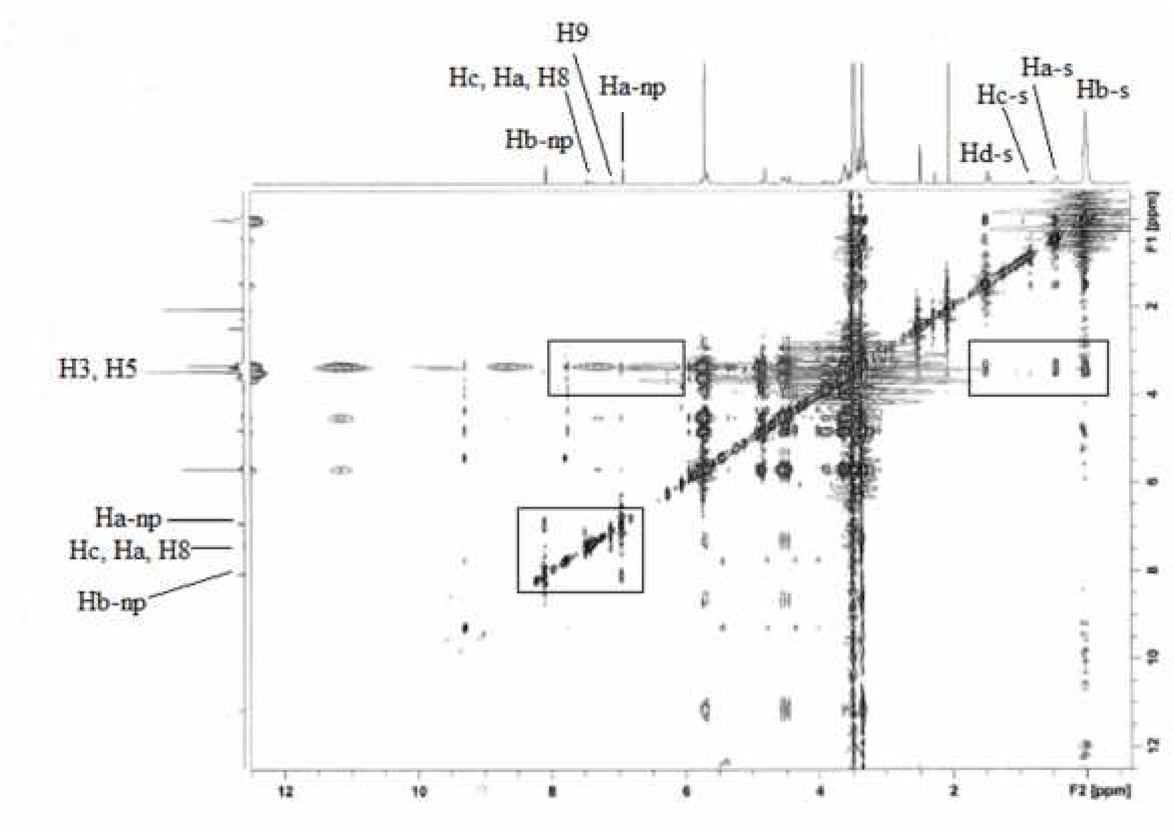
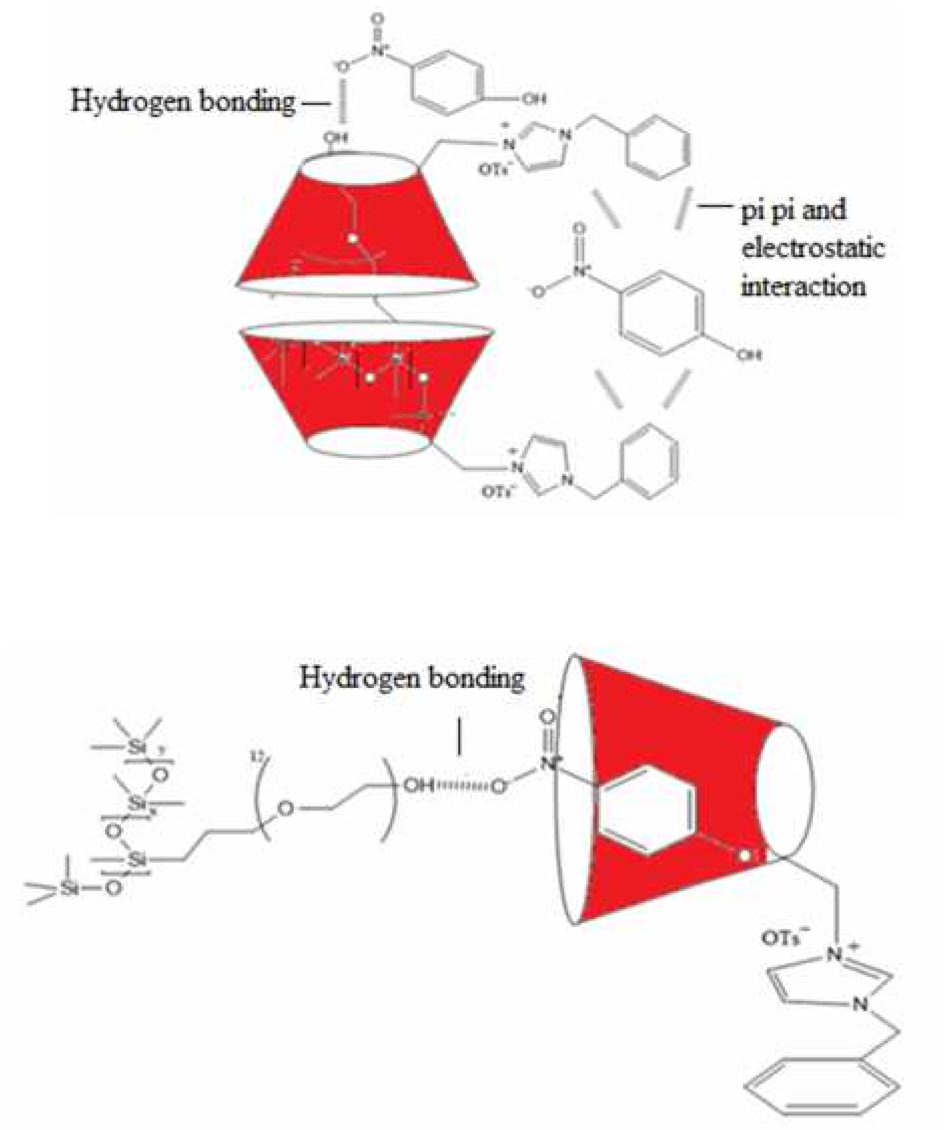


Figure 4.16: Two−dimensional NOESY spectrum of the βCD−IL−DC193C−NP complex in DMSO−d_6.

Hence, the possible formations of the inclusion complex structure of molecular form of 4−NP and DC193C with βCD−IL are shown in Figure 4.17 (a) and (b) and have been proposed by taking account of the hydrogen bonding between DC193C and 4−NP, π – π interaction, electrostatic attraction between the imidazolium ring of the βCD−IL and 4−NP, as well as the inclusion complexes between the βCD−IL with DC193C and/or βCD−IL with 4−NP.



(a)

(b)

Figure 4.17 (a) and (b): Schematic illustration of the complexation between molecular form of 4−NP and DC193C with βCD−IL.

4.3 Isotherm study.

4.3.1 Solubilization isotherm.

Solubilization isotherm is useful for understanding the mechanism of the surfactant solubilization. Solubilization properties and equilibrium parameters, commonly known as solubilization isotherm, describe how the surfactants interact with solute or solubilizate, and contribute towards a comprehensive understanding of the nature of interaction. Isotherm study helps to provide knowledge about the optimum use of surfactant. Thus, it is essential to establish the most appropriate correlation for the equilibrium curve, in order to optimize the design of a solubilization isotherm system for the removal of phenolic compounds from aqueous solutions. There are several isotherm equations available for analyzing experimental solubilization equilibrium parameters. However, the most common types of isotherms are the Langmuir and Freundlich models (Nandi *et al*., 2009).

The Langmuir solubilization isotherm has been successfully applied to many pollutant solubilization processes. It has also been the most widely used model to describe the solubilization of a solute from an aqueous solution into surfactant. A basic assumption of the Langmuir theory is that solubilization takes place at specific homogeneous sites on the surface of the surfactant. It is then assumed that once a solubilizate occupies a site, no further solubilization can take place at that site. The rate of solubilization 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 of surfactant (Chen *et al*., 2009; Rawajfih and Nsour, 2006). The Langmuir type solubilization isotherm model has been used to explain the solubilization of the three phenolic compounds into the non−ionic surfactant of DC193C in the different CPE systems due to its success in describing many solubilization 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 phenolic compounds solubilized per mole of DC193C surfactant at equilibrium (mol mol^{-1}). C_e is the dilute phase equilibrium (mol L^{-1}) of the phenolic compounds. The constant m and n are the Langmuir constants signifying the solubilization capacity (mol mol^{-1}) and energy of solubilization (L mol^{-1}), respectively (Purkait *et al*., 2006a, 2006b). The values of m and n in the three CPE systems can be calculated by the regression analysis using experimental data for the phenolic compounds.

4.3.2 Evaluating the values of *m* and *n*.

The Langmuir equation can be linearized into the following form;

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

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).

Figures 4.18, 4.19 and 4.20 show the solubilization isotherm in the three CPE systems for 2,4−DCP; 2,4,6−TCP and 4−NP, respectively, which is illustrated by plotting q_e vs. C_e. 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 in the three CPE systems were calculated by plotting $1/q_e$ vs. $1/C_e$ as shown in Figures 4.21 4.22 and 4.23 for 2,4−DCP; 2,4,6−TCP and 4−NP, respectively. The Langmuir model parameters and the statistical fits of the solubilization data to this equation in the three CPE systems for the phenolic compounds were given in Table 4.4.

The values of m and n vary with the temperature, which is a characteristic of both the surfactant and solute. However, when the aqueous in the CPE is separated into two phases at a fixed temperature, the solubilization capacity (m) and the energy of solubilization (n) are constant. Aforementioned, the 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 (Jianwei Chen, et al., 2009). According to the Rawajfih and Nsour (2006), the solubilization conforms to the Langmuir model when the value of the correlation coefficient (R^2) is greater than 0.89. Thus, the R^2 values obtained are shown in Table 4.4 which was greater than 0.89 for the phenolic compounds in the three CPE systems, indicating that the isotherms were consistent with the Langmuir model.

Table 4.4: The values of *m* and *n* with correlation coefficient (R^2) in the different CPE systems for the phenolic compounds are given below.

Analytes	Parameters	CPE	CPE−βCD	CPE−βCD−IL
2,4−DCP	m (mol mol^{-1})	3.33×10^{-3}	7.70×10^{-3}	7.09×10^{-3}
	n (L mol^{-1})	5.67×10^{3}	4.03×10^{3}	4.38×10^{3}
	R^2	0.995	0.998	0.998
2,4,6−TCP	m (mol mol^{-1})	4.75×10^{-3}	1.03×10^{-2}	9.52×10^{-3}
	n (L mol^{-1})	3.90×10^{3}	3.01×10^{3}	3.27×10^{3}
	R^2	0.995	0.998	0.999
4−NP	m (mol mol^{-1})	2.27×10^{-3}	2.23×10^{-3}	4.00×10^{-3}
	n (L mol^{-1})	7.00×10^{3}	7.03×10^{3}	4.44×10^{3}
	R^2	0.995	0.995	0.998

The solubilization isotherms in the three CPE systems for the phenolic compounds exhibited Langmuir behavior which indicates monolayer coverage. The solubilization capacity, which is a measure of the capacity of the surfactant to retain the solute, suggests that DC193C surfactant would be effective as the surfactant of the phenolic compounds in the three CPE systems. The solubilization capacity (*m*) increased on the increasing solute molecule hydrophobicity according to the following order; 4−NP < 2,4−DCP < 2,4,6−TCP in the three CPE systems. This tendency can be observed in Table 4.4. The monolayer solubilization capacity was greater for the chlorophenols than the nitrophenol due to the different phenolic compounds. The trichlorinated phenol is more hydrophobic than the dichloronated phenol due to the increasing numbers of chlorine atoms in the molecular structure. The octanol/water (o/w) partition coefficient (log K_{ow}) of chlorophenols, which could be measured of solvent hydrophobicity, increased with the degree of chlorination. The log K_{ow} values for 2,4,6−TCP and 2,4−DCP were 3.69 and 3.08 respectively. The strength of the hydrogen bonds was stronger if there were more chlorine atoms attached to the phenyl ring. The number of chlorine atoms for TCP and DCP was 3 and 2, respectively, so the order of strength of hydrogen bonds was TCP > DCP (Li *et al*., 2012).

The solubilization capacity (*m*) of the CPE (3.33×10^{-3}; 4.75×10^{-3}) system was lower than the CPE−βCD (7.70×10^{-3}; 1.03×10^{-2}) systems for 2,4−DCP and 2,4,6−TCP, respectively. Based on these results, the value of *m* in the CPE−βCD system was higher than the *m* value in the CPE system for 2,4−DCP and 2,4,6−TCP. In contrast, 4−NP showed no significant effect between the solubilization capacity (*m*) in the CPE (2.27×10^{-3}) and CPE−βCD (2.23×10^{-3}) systems. Generally, host cyclodextrin molecules possessed a greater inclusion affinity for more hydrophobic guest or solute molecules (Li *et al*., 2009). Due to this, the modifier of β−CD play their role in enhance the solubilization of hydrophobic solutes in the CPE system.

The solubilization capacity of 2,4−DCP and 2,4,6−TCP into the surfactant rich phase enhance in the presence of β−CD modifier in the CPE−βCD compared to the CPE system. Due to the proper size of 2,4−DCP and 2,4,6−TCP to fit into the β−CD's cavity, the solubilization capacity can be enhanced by expelling all water molecules will exhibit the greatest interaction as well as the mechanism interaction between β−CD modifier and DC193C surfactant. This "tightness of fit" trend may be explained by examining the hydrophobic inclusion process, which is the primary binding interaction involved between the hydrophobic solute molecule and β−CD in aqueous solutions. In order for the hydrophobic solute to include within the β−CD cavity, water molecules present within the cavity must be expelled (Li *et al*., 2009). The nucleophilic Cl and hydroxyl atoms in 2,4−DCP and 2,4,6−TCP can form hydrogen bonding with hydroxyl atoms in the both of β−CD as well as βCD−IL modifier and DC193C surfactant. There were large amount of 2,4−DCP and 2,4,6−TCP in interspace between the β−CD and/or βCD−IL modifier and DC193C surfactant. Thus, 2,4−DCP and 2,4,6−TCP can be solubilized tightly around β−CD and/or βCD−IL modifier to form columnar structure (Li *et al.*, 2009).

However, the presence of the β−CD modifier did not improve the extraction performance of 4−NP in the CPE−βCD system. This is because of the 4−NP molecules are not large enough to expel most (if not all) of the water molecules from the β−CD's cavity upon binding, the overall hydrophobic nature of the cavity environment is decreased. The binding between the β−CD and the 4−NP molecules are not fixed or permanent, but rather come in dynamic equilibrium. Furthermore, the electrophilic property of oxygen in $–NO_2$ of 4−NP leads nitrogen atom to difficulty form hydrogen bonding with hydroxyl in the β−CD. Even though –OH in 4−NP may form hydrogen bonding with hydroxyl in the β−CD, it is difficult to lead 4−NP to tightly solubilize around the β−CD (Li *et al.*, 2009). Thus, the solubilization capacity of 4−NP into the β−CD's cavity of modifier in the CPE−βCD system was lower than 2,4−DCP and 2,4,6−TCP.

In the CPE−βCD−IL system, the solubilization capacity decreases for the 2,4−DCP and 2,4,6−TCP. The values of m (7.09×10^{-3}; 9.52×10^{-3}) in the CPE−βCD−IL system was lower than in the CPE−βCD system for 2,4−DCP and 2,4,6−TCP, respectively. It is obviously shows that the presence of IL did not improve the solubilization of hydrophobic and larger solutes of 2,4−DCP and 2,4,6−TCP into the surfactant rich phase. However, the solubilization capacity (4.00×10^{-3}) of 4−NP has been enhanced in the CPE−βCD−IL system.

The functionalized of the β−CD often alters the binding properties of the native β−CD by potentially introducing steric hindrance for cavity inclusion, extending the depth of the hydrophobic cavity, or altering the number of sites available for hydrogen bonding and dipole interactions (Flaherty *et al.*, 2013). In addition, the solubilization might be also explained to proceed via the inter−molecular hydrogen bonds between –NH and/or –OH groups of the βCD−IL and –OH group of the phenolic compounds (Li *et al.*, 2012). The performance solubilization of 2,4−DCP and 2,4,6−TCP slightly decrease in the presence of the functionalized β−CD with IL modifier due to the $\pi - \pi$ interaction as discussed in Section 4.1.6. As opposed to 4−NP, the binding performance was improved in the CPE−βCD−IL system. This result indicates that in the presence of IL functionalized to the β−CD, the cavity of β−CD already alters for better binding with 4−NP.

The values of energy of solubilization (*n*) were reversible to the values of solubilization capacity (*m*) for the three phenolic compounds in the three CPE systems. The values of *n* obtained in the CPE−βCD (4.03×10^3; 3.01×10^3) system were lowered compared to the CPE (5.67×10^3; 3.90×10^3) system for the 2,4−DCP and 2,4,6−TCP, respectively. However, there was no significant effect of the *n* values between the CPE (7.00×10^3) and CPE−βCD (7.03×10^3) systems for 4−NP. The energy of solubilization for 2,4−DCP and 2,4,6−TCP were slightly higher in the CPE−βCD−IL system (4.38×10^3; 3.27×10^3) than in the CPE−βCD system. On the other hand, the value of *n* was obviously decreases in the CPE−βCD−IL (4.44×10^3) system compared to the CPE−βCD system for 4−NP. These results might be explained via the interaction between solutes, modifier and surfactant as explain previously in the binding interaction of *m* value. It can be concluded, the least binding interaction between the solutes, modifier and surfactant, the more energy was required to solubilize solutes into the surfactant rich phase.

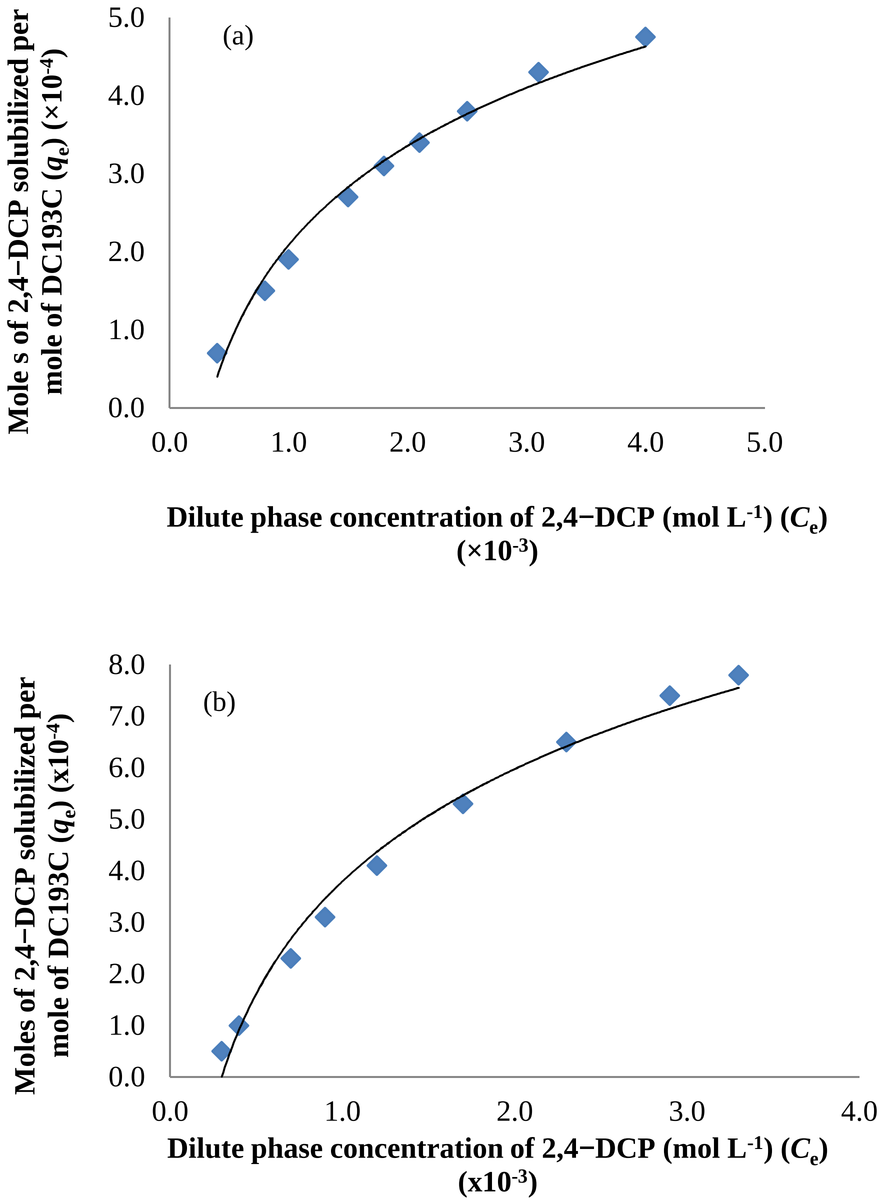
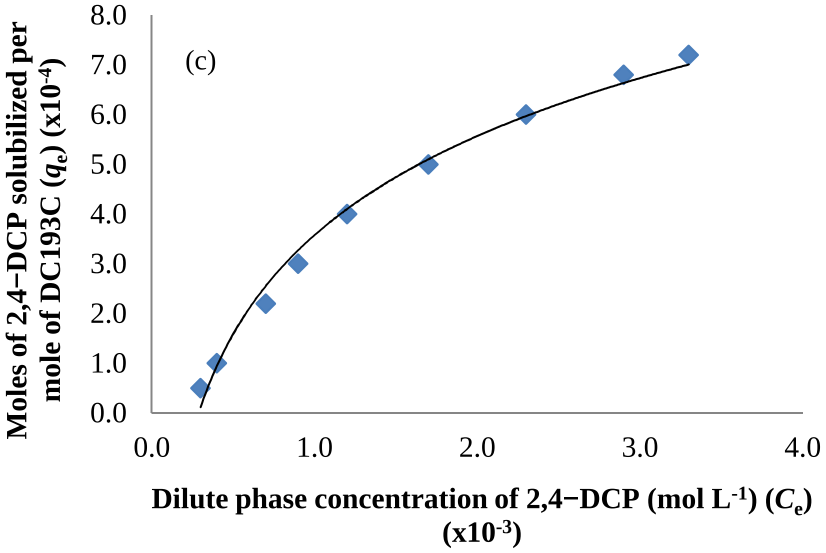


Figure 4.18: Solubilization isotherm of the 2,4−DCP over DC193C surfactant: (a) CPE (b) CPE−βCD (c) CPE−βCD−IL.



'**Figure 4.18**, continued'.

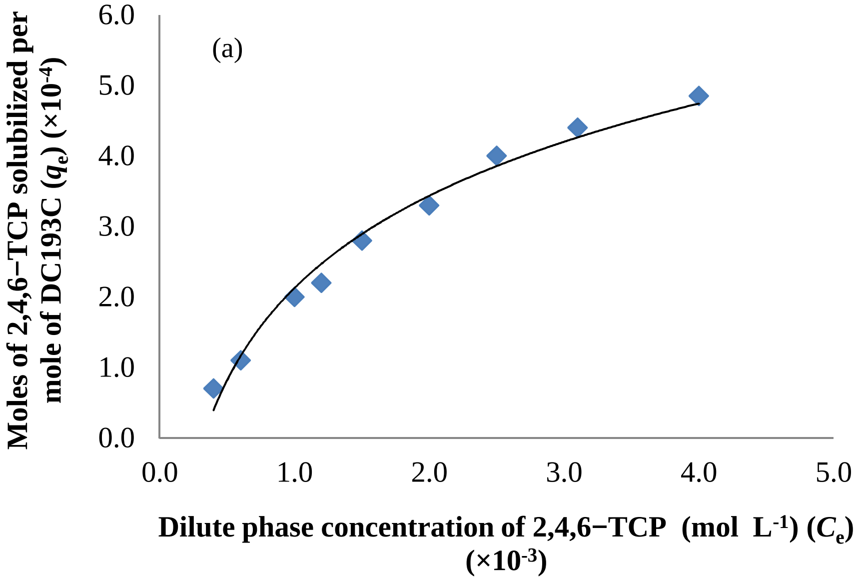
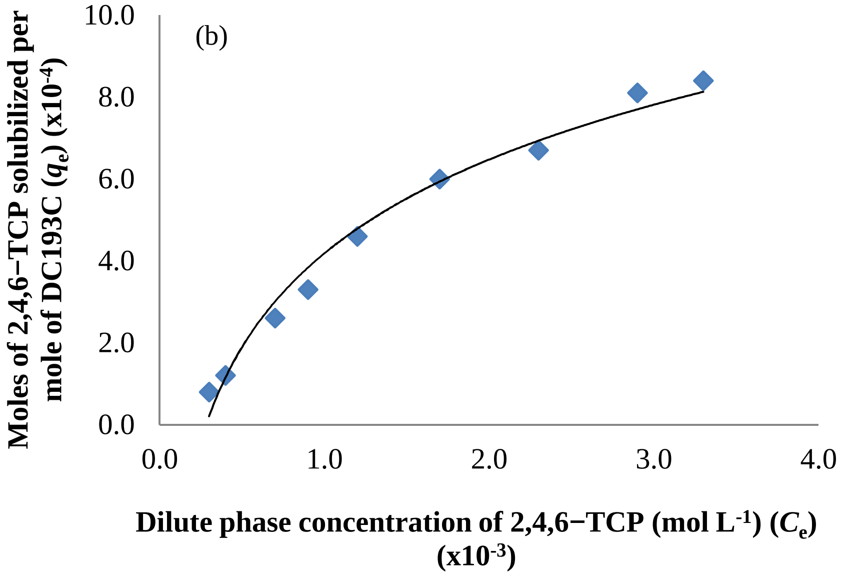
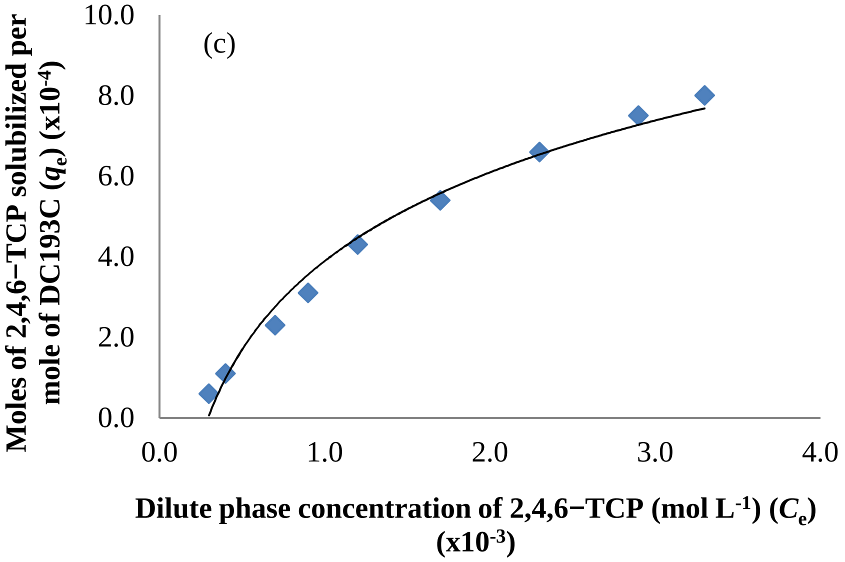


Figure 4.19: Solubilization isotherm of 2,4,6−TCP over DC193C surfactant: (a) CPE (b) CPE−βCD (c) CPE−βCD−IL.





‘**Figure 4.19**, continued’.

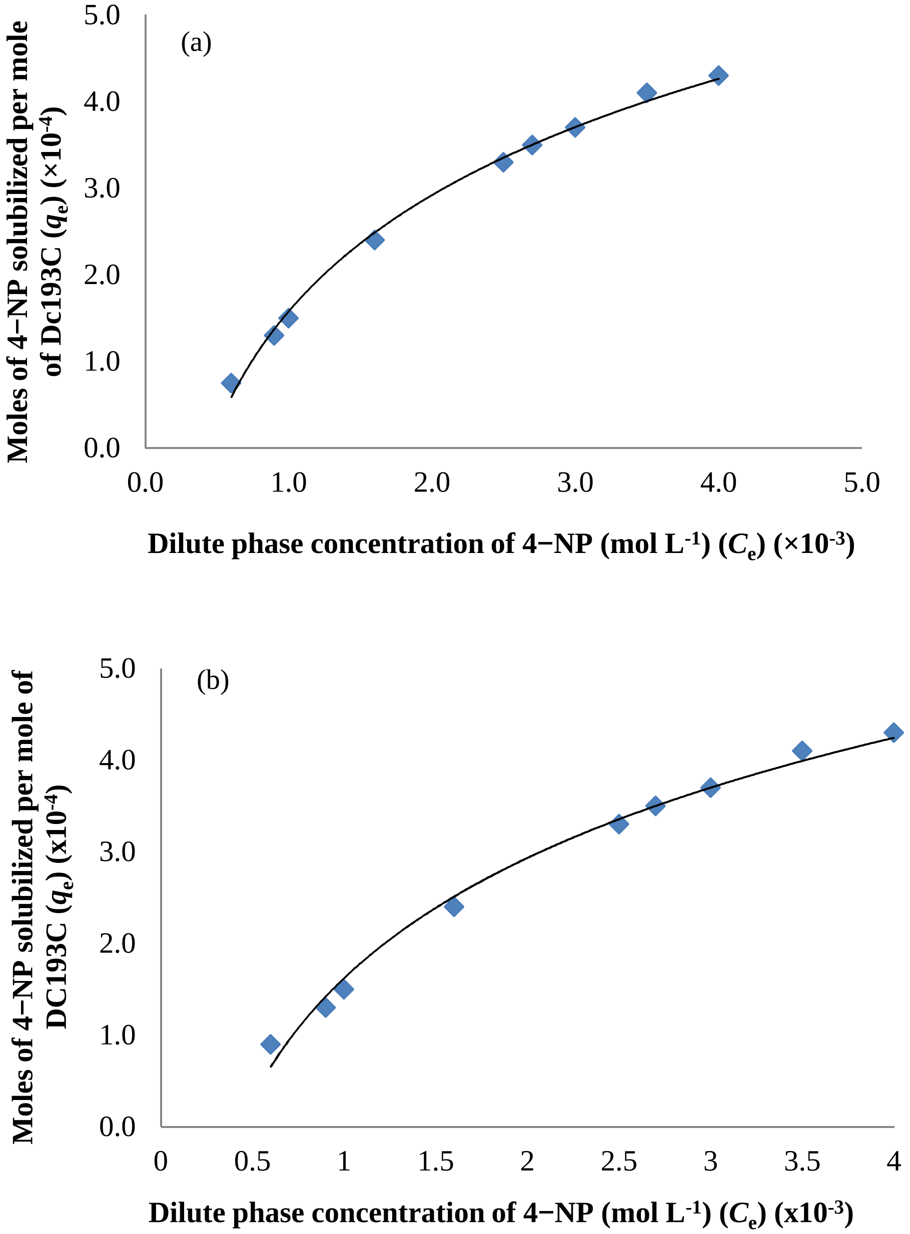
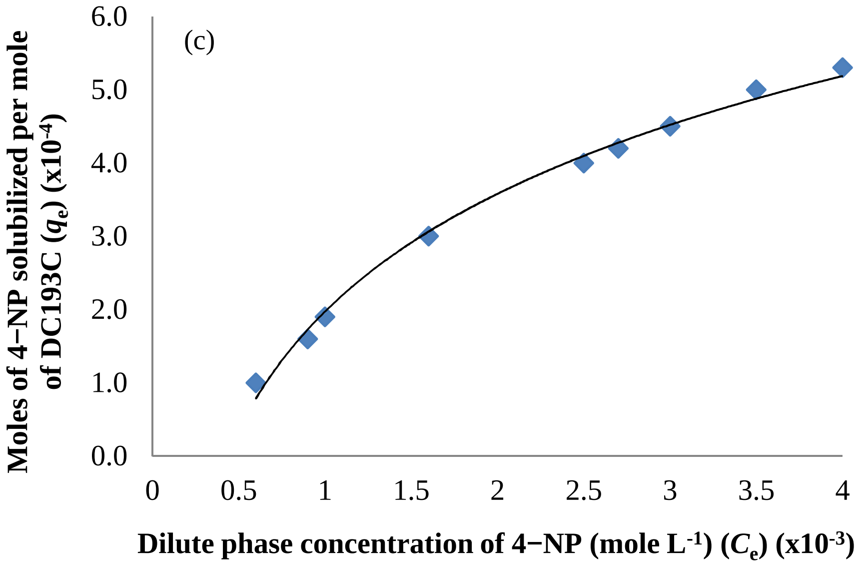


Figure 4.20: Solubilization isotherm of 4−NP over DC193C surfactant: (a) CPE (b) CPE−βCD (c) CPE−βCD−IL.



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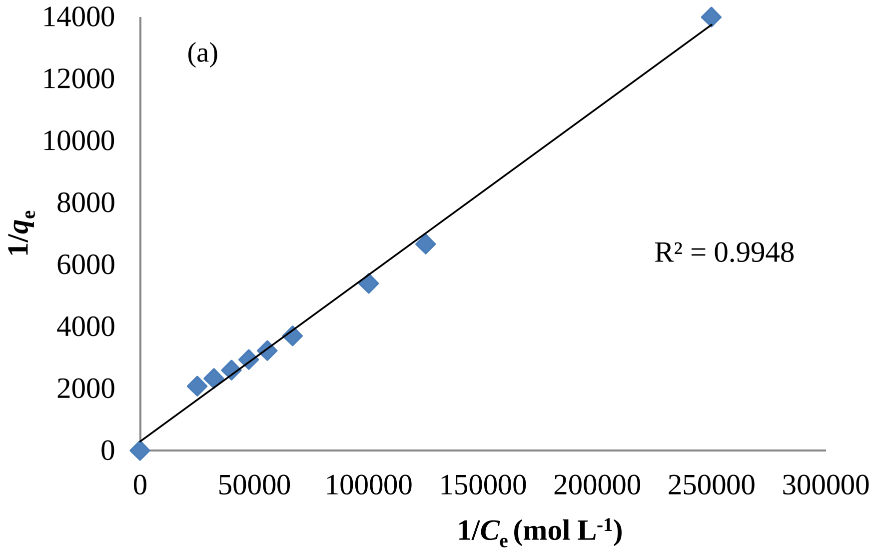
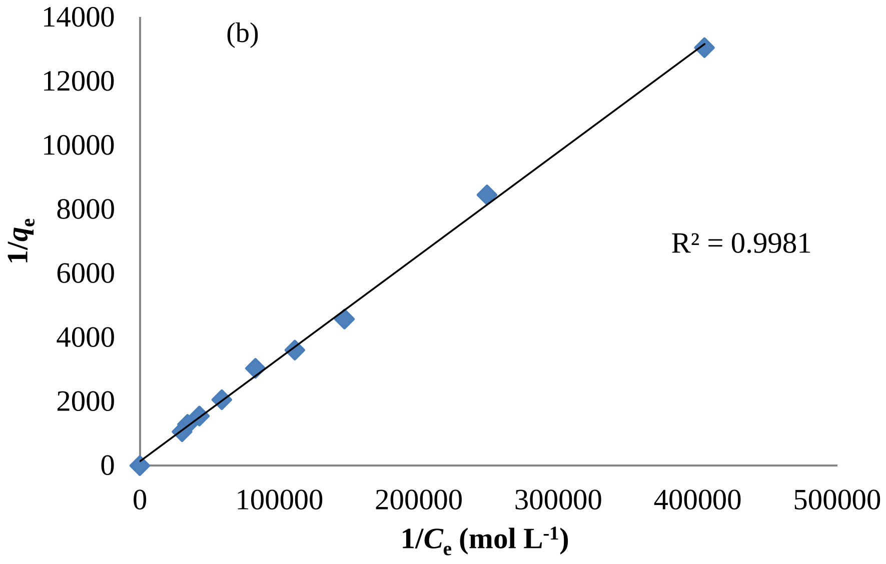
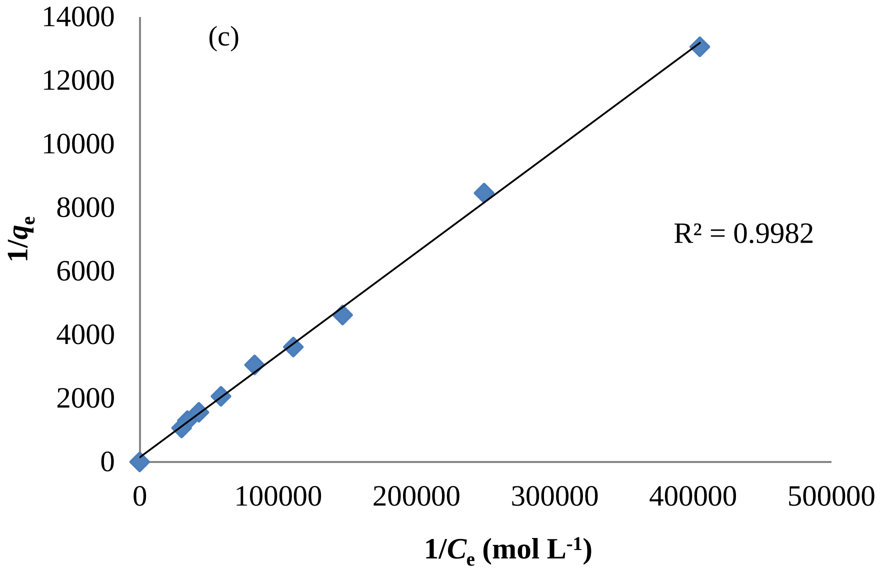
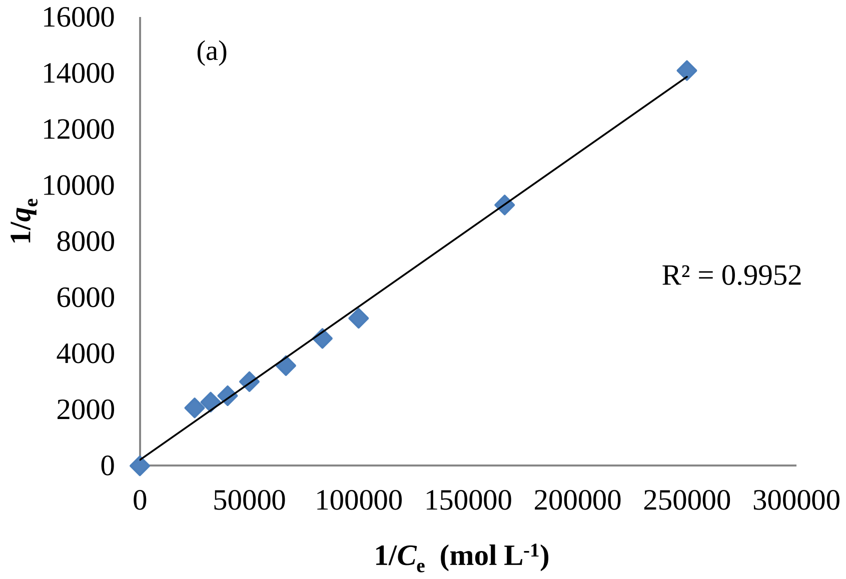


Figure 4.21: Plotting $1/q_e$ vs. $1/C_e$ for m and n calculations for 2,4−DCP: (a) CPE (b) CPE−βCD (c) CPE−βCD−IL.





‘**Figure 4.21**, continued’.



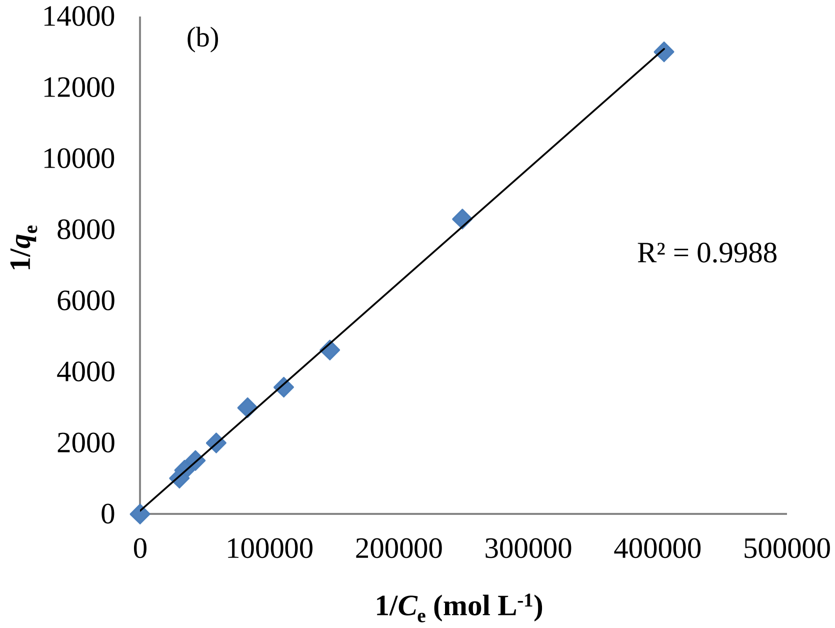
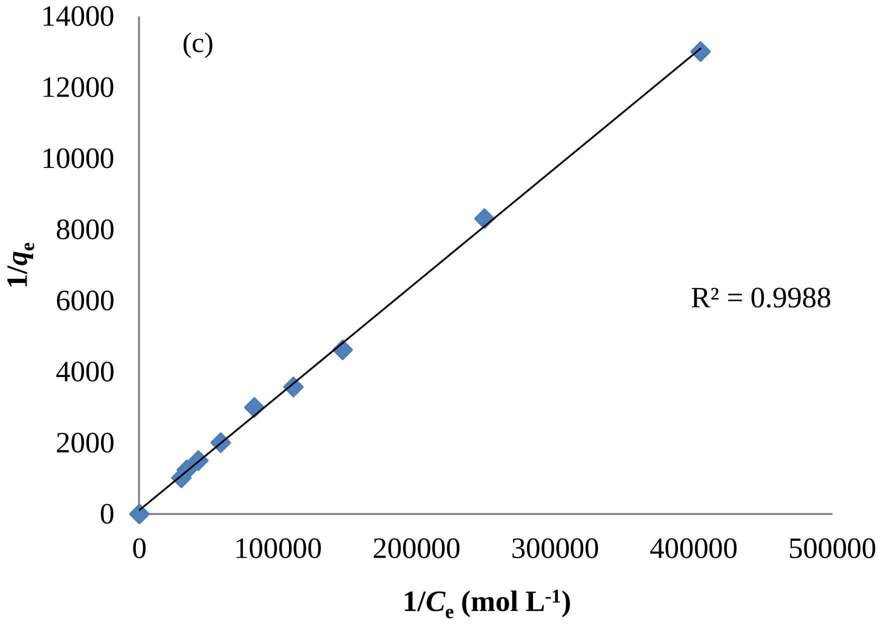


Figure 4.22: Plotting 1/q_e vs. 1/C_e for *m* and *n* calculations for 2,4,6−TCP: (a) CPE (b) CPE−βCD (c) CPE−βCD−IL.



'**Figure 4.22**, continued'.

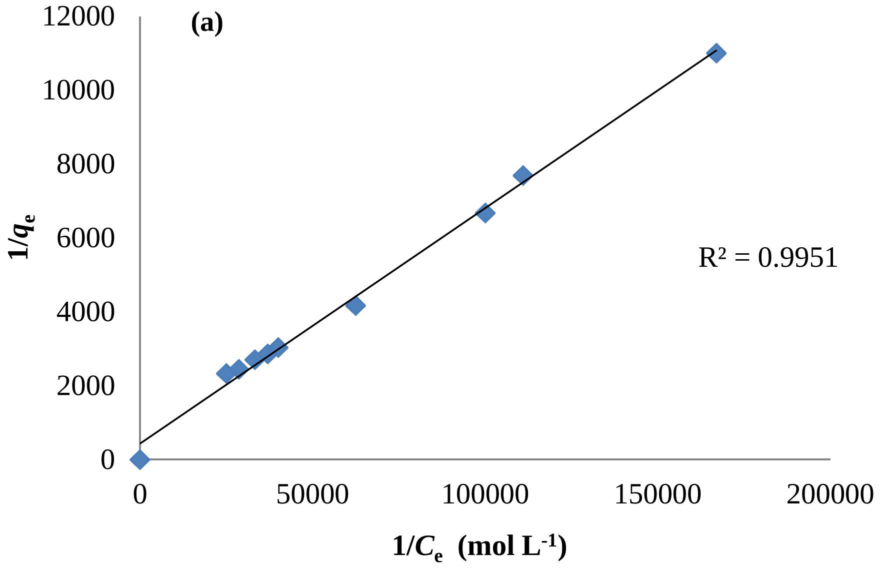
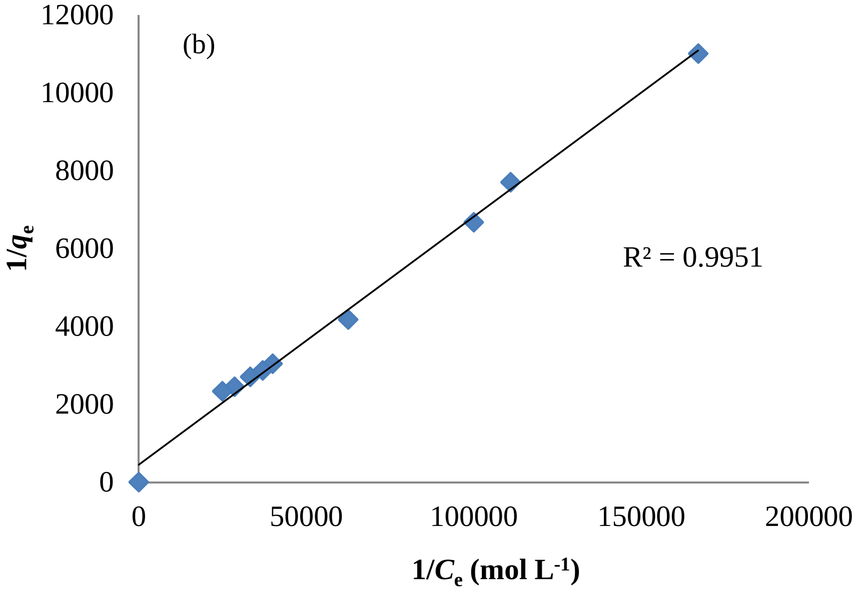
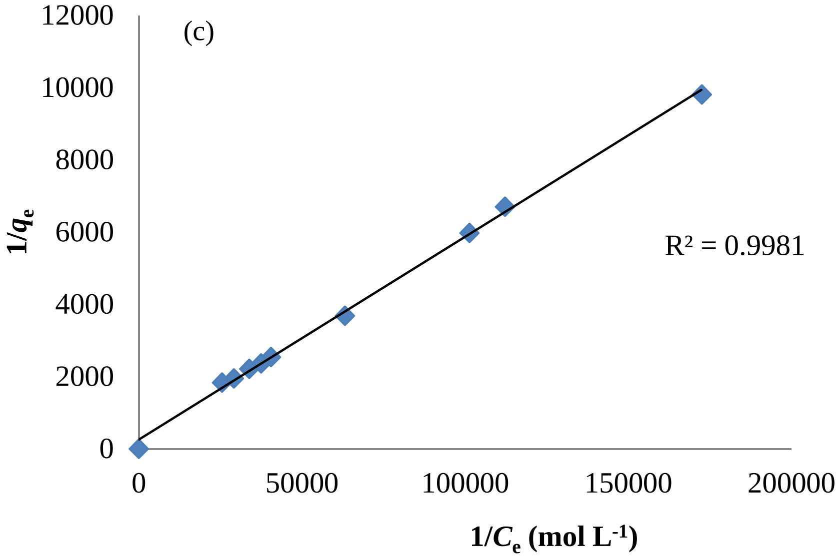


Figure 4.23: Plotting 1/q_e vs. 1/C_e for *m* and *n* calculations for 4−NP: (a) CPE (b) CPE−βCD (c) CPE−βCD−IL.





‘**Figure 4.23**, continued’.

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

A calculation procedure is outlined by using Eq. (4) to determine the amount concentration of surfactant required for the extraction efficiency up to the desired level. The amount of solubilization is defined as;

$$q_e = \frac{Q_d}{Gs} \tag{4}$$

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

$$E = \frac{Q_d}{Q_o} \tag{5}$$

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

$$C_e = \frac{Q_d\,(1-E)}{V_d} \tag{6}$$

where V_d is the volume of the dilute phase.

There are some assumptions have been made for determining the amount of the DC193C 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 its concentration too small compared to in the surfactant rich phase which is thousand times. Thus, G_s can represent the amount of the surfactant used in the feed (G_o) (Chen *et al.*, 2009; Wang *et al.*, 2003); and V_d (volume of the dilute phase) can approximate the volume of the initial solution before CPE (V_o) due to its volume so large. Based on these assumptions, the combining Eqs. (4) − (6) leads to:

$$\frac{G_o}{EQ_o} = \frac{1}{m} + \frac{V_o}{mnQ_o(1-E)} \quad (7)$$

$$\frac{G_o}{V_o} = Cos \quad (8)$$

$$\frac{Q_o}{V_o} = C_o \quad (9)$$

where Cos and C_o are the concentrations of the surfactant and solute in the feed, respectively. Combining Eqs. (7) − (9) in turn, leads to:

$$Cos = \frac{EC_o}{m} + \frac{E}{mn(1-E)} \quad (10)$$

Cos is function of C_o. The values of *m* and *n* were calculated for the aforementioned phenolic compounds in the three CPE systems. Therefore, using the concentration of the phenolic compounds in the feed and a desired level of extraction efficiency (E), Eq. (10) can be solved to obtain DC193C surfactant concentration required (Cos). Figure 4.24 (a), (b) and (c) shows the required DC193C surfactant concentrations in the three CPE systems for the phenolic compounds at 50ºC in the CPE processes with the desired extraction efficiency of 90 %.

As shown in Figure 4.24 (a), (b) and (c), more surfactant concentration was required as the concentration of feed in the three CPE systems increased so the desired extraction efficiency of 90% can be achieved. Generally, the solubilization behavior of organic compounds on non−polar and moderately polar polymeric adsorbent in aqueous solution is related to the hydrophobicity of solute; whereby the hydrophobic the solute, the more readily it can be solubilized (Li *et al.*, 2002). It can be related to Figure 4.24 (a), (b) and (c), the higher amount of DC193C surfactant was required for the hydrophilic 4−NP as compared to both hydrophobic compounds of 2,4−DCP and 2,4,6−TCP in the three CPE systems.

More DC193C surfactant was required in the CPE system for 2,4−DCP and 2,4,6−TCP compared to the CPE−βCD and CPE−βCD−IL systems. There were no much difference in the amount of DC193C surfactant required between the CPE−βCD and CPE−βCD−IL systems for 2,4−DCP and 2,4,6−TCP. Similarly there were no much difference in the amount of DC193C surfactant required in the CPE and CPE−βCD system for 4−NP. However, less amount of DC193C surfactant was required in the CPE−βCD−IL system. By comparing the three CPE systems, it can be concluded that more amount of DC193C surfactant was required for least interaction binding between solute, DC193C surfactant and modifier in CPE process.

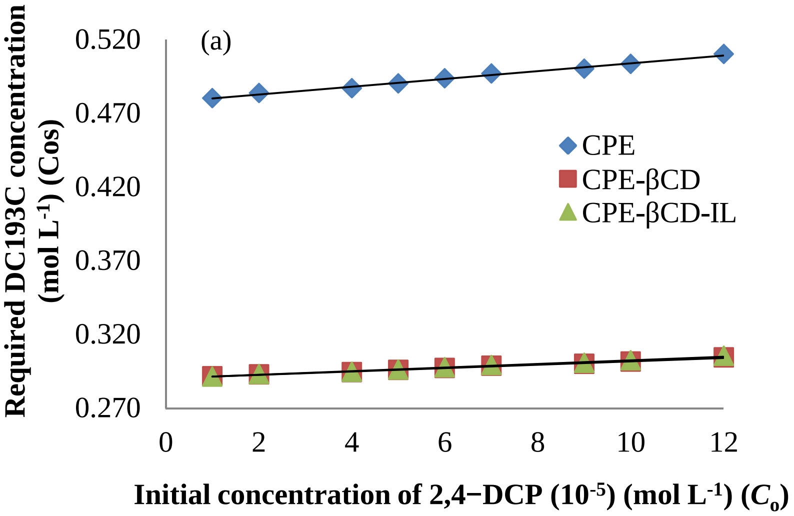
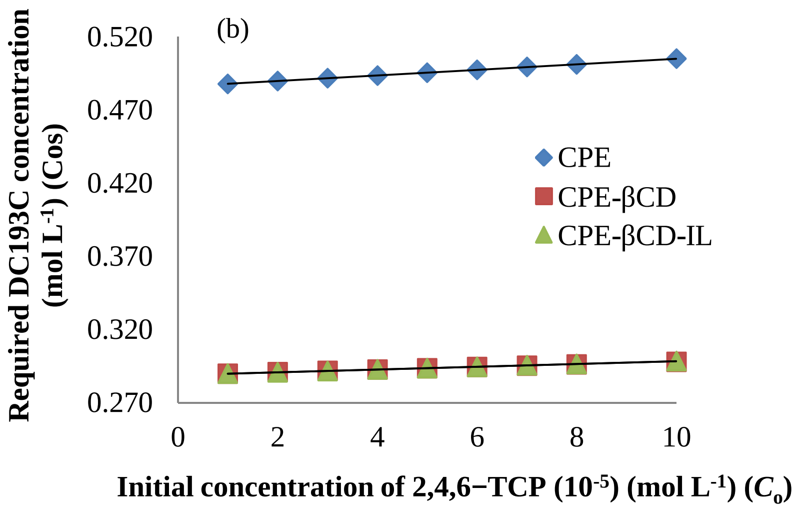
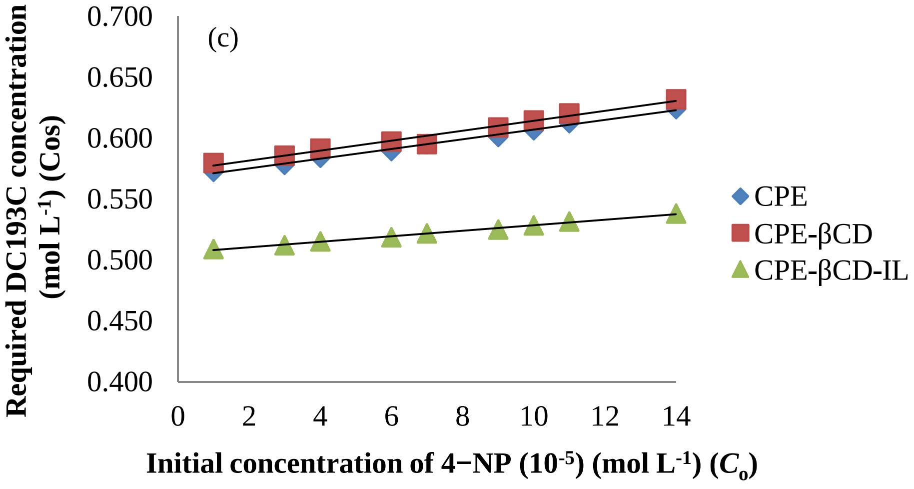


Figure 4.24: Variation of required surfactant concentration for different feed concentration of the phenolic compounds (a) 2,4−DCP (b) 2,4,6−TCP and (c) 4−NP in the different CPE systems with the desired extraction efficiency of 90 %.





‘**Figure 4.24**, continued’.

4.4 Thermodynamic study.

4.4.1 Determination of Thermodynamic parameters.

At certain temperature, an aqueous solution of DC193C surfactant system becomes turbid. This temperature is known as the cloud point temperature (CPT). Above the CPT, in the aqueous solution of the DC193C 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 in the three CPE systems for the phenolic compounds. The effect of the temperature on the extraction of the phenolic compounds in the three CPE systems using the DC193C surfactant has been discussed in Section 4.1.4. It is observed that the extraction efficiency increased significantly with the temperature. The thermodynamic parameters of ΔG^o, ΔH^o and ΔS^o for this extraction process are determined using the following equations for the phenolic compounds in the three CPE systems;

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \tag{11}$$

$$\log (q_e/C_\mathrm{e}) = \frac{\Delta S^o}{2.303R} + \frac{\Delta H^o}{2.303RT} \tag{12}$$

$$q_e = \frac{\text{Moles of phenol solubilized}}{\text{Moles of DC193C used}} = \frac{A}{X} \tag{13}$$

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

$$A = V_oC_o - V_dC_e \tag{14}$$

$$X = C_sV_o \tag{15}$$

where q_e is the mole of the phenolic compounds solubilized per mole of the DC193C surfactant. C_e is the equilibrium concentration of the phenolic compounds (mol L^{-1}) after the completion of the two phases and T is the temperature in Kelvin. q_e/C_e is called the solubilization affinity. A is the moles of phenol solubilized onto DC193C surfactant. 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 is the concentration of the surfactant in feed. The thermodynamic parameters ΔG^o, ΔH^o and ΔS^o are in the linear range of q_e versus the C_e plot that can be calculated by experimental data in the three CPE systems for the phenolic compounds. Referring to the Eq. (11), the values of Gibbs free energy (ΔG^o)

can be calculated by knowing the enthalpy of solubilization (ΔH^o) and the entropy of solubilization (ΔS^o). Eq. (12) has been used to calculate ΔH^o and ΔS^o that are obtained from a plot of log (q_e/C_e) versus 1/T (Purkait *et al*., 2009). The values of ΔG^o, ΔH^o and ΔS^o in the three CPE systems for the phenolic compounds were calculated at different temperatures and reported systematically.

4.4.2 Variation of Gibbs free energy (ΔG^o) during the CPE of the phenolic compounds.

Figure 4.25 show the variation of ΔG^o with different temperatures at constant surfactant concentration and the phenolic compounds concentration in the three CPE systems. It has been noted from the figure that the solubilization increases linearly with the temperature in the three CPE systems for the phenolic compounds. This increase in solubilization of the phenolic compounds with a rise in temperature can be explained on the basis of thermodynamic parameters such as the change in standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o). The thermodynamic parameters were shown in Table 4.5, 4.6 and 4.7 in the three CPE systems for 2,4−DCP, 2,4,6−TCP and 4−NP, respectively.

The negative values of ΔG^o for the phenolic compounds in the three CPE systems indicate that of these compounds solubilization process was spontaneous and thermodynamically favorable. The increase in the negative values of ΔG^o with temperature implies the greater driving force of solubilization which is confirmed by the greater extent of the extraction of these phenolic compounds in the three CPE systems with the increase in temperature.

The positive values of ΔH^o indicate that the solubilizations of the phenolic compounds in the three CPE systems were endothermic in nature. It has been supported by the increasing of the phenolic compounds solubilization in the three CPE systems with the increasing solution temperature studied within 25ºC – 80ºC. Increasing the temperature was known to indicate the rate of diffusion of the phenolic compounds molecules across the external boundary layer of the surfactant, owing to the decrease in the viscosity of the solution. The enhancement in the amount of solubilization might be due to the chemical interaction between DC193C surfactant and also modifier with the phenolic compounds molecules, creation of new binding sites or increased rate of intraparticle diffusion of these molecules into the surfactant at higher temperature (Tan *et al*., 2009). Purkait *et al*. (2009)., also noted similar observations and they suggested that the increase in the amount of solubilization with increase in temperature, might be due to the possibility of an increase in the numbers of binding sites for the solubilization as well as an increase in the mobility of the solutes molecules (Purkait *et al*., 2009).

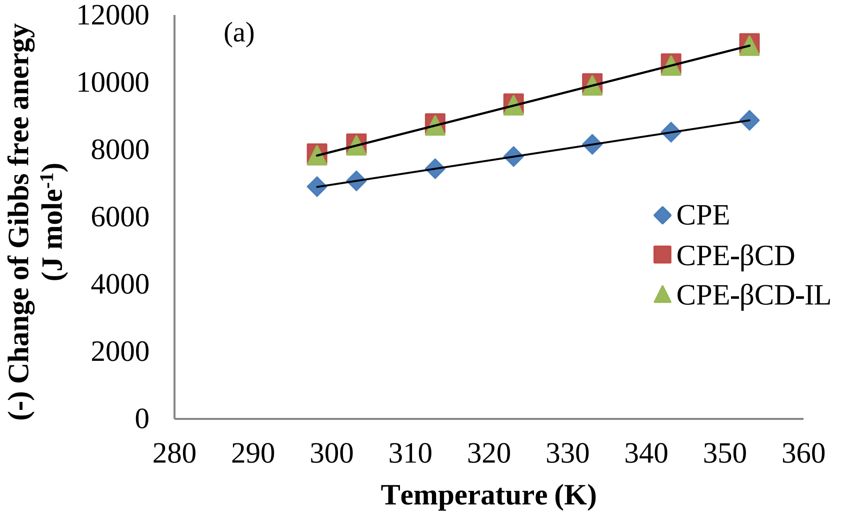
As discussed in Section 4.1.4, the operating temperature increases in the three CPE systems as the extraction efficiency of the phenolic compounds increased. This is due to high solubilization of these compounds with rising temperature. The effect of temperature can be explained on the basis of hydrogen bonding. In aqueous solutions of the phenolic compounds, there exists extensive hydrogen bonding between the phenolic compounds molecules and the water resulting in appreciable solubility. These hydrogen bonds get broken at higher temperature, and this would cause phenolic compounds to be less soluble and therefore exhibit higher tendency to surfactant surface and get solubilized rather than remaining in the solution. This would result in higher solubilization at higher temperature (Jain *et al*., 2004).

Meanwhile, the positive ΔS^{o} corresponds to a decrease in the degree of freedom of the solubilized species and that reflects good affinity of the phenolic compounds in the three CPE systems towards surfactant. The values of ΔG^{o}, ΔH^{o} and ΔS^{o} increase with the increased hydrophobicity of the phenolic compounds in the order; 4−NP < 2,4−DCP < 2,4,6−TCP in the three CPE systems. However, a different trend of order was observed in the three CPE systems for the phenolic compounds. The values of Δ*G*º, Δ*H*º and Δ*S*º in the three CPE systems for 2,4−DCP and 2,4,6−TCP increase and are stated as follows; CPE−βCD−IL ≈ CPE−βCD > CPE. Meanwhile, the values of Δ*G*º, Δ*H*º and Δ*S*º increase in the three CPE systems as the following order; CPE−βCD−IL > CPE−βCD ≈ CPE for 4−NP.

There must be a favorable net energetic driving force that pulls the guest into the β−CD's cavity to form inclusion complex (Del Valle, 2004). The thermodynamic parameters such as the standard free energy (Δ*G*º), the standard enthalpy change (Δ*H*º), and the standard entropy change (Δ*S*º) of the binding reaction are important to confirm the force of interaction of phenolic compounds with β−CD modifier as well as the βCD−IL modifier in the CPE system. Several interactions involved were hydrogen bonding, $\pi - \pi$ interaction, electrostatic attraction and inclusion complex between the βCD−IL with substrates were proposed previously in Section 4.2. A different behavior was observed for the phenolic compounds or DC193C surfactant complex with the βCD−IL; where upon complexation both positive enthalpic changes and entropic values were obtained, indicating that this inclusion is mainly entropically driven.

Apparently, when the phenolic compounds or DC193C surfactant was free in solution, it seems to have a strong interaction with its solvent shell. Upon binding, this solvent shell is broken up, leading to the partly unfavorable enthalpic change (Brewster and Loftsson, 2007; Jullian *et al.*, 2010). The positive values of Δ*H*º indicate that sorption process was endothermic. The apparent endothermic nature of the solubilization may contradict the well−known criteria of the spontaneity of the solubilization. In fact, the sorptions enthalpies solubilize do not enforce the reversible reaction but are consumed in the dehydration of the β−CD's cavity This is supported by the positive value of Δ*S*º that is related to the increased randomness of the system due to the liberation of water from the β−CD cavities during the sorption (Li *et al.*, 2010).

Similar interaction occurred between the phenolic compounds or DC193C surfactant complex with β−CD excludes electrostatic attraction.



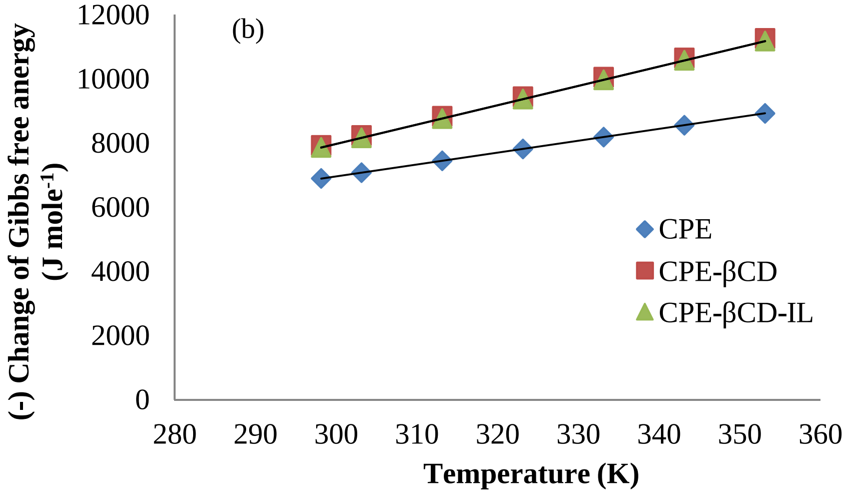
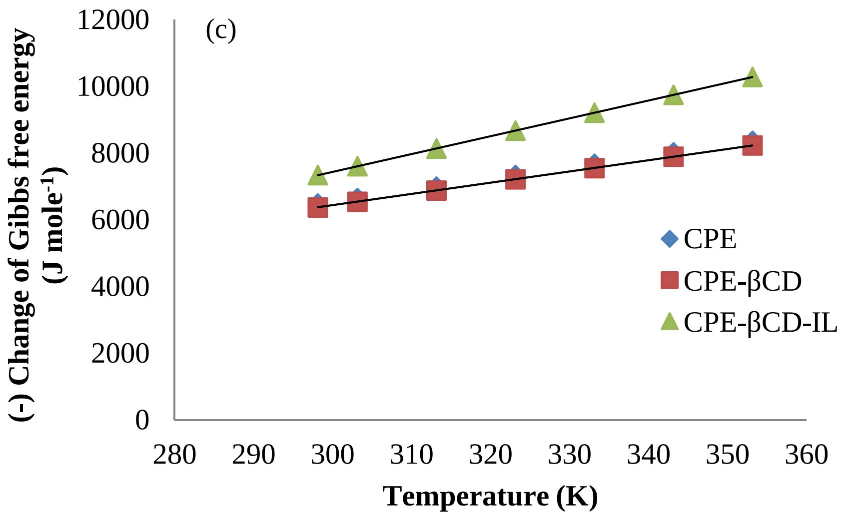


Figure 4.25: Variation of Gibbs free energy change (ΔG^{o}) with temperature at constant (a) 2,4−DCP, (b) 2,4,6−TCP and (c) 4−NP species concentration in the three CPE systems.



‘**Figure 4.25**, continued’.

Table 4.5:
Thermodynamic parameters in the three CPE systems for 2,4−DCP at different temperatures.

Systems	Temperature (K)	−Δ*G*º (J mol^{-1}) (x 10^{3})	Δ*H*º (J mol^{-1}) (x10^{3})	Δ*S*º (J mol^{-1} K^{-1}) (x 10^{1})
CPE	298.15	6.90	3.83	3.60
	303.15	7.08		
	313.15	7.44		
	323.15	7.80		
	333.15	8.16		
	343.15	8.52		
	353.15	8.88		
CPE−βCD	298.15	7.88	9.85	5.95
	303.15	8.18		
	313.15	8.78		
	323.15	9.37		
	333.15	9.96		
	343.15	10.56		
	353.15	11.15		
CPE−βCD−IL	298.15	7.83	9.85	5.93
	303.15	8.13		
	313.15	8.72		
	323.15	9.32		
	333.15	9.91		
	343.15	10.50		
	353.15	11.10		

Table 4.6:
Thermodynamic parameters in the three CPE systems for 2,4,6−TCP at different temperatures.

Systems	Temperature (K)	$-\Delta G^{o}$ (J mol^{-1}) (x 10^{3})	ΔH^{o} (J mol^{-1}) (x10^{3})	ΔS^{o} (J mol^{-1} K^{-1}) (x 10^{1})
CPE	298.15	6.90	4.14	3.70
	303.15	7.08		
	313.15	7.45		
	323.15	7.82		
	333.15	8.19		
	343.15	8.56		
	353.15	8.93		
CPE−βCD	298.15	7.94	10.12	6.06
	303.15	8.23		
	313.15	8.84		
	323.15	9.45		
	333.15	10.06		
	343.15	10.66		
	353.15	11.27		
CPE−βCD−IL	298.15	7.87	10.12	6.03
	303.15	8.17		
	313.15	8.78		
	323.15	9.38		
	333.15	9.98		
	343.15	10.59		
	353.15	11.19		

Table 4.7:
Thermodynamic parameters in the three CPE systems for 4−NP at different temperatures.

Systems	Temperature (K)	$-\Delta G^{o}$ (J mol^{-1}) (x 10^{3})	ΔH^{o} (J mol^{-1}) (x 10^{3})	ΔS^{o} (J mol^{-1} K^{-1}) (x 10^{1})
CPE	298.15	6.49	3.69	3.41
	303.15	6.66		
	313.15	7.00		
	323.15	7.34		
	333.15	7.68		
	343.15	8.02		
	353.15	8.37		
CPE−βCD	298.15	6.38	3.69	3.38
	303.15	6.54		
	313.15	6.88		
	323.15	7.22		
	333.15	7.56		
	343.15	7.90		
	353.15	8.23		
CPE−βCD−IL	298.15	7.34	8.62	5.35
	303.15	7.61		
	313.15	8.14		
	323.15	8.68		
	333.15	9.21		
	343.15	9.75		
	353.15	10.28		

CHAPTER 5

CONCLUSION

5.1 Conclusion.

The CPE technique combined with spectrophotometry offers several advantages such as low cost and safer with good extraction efficiency. The three CPE systems namely CPE, CPE−βCD and CPE−βCD−IL systems were successfully optimized for removal of the phenolic compounds from aqueous solution. Several parameters were evaluated such as the effect of DC193C surfactant concentration and volume, pH, β−CD and βCD−IL modifiers concentration and volume, equilibrium temperature and time, concentration of salt and analyte, and water content. Our experimental results indicate that high recoveries can be obtained at the optimized condition; 0.5 mL of 0.5 v/v% DC193C surfactant; 1.5 mol L^{-1} of Na_2SO_4; 50°C and 15 min incubation time; and 10 mg L^{-1}, 100 µL of the β−CD and βCD−IL modifiers for the removal of the phenolic compounds from aqueous in the three CPE systems.

In the CPE−βCD system, the results obtained has clearly shown the enhancement of 2,4−DCP and 2,4,6−TCP extraction compared to the CPE system. However, the extraction of 4−NP did not improve in the presence of β−CD modifier in the CPE−βCD system. The size of the hydrophilic 4−NP was incompatible with the β−CD’s cavity. Apart from that, the hydrophobic host of β−CD was favorable for hydrophobic guest to form inclusion complex. Due to these properties, the hydrophobic 2,4−DCP and 2,4,6−TCP were favorable to form inclusion complex with β−CD. Hence, the extraction efficiency of 2,4−DCP and 2,4,6−TCP can be enhanced in the presence of the β−CD modifier.

By adding the modifier of the βCD−IL to the CPE system, the $\pi - \pi$ interactions and electrostatic attraction may occur between the imidazolium ring and aromatic ring of the phenolic compounds. A better extraction performance of the 4−NP was attained in the presence of βCD−IL modifier as compared to the β−CD modifier. Nevertheless, the βCD−IL modifier did not improve the extraction of 2,4−DCP and 2,4,6−TCP due to the weak $\pi - \pi$ interactions. The $\pi - \pi$ interactions were enhanced with the increase of the number of nitro and chloro which are both in the electron−withdrawing groups. Since nitro has stronger electron−withdrawing ability than the chloro group, thus, the $\pi - \pi$ interactions can be enhanced by reducing the electron density of π electrons, diminishing the repulsive electrostatic interactions between the aromatic rings.

In the solubilization isotherm study, it was found that the experimental data of the solubilization amounts and concentration solutes had fitted the Langmuir type isotherm for the phenolic compounds in the three CPE systems. The straight line was 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 surfactant for the phenolic compounds in the three CPE systems. The values of monolayer solubilization capacity (*m*) of the DC193C surfactant with the phenolic compounds were found in proportion to their hydrophobicity, according to the following order; 4−NP < 2,4−DCP < 2,4,6−TCP in the three CPE systems. However, the energy of solubilization (*n*) was reversible to the values of *m* for the phenolic compounds in the three CPE systems. By comparing to the three CPE systems, the values of *m* and *n* depend on the capability of the CPE systems to extract the solutes. Based on the results, the extraction of the 2,4−DCP and 2,4,6−TCP can be enhanced in the presence of the β−CD modifier. On the other hand, the extraction of 4−NP can only be enhanced in the presence of the βCD−IL modifier. The phenolic compounds solubilize more into the surfactant rich phase if the extraction efficiency of phenolic compounds is high.

Thermodynamic parameters such as the change in Gibbs free energy ($\Delta G°$), change in enthalpy ($\Delta H°$) and change in entropy ($\Delta S°$) of the DC193C−phenolic compounds were studied. The results showed that the process was feasible from the thermodynamic studied. The spontaneity of the above phenolic compounds extraction was governed by the negative value of ΔG^o in the three CPE systems. The positive values of ΔS^o dictated that the solubilized phenolic compounds molecules were organized in a more random fashion on the mantle of an aqueous hydrophilic chain in the three CPE systems. The extraction processes were endothermic in nature, the fact also proven by the positive value of ΔH^o in the three CPE systems. The values of ΔG^o, ΔH^o and ΔS^o in the different systems for the 2,4−DCP and 2,4,6−TCP increases in this order; CPE−βCD−IL ≈ CPE−βCD > CPE. Meanwhile the values of ΔG^o, ΔH^o and ΔS^o increases in the different systems in this order; CPE−βCD−IL > CPE−βCD ≈ CPE for the 4−NP. However, the values of ΔG^o, ΔH^o and ΔS^o increase with the increased hydrophobicity of the phenolic compounds in the order; 4−NP < 2,4−DCP < 2,4,6−TCP in the three CPE systems.

In conclusion, the extraction of phenolic compounds in the CPE system can be enhanced by adding the modifiers depend on species. The hydrophobic of 2,4−DCP and 2,4,6−TCP extraction performance were enhanced in the presence of β−CD modifier. However, the extraction performance did not improve when the βCD−IL modifier was added. On the contrary, the βCD−IL modifier improves the performance of hydrophilic 4−NP compared to the native of β−CD modifier. Based on these findings, by adding the βCD−IL modifier in the CPE system, the removal of organic pollutant from aqueous solution can be enhanced due to their unique structure that can entrap hydrophobic as well as hydrophilic organic pollutant. On the other hand, non−ionic DC193C surfactant has low water content which can enhance the extraction efficiency. In addition, non−ionic DC193C surfactant and modifiers used in the CPE has made the micellar extraction procedure simple, greener and economical as highly desired for removal phenolic compounds from aqueous solution.

5.2 Future works.

A new method of dispersive cloud point micro−extraction (DCPME) termed temperature controlled non−ionic surfactant will be developed based on dispersive liquid−liquid micro−extraction (DLLME) for determination of organic pollutant in biological and water samples. In this approach, βCD−IL modifier will be used as a complexing agent and non−ionic of DC193C surfactant will be used as extraction and dispersive solvent. This method is expected to be simple, inexpensive and has higher enrichment factor. In addition, the method should be minimized in preparation time and consumption of toxic organic solvent.

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1. N. N. M. Zain, N. K. Abu Bakar, S. Mohamad & N. Md. Saleh. Optimization of a greener method for removal phenolic compounds by cloud point extraction and spectrophotometry. Journal of Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 118 (2014) 1121-1128.

2. N. N. M. Zain, N. K. Abu Bakar, S. Mohamad. Study of removal of phenol species by adsorption on non-ionic silicon surfactant after cloud point extraction methodology. Journal of Desalination and Water Treatment. (2014) 1-12. doi: 10.1080/19443994.987176.

3. Sharifah Mohamad, Nor Kartini Abu Bakar, Ahmad Razali, Hemavathy Surikumaran, Kaviraja Pandian, Muggundha Raoov, Nur Nadhirah Mohamad Zain and Kumuthini Chandrasekaram. Removal of Phosphate by Paper Mill Sludge: Adsorption Isotherm and Kinetic Study. Asian Journal of Chemistry. 26 (2014) 3545-3552.

4. N. N. M. Zain, N. K. Abu Bakar, S. Mohamad. Enhanced solubilization of chlorophenols from aqueous sample by β−cyclodextrin in cloud point extraction. (under review)

5. N. N. M. Zain, M. Raoov, N. K. Abu Bakar, S. Mohamad. Comparative studies of chlorophenol and nitrophenol towards β−cyclodextrin functionalizedionic liquid as modifier in cloud point extraction. (under review)

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1. Nur Nadhirah Mohamad Zain, Nor Kartini Abu Bakar & Sharifah Mohamad. 2012. Synthesis and characterization of Ionic Liquid-Modified Nanosilica for Inorganic and Organic Selenium Species. Universiti Malaysia Terengganu Annual Seminar (UMTAS 2012), 9-11 July 2012, Riyaz Heritage Marina & Spa, Kuala Terengganu, Malaysia. (Poster)

2. Nur Nadhirah Mohamad Zain, Nor Kartini Abu Bakar & Sharifah Mohamad. 2013. Development of Cloud Point Extraction Combined with Spectrophotometric Determination of Phenolic Compounds in Environmental Samples with Silicone Surfactant. The 2013 Asia-Pacific International Congress on Engineering & Natural Sciences (APICEN 2013), 16-18 April 2013, Bangkok, Thailand. (Oral)

3. Nur Nadhirah Mohamad Zain, Nor Kartini Abu Bakar & Sharifah Mohamad. 2013. Optimization of a Greener Method for Extraction Phenol Species by Cloud Point Extraction and Beta-Cyclodextrin as a Modifier and Spectrophotometry. Malaysian Polymer International Conference 2013 (MPIC 2013), 25-26 September 2013, Hotel Equatorial Bangi-Putrajaya, Bangi, Malaysia. (Poster)

4. Nur Nadhirah Mohamad Zain, Nor Kartini Abu Bakar & Sharifah Mohamad. 2013. Optimization of a greener method for extraction phenol species by cloud point extraction and beta-cyclodextrin attach with Ionic Liquid as a Modifier Combined with UV-Vis Spectrophotometry. International Conference

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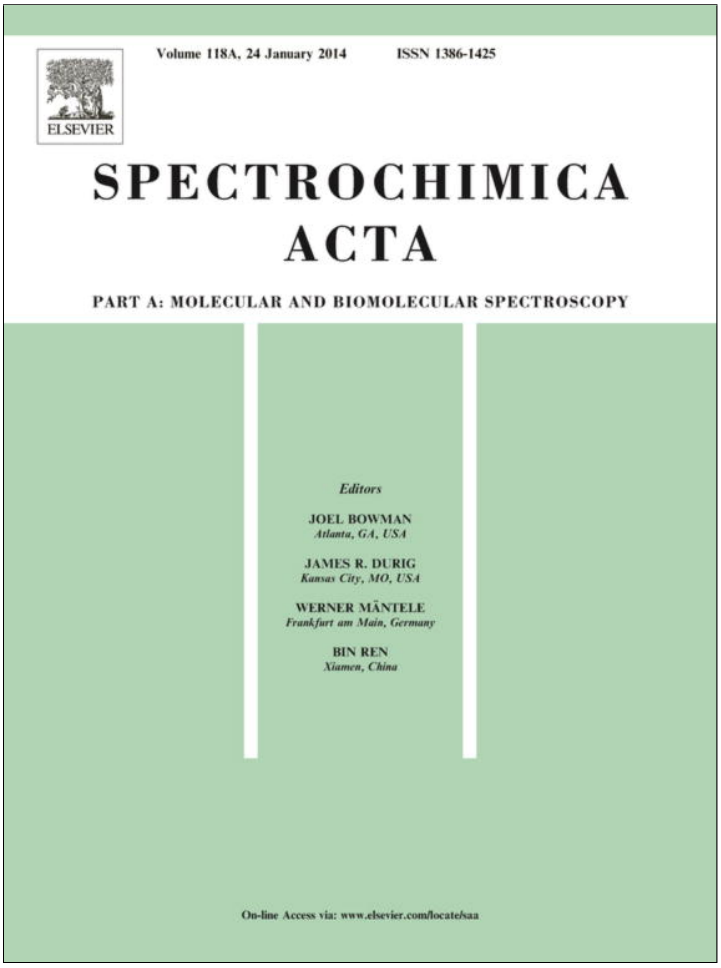
5. Nur Nadhirah Mohamad Zain. 1 Day Course on HPLC Method Development & Troubleshooting. 23rd February 2012 at Theater Hall, Ibnu Sina Institurte for Fundamental Science Studies, Universiti Teknologi Malaysia. (Participate)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Optimization of a greener method for removal phenol species by cloud point extraction and spectrophotometry

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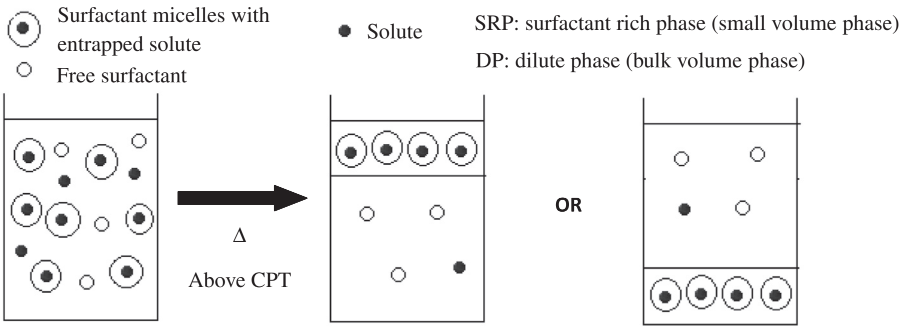
HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT

Schematic of cloud point extraction process.



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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

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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 copolyols, 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 polyethyleneglycol (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, λ_{max}: 318 nm), 2,4-dichlorophenol (molecular weight: 163, λ_{max}: 285 nm) and 2,4,6-trichlorophenol (molecular weight: 197.45, λ_{max}: 295 nm) that were purchased from Aldrich. Standard stock solutions of chlorophenols (1000 mg L^{-1}) were prepared in methanol and 4-nitrophenol (1000 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 compounds were used without further purification. HCl and NaOH were used for pH adjustment. Na_2SO_4 was prepared by dissolving an appropriate amount in distilled water.

Procedure

An aliquot of 1.0 mL of a sample or standard solution containing the analyte (10 mg L^{-1}), surfactant of DC193C (0.5 v/v%) and

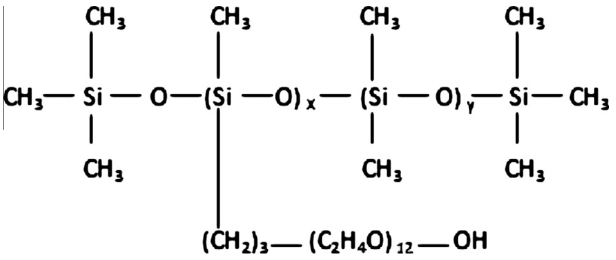

Fig. 1. The structure of silicone surfactant (DC193C).

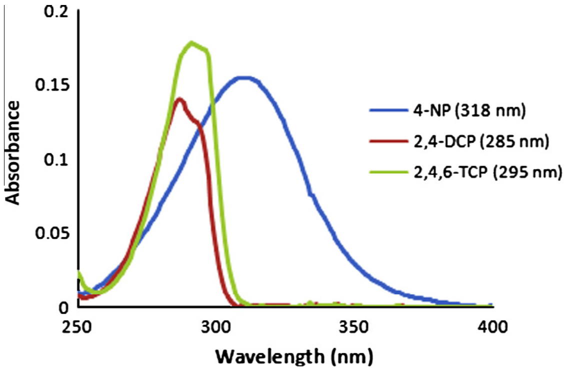

Fig. 2. The absorption of the UV–Vis spectra for individual phenol species at the respective absorption maxima in the surfactant rich phase after CPE.

1.5 mol L^{-1} of Na_2SO_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 Titiwangsa 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];

$$\text{Extraction efficiency, } (\%) = \frac{C_s V_s}{C_o V_o} \times 100$$

where C_s represents the phenol species concentration in the surfactant rich phase of volume V_s; C_o represents the phenol species concentration in the sample-surfactant mixture of volume V_o.

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.

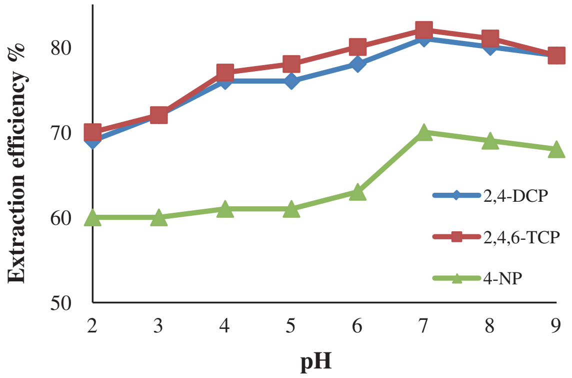

Fig. 3. Effect of pH on the extraction efficiency. Conditions: 10 mg L^{-1} of phenol species concentration, 0.5 (v/v%) DC193C, 1.5 mol L^{-1} Na_2SO_4 at 50 °C.

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_s/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_s) 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.

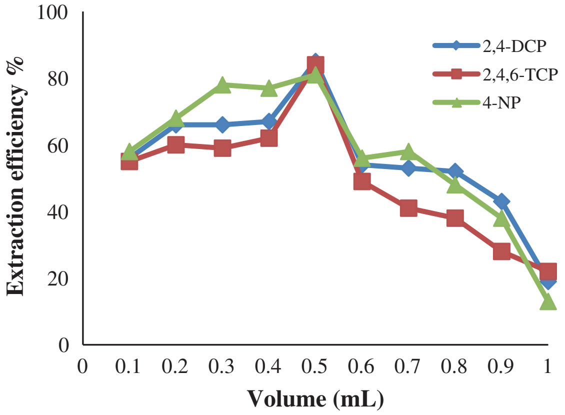

Fig. 5. Effect of amount surfactant on the extraction efficiency. Conditions: 10 mg L^{-1} of phenol species concentration, pH 7.0, 0.5 (v/v%) DC193C, 1.5 mol L^{-1} Na_2SO_4 at 50 °C.

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 80C 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_s) [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 tempera-

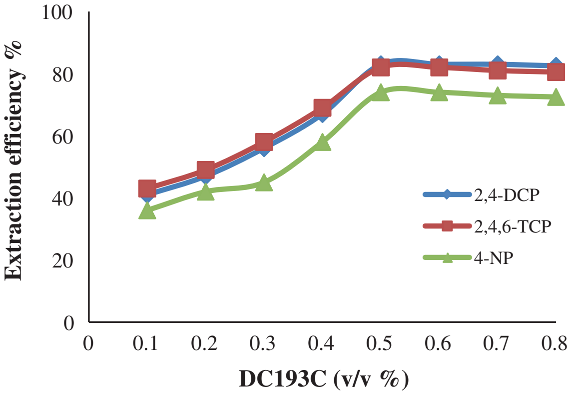

Fig. 4. Effect of concentration surfactant on the extraction efficiency. Conditions: 10 mg L^{-1} of phenol species concentration, pH 7.0, 1.5 mol L^{-1} Na_2SO_4 at 50 °C.

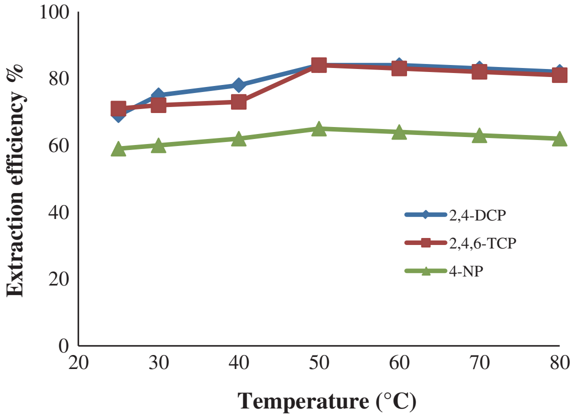

Fig. 6. Effect of temperature on the extraction efficiency. Conditions: 10 mg L^{-1} of phenol species concentration, pH 7.0, 0.5 (v/v%) DC193C, 1.5 mol L^{-1} Na_2SO_4.

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, 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 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, Na_2SO_4, NaOH, 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 behavior 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 $\leqslant$2.0 mg L^{-1} such as NaCl, NaOH, K_3PO_4, KCl and KI. This phenomenon is probably a solvophobic one. The kosmotropic ions, e.g. SO_4^{2-}, OH^-, Na^+ and PO_4^{3-}, which exhibit a stronger interaction with water molecule than water with itself are therefore capable of breaking water–water hydrogen bonds and beneficial to the phase separation formation. However, the chaotropic ions, e.g. Cl^-, K^+, I^- have the opposite effect because of their exhibiting weaker interactions with water than water itself and thus interfering little in the hydrogen bonding of the surrounding water. The effect of the cation nature is usually smaller than that of the anion. According to Ferreira and Teixeira (2010), the salting-out ability of the cations follows the Hofmeister series ($Na^+ > K^+$) and can be related to the ions from Gibbs' free energy of hydration (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^+ [43]. Therefore, Na_2SO_4 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 Na_2SO_4 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 (SO_4^{2-}); 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 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. 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 Na_2SO_4 is not always favorable. The addition of excessive Na_2SO_4 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

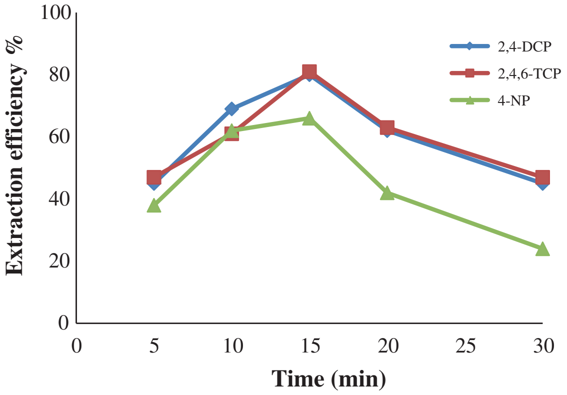

Fig. 7. Effect of incubation time on extraction efficiency. Conditions: 10 mg L^{-1} of phenol species concentration, pH 7.0, 0.5 (v/v%) DC193C, 1.5 mol L^{-1} Na_2SO_4 at 50 °C.

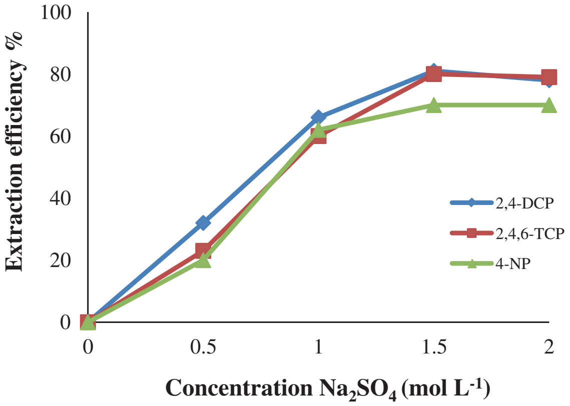

Fig. 8. Effect of concentration salt on the extraction efficiency. Conditions: Conditions: 10 mg L^{-1} of phenol species concentration, pH 7.0, 0.5 (v/v%) DC193C at 50 °C.

rich phase. The more concentration of Na_2SO_4, 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 cholorophenols (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^-, CO_3^{2-}, OH^-, I^- and NO_2^- 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.

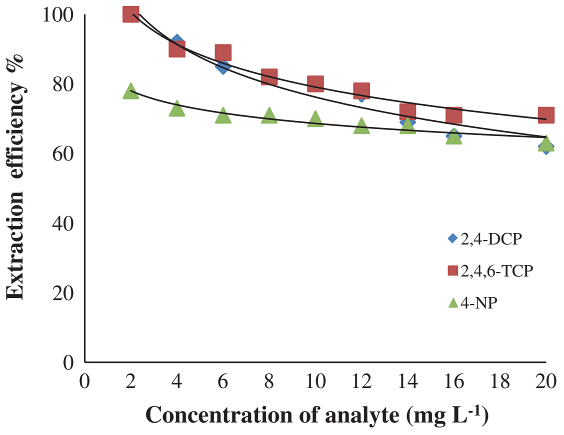

Fig. 9. Effect of concentration analytes on the extraction efficiency. Conditions: pH 7.0, 0.5 (v/v%) DC193C, 1.5 mol L^{-1} Na_2SO_4 at 50 °C.

Table 1
Interference study.

Ions	Concentration (mg L^{-1})	Extraction efficiency (%)		
		2,4-DCP	2,4,6-TCP	4-NP
Na^+	500	80	81	65
K^+	500	80	81	61
Cl^-	500	80	80	63
Br^-	500	83	84	61
CO_3^{2-}	500	80	80	68
OH^-	500	80	80	63
I^-	500	83	83	62
NO_2^-	500	81	81	60

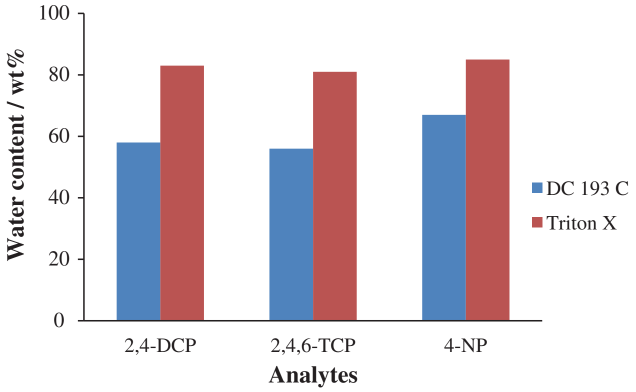

Fig. 10. Water content in the surfactant rich phase obtained by the CPE process with DC193C and Triton X at 0.5 (v/v%) surfactant concentration.

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;

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

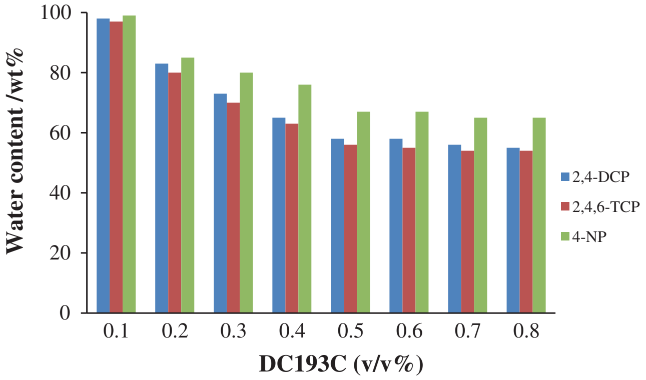

Fig. 11. Water content in the surfactant rich phase obtained by the CPE process with DC193C at different surfactant concentration.

Table 2
Method validation of the spectrophotometric of the phenol species using the CPE procedure.

Analytes	Linear range (mg L^{-1})	Correlation coefficient, R^2	% RSD, $n = 3$
2,4-DCP	0.4–2.0	0.997	0.15–1.40
2,4,6-TCP	0.4–2.0	0.993	0.16–0.60
4-NP	0.4–2.0	0.998	0.05–0.42

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.

Table 3
Recoveries of the three phenol species in spiked water samples.

Analyte	Sample[a]	Correlation coefficient, R^2	Spiking (mg L^{-1})	Recovery (% mean ± RSD, $n = 3$)
2,4-DCP	1		0.4	91 ± 1.5
		0.997	1.2	88 ± 2.4
	2		0.4	91 ± 2.8
			1.2	85 ± 2.2
2,4,6-TCP	1		0.4	96 ± 1.3
		0.993	1.2	86 ± 1.7
	2		0.4	97 ± 2.3
			1.2	87 ± 1.4
4-NP	1		0.4	77 ± 1.8
		0.998	1.2	69 ± 1.1
	2		0.4	81 ± 1.6
			1.2	70 ± 1.3

[a] Samples 1, 2 from lakes water.

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_2SO_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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Study of removal of phenol species by adsorption on non-ionic silicon surfactant after cloud point extraction methodology

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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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*Corresponding author.

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 ($1{,}000\ \text{mg L}^{-1}$) were prepared in methanol and 4-nitrophenol ($1{,}000\ \text{mg L}^{-1}$) 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.

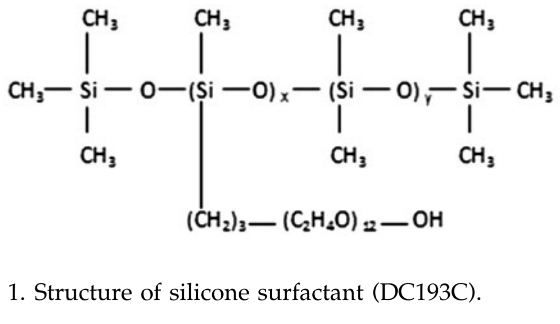

Fig. 1. Structure of silicone surfactant (DC193C).

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 ($10\ \text{mg L}^{-1}$), non-ionic surfactant of DC193C ($0.16\ \text{mol L}^{-1}$) and $1.5\ \text{mol L}^{-1}$ 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 $2.0–20.0\ \text{mg L}^{-1}$ 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];

$$\begin{aligned}\text{Extraction efficiency\%} &= \frac{C_s V_s}{C_o V_o} \times 100 \\ &= \frac{C_o V_o - C_w V_w}{C_o V_o} \times 100 \qquad (1)\end{aligned}$$

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].

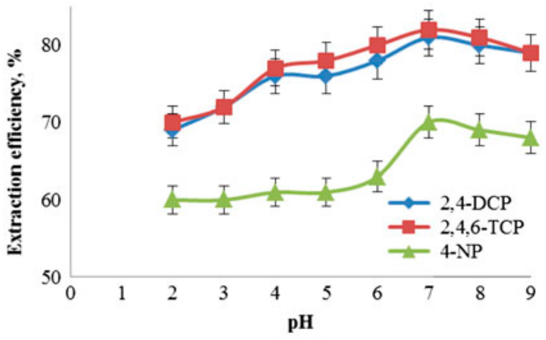

Fig. 2. Effect of pH on the extraction efficiency. Conditions: 10 mg L^{-1} of phenol species concentration, 0.5 (v/v%) DC193C, 1.5 mol L^{-1} Na_2SO_4 at 50˚C.

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

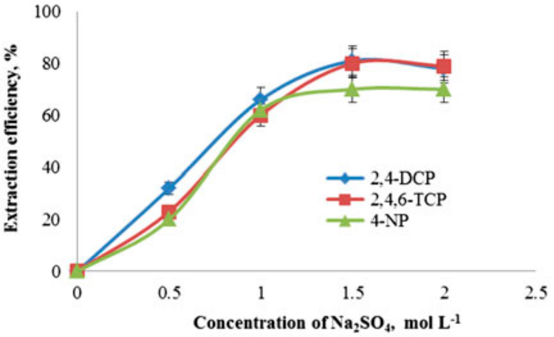

Fig. 3. Effect of concentration salt on the extraction efficiency. Conditions: 10 mg L^{-1} of phenol species concentration, pH 7.0, 0.5 (v/v%) DC193C at 50°C.

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 $\cdot$ 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.

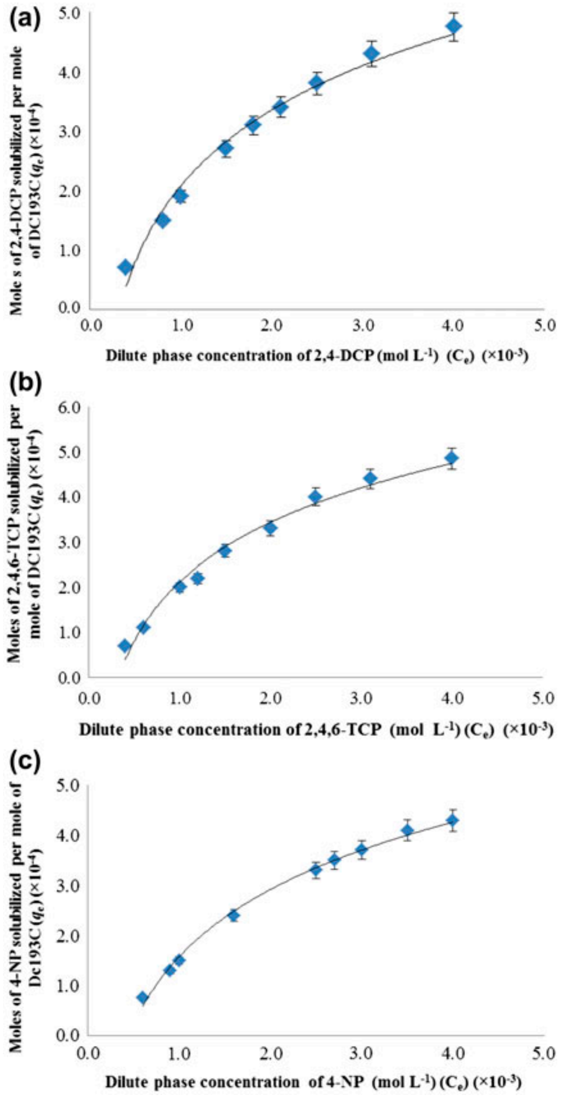

Fig. 4. Solubilization isotherm of the three phenol species over the DC193C surfactant: (a) DC193C-DCP, (b) DC193C-TCP, and (c) DC193C-NP.

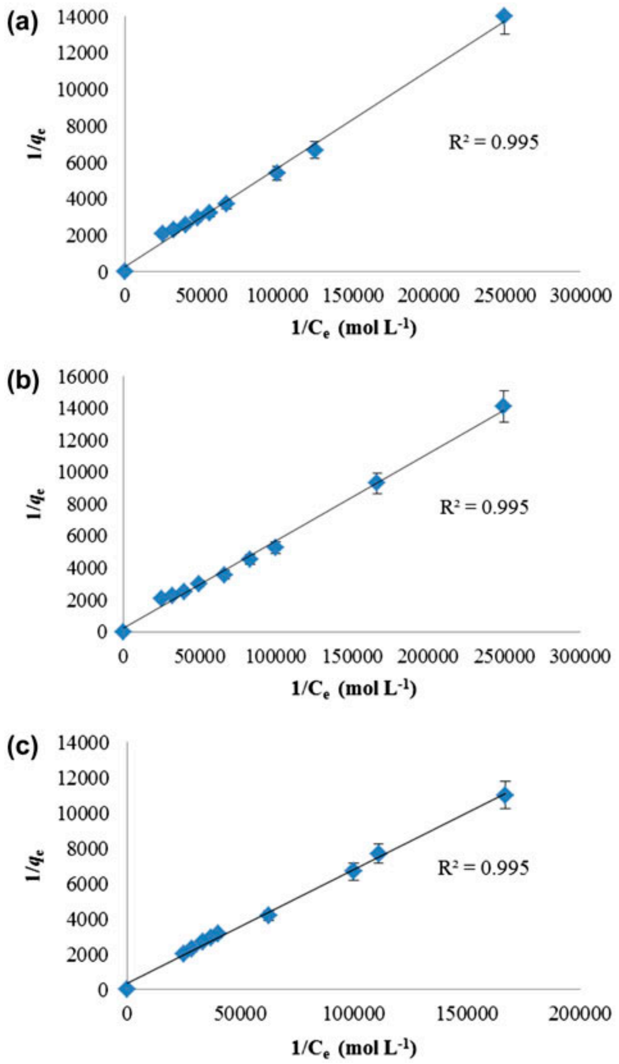

Fig. 5. Plotting $1/q_e$ vs. $1/C_e$ for m and n calculations: (a) 2,4-DCP, (b) 2,4,6-TCP, and (c) 4-NP.

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;

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

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

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

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.

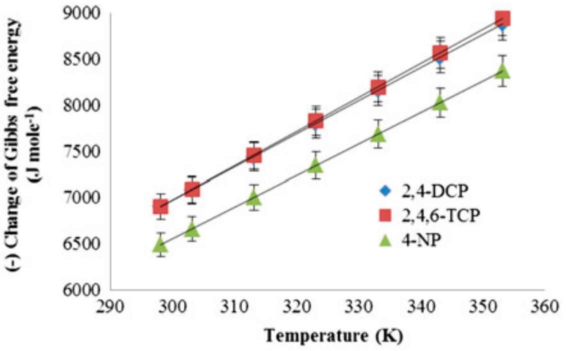

Fig. 6. Variation of Gibbs free energy change (ΔG°) with temperature at constant phenol species concentration for the three phenol compounds.

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}) ($\times 10^3$)	ΔH° (J mol^{-1}) ($\times 10^3$)	ΔS° (J mol^{-1} K^{-1}) ($\times 10^1$)
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

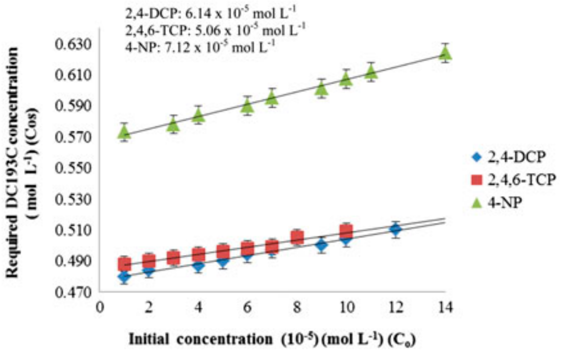

Fig. 7. Variation of required surfactant concentration for different feed concentrations of phenol compounds with the desired extraction efficiency of 90%.

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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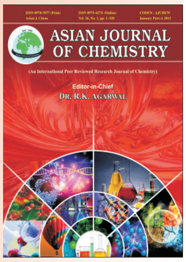

Removal of Phosphate by Paper Mill Sludge: Adsorption Isotherm and Kinetic Study

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Phosphate ions have been removed from aqueous solution by paper mill sludge. The influences of experimental conditions such as pH, amount of adsorbent, initial concentration of phosphate, adsorption isotherm and adsorption kinetics of paper mill sludge were studied. The adsorption of phosphate was more efficient in the basic pH region (pH 12). Pseudo second-order model fits better than the pseudo first-order model for adsorption kinetic data and indicates the adsorption process is based on chemisorptions. The calculated activation energy (E_a) is 37.01 J/mol which further suggests that the sorption of phosphate by paper mill sludge was based on chemical adsorption. Consequently, the equilibrium isotherm data were fitted well to Langmuir isotherm with maximum adsorption capacity of 12.65 mg/g. From the study, it showed that paper mill sludge has the potential to be utilized as a cost effective and high capability adsorbent for removal of phosphate from aqueous solutions.

Keywords: Paper mill sludge, Phosphate, Removal, Kinetics, Adsorption.

INTRODUCTION

Industrial sectors play an important role in the growth of the world economy by providing services and products that improve the quality of people's lifestyle. However, the rapid industrialization generates huge amounts of wastes which greatly affect the environment. The increasing amounts of industrial wastes require a larger space of landfill and expensive treatment for disposal. This causes a detrimental pollution effect on the soil, water and air[1]. One of the industries that generate quite large amounts of industrial waste is the pulp and paper production. This industry produces large amount of sludge as a result from their wastewater treatment plant. The primary method of disposal for paper mill sludge is mainly through land application and land filling[2]. Land filling costs are rising because of stringent regulation, taxes and declining capacity. With landfill space becoming scarce and expensive, sludge are being burned or incinerated to reduce their volume and to recover part of the energy that they contain[3]. Expensive treatment of land disposal necessitates other means of treatment which is more economical and other alternatives used of these waste for beneficial application.

A recent alternative method to overcome this problem is by utilization of the industrial waste for other valuable applications. This alternative method allows the industrial sector to reduce the cost of disposal and at the same time reduces the cost of the manufacturing process, enhances the efficiency of resource utilization and most importantly reduces the negative impacts on the environment and human health. Utilization of waste material for other valuable applications will balance the increasing demands of limited natural resources by providing alternative resources and reduces the dependency on natural resources[1].

Paper mill sludge is mainly composed of organic matter which is added to the paper or pulp whereas inorganic compounds (mainly calcium carbonate, kaolinite and talc) are used as fillers and coating[4]. Some studies had been done using material containing calcium such as fly ash and calcite to remove phosphate from waste water[5]. In view of the fact that the calcium content in the paper mill sludge is high, hence we investigated the efficiency of paper mill sludge as adsorbent for removal of phosphate from aqueous solution. Phosphate wastes are usually being discharged into rivers causing harmful effects to the environment and human health[6]. The excess of phosphate will cause eutrophication which will lead to imbalance to an ecosystem. Recently, phosphate is treated using chemical, biological and physical treatment processes which have their own advantages and disadvantages. However, these processes are expensive. In addition, employing environmental friendly methods for treatment is emphasized much more these days. The utilization of paper mill sludge as adsorbent for phosphate removal could help in this regard, in addition to re-using of these waste materials, which can be an advantage.

Considering the environmental problems from both solid waste of paper mill sludge and phosphate contamination, the removal of phosphate using paper mill sludge will be a good solution for both problems. Most researchers studied the removal of phosphate by modification of paper mill sludge before using it for phosphate removal[7-10]. Nevertheless, in this study, raw paper mill sludge was used for phosphate adsorption without any modification. The use of paper mill sludge as an adsorbent was studied and optimized under different controlling parameters including the effects of pH, initial concentration of phosphate, dosage of paper mill sludge and the contact time. The adsorption kinetics and adsorption isotherm of phosphate were also investigated.

EXPERIMENTAL

Functional groups of adsorbent were investigated using the fourier transform infrared spectrometry (FTIR). The spectra were recorded on a Perkin Elmer FTIR RX1 Spectrophotometer at ambient temperature using a KBr disk method. Qualitative analysis of calcite using X-ray diffraction (XRD) was carried out by using XRD Siemens D5000 diffraction with CuK_α radiation ($\lambda = 0.15406$ nm).

Artificial orthophosphate standard solutions were used throughout the adsorption test. A stock solution of 1000 mg/L in orthophosphate was prepared by dissolving a certain amount of chemically pure sodium dihydrogen orthophosphate in ultrapure water. An aliquot of the stock solution was further diluted with ultrapure water to prepare the desired experimental concentrations. All standards are daily prepared to avoid possible precipitation of phosphate species. IC effluent was prepared using sodium bicarbonate and sodium carbonate in the ratio of 8:1. The effluent was daily prepared to maintain effluent quality and condition for phosphate quantification.

Sampling of paper mill sludge: Paper mill sludge sample was collected from Union Paper Industries Sdn. Bhd. in Bentong, Pahang, Malaysia. The paper mill sludge was collected randomly and packed in plastic bags before keeping it in the freezer prior to experimental steps.

Preparation of adsorbent material: Paper mill sludge was first crushed mechanically with a jaw crusher then it was dried in an oven at 110 °C for 24 h and then crushed again. Samples were sieved and stored in the desiccators.

Adsorption measurement: The batch experiment was carried out with a defined amount of adsorbent sample in a 100 mL bottle sample. A defined volume of the phosphate concentration was prepared from a stock solution by adding ultra pure water. The pH of the phosphate solution was then adjusted to the desired value and added to the bottle container. The mixture was stirred at 200 rpm for a defined period. After a certain period of stirring, filtering process was applied to separate solid from liquid. The supernatant was then subjected to ion chromatography for analysis. The amount of phosphate adsorbed per unit mass of the adsorbent (Q_e) was calculated as follows:

$$Q_e = \frac{(C_o - C_e)V}{W} \qquad (1)$$

The percentage of adsorbate adsorbed on the polymer (removal efficiency, R (%)) was calculated by the following equation:

$$R\ \% = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

where, C_o and C_e are the intial and equilibrium concentration of solutions (mg/L), respectively. V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used.

RESULTS AND DISCUSSION

To ascertain the presence of functional groups in the paper mill sludge, FT-IR spectra was employed. Fig. 1 shows the FTIR spectrum of paper mill sludge. The observed features between 3500-3000 cm^{-1} and the band around 2900-2800 cm^{-1} could be attributed to O-H group of cellulose and the CH_2 groups, respectively. The bond at 1630 cm^{-1} was mainly assigned to the O-H group. This O-H group is the characteristic of the deformation vibration of O-H group. The presence of $CaCO_3$ leads to a broad band at 1416 cm^{-1} indicates the abundance of calcite in the paper mill sludge. Meanwhile an absorption band at 1161 cm^{-1} and 1107 cm^{-1} could be attributed to the C-O-C bond while the band 1031 cm^{-1} is the vibration of glucose unit ring involving stretching of C-O and O-H. Finally, the absorption band at 872 cm^{-1} corresponds to the C-O-C bond[11].

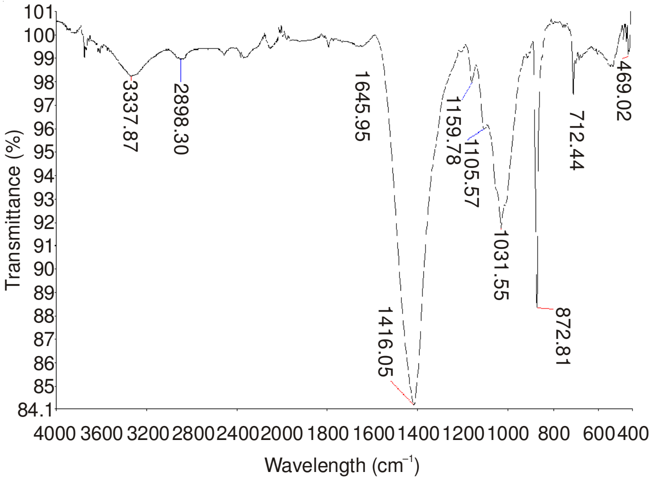

Fig. 1. FTIR spectrum of paper mill sludge

The XRD pattern of paper mill sludge (Fig. 2) shows the main crystalline constituent is calcite. The most intense peak of calcite is at $2\theta \approx 30°$. XRD result confirmed the abundance of $CaCO_3$ in the paper mill sludge. The abundance of calcite in paper mill sludge is important for phosphate adsorption from water solution since its presence will enhance the reaction of calcium phosphate precipitation[5].

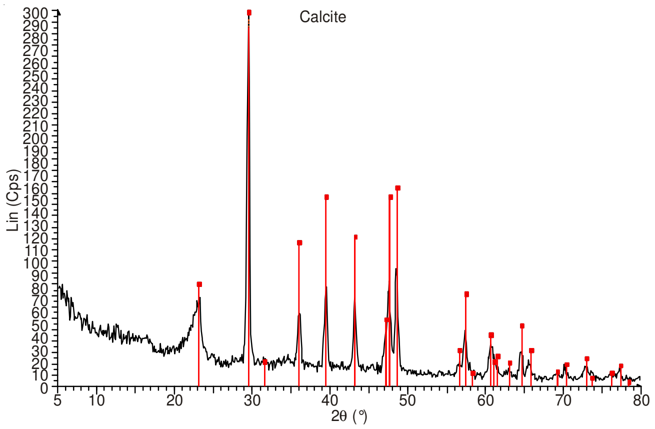

Fig. 2. XRD pattern of calcite in the paper mill sludge

Adsorption properties of adsorbent

Effect of pH on phosphate removal by paper mill sludge: The pH of the system is an important parameter in adsorption studies. The protonation reaction of phosphate is reported elsewhere[5]. It is stated that increasing of pH produces more negative charge to the phosphate species. $H_2PO_4^-$ and HPO_4^{2-} species are present in the pH region 5-10. The concentration of $H_2PO_4^-$ species is higher for acidic pH while HPO_4^{2-} species is higher in pH region 7-10. For pH between 10 and 12, HPO_4^{2-} predominates, the PO_4^{3-}, but when the pH is higher than 12.5, the concentration of PO_4^{3-} becomes more significant. In this work, the effect of pH was examined in the pH region between 7 and 12. The relationship between the initial pH of the solution with the adsorption capacity of phosphate is shown in Fig. 3. The adsorption capacity was increased from 0.56 to 2.21 mg/g with increasing initial pH from 7 to 12. Higher content of calcite in paper mill sludge enables it to interact with phosphate species. With the increase of pH, the deprotonation reaction of phosphate obtained more negative charges which enhance the electrostatic interaction between phosphate species and calcite in the paper mill sludge[5]. Therefore, pH 12 was selected as the optimum pH for phosphate removal from solutions. The adsorption process could be possibly described by the following reaction:

$$Ca^{2+} + H_2PO_4^- \longrightarrow CaH_2PO_4^+$$
$$Ca^{2+} + HPO_4^{2-} \longrightarrow CaHPO_4$$
$$Ca^{2+} + PO_4^{3-} \longrightarrow CaPO_4^-$$

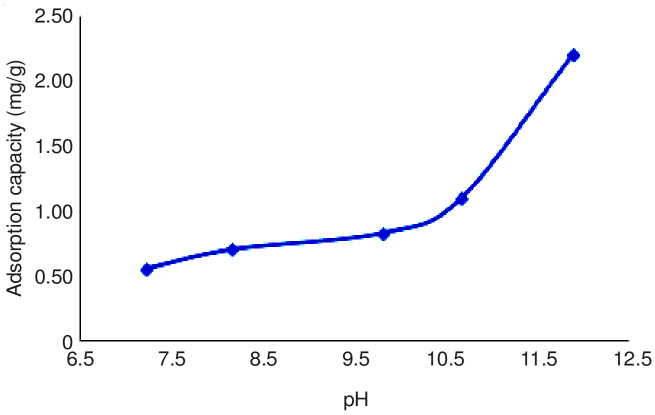

Fig. 3. Adsorption capacity of phosphate removal by paper mill sludge at various pH conditions

Effect of adsorbent dosage of paper mill sludge on phosphate removal: The effect of the adsorbent dosage was determined at pH 12 with shaking time of 0.5 h at room temperature and 100 mg/L of initial phosphate concentration by varying the mass of adsorbent. Fig. 4 showed that the percentage of phosphate removal increased rapidly from 46 to 85 % with increasing the adsorbent mass from 0.2 to 1 g. However, the adsorption capacity decreased from 4.27 to 1.62 mg/g, respectively. The phosphate removal was greater with the increase in paper mill sludge due to the increase in surface area and adsorption sites available for adsorption. The decline in adsorption capacity is basically due to the site remaining unsaturated during the adsorption process[12]. The amount of paper sludge for further adsorption experiments was selected as 0.5 g because the phosphate removal and adsorption capacity were found to be optimum at 71 % and 2.7 mg/g, respectively.

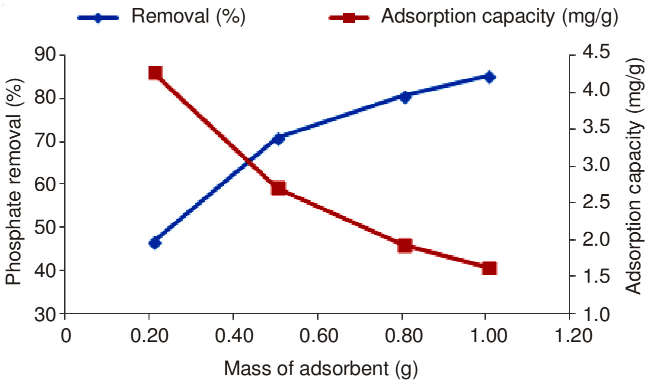

Fig. 4. Effect of adsorbent dosage of paper mill sludge on the adsorption capacity and percentage removal of phosphate

Effect of initial concentration of phosphate on adsorption: The adsorption experiments were performed to study the effect of initial phosphate concentration by varying it from 50 to 300 mg/L while maintaining the amount of paper mill sludge (0.5 g). Fig. 5 shows that with the increase in phosphate concentration, the percentage of removal decreased from 95 to 83 % and adsorption capacity increased from 2.07 to 9.97 mg/g. The decrease in percentage removal can be explained by the fact that the adsorbent had a limited number of active sites which would become saturated above a certain concentration. The increasing phosphate concentration in paper mill sludge influences supersaturating and decreases the efficiency of the precipitating system[13]. The greater value in adsorption capacity was experienced with the increase in phosphate concentration due to the utilization of more active sites available in the paper mill sludge for the adsorption at higher concentration[14].

Kinetics of phosphate adsorption by paper mill sludge: The rate of phosphate adsorption by paper mill sludge was measured as a function of shaking time at three different temperatures (30, 45 and 70 °C). The adsorption process of phosphate was rapid at the initial stage and slowed when approaching equilibrium (Fig. 6). The equilibrium time for phosphate adsorption can be considered at 24 h and becoming stable after longer reaction times. The kinetics results indicated that the sorption process was increased with the increase in the solution temperature from 30 to 70 °C.

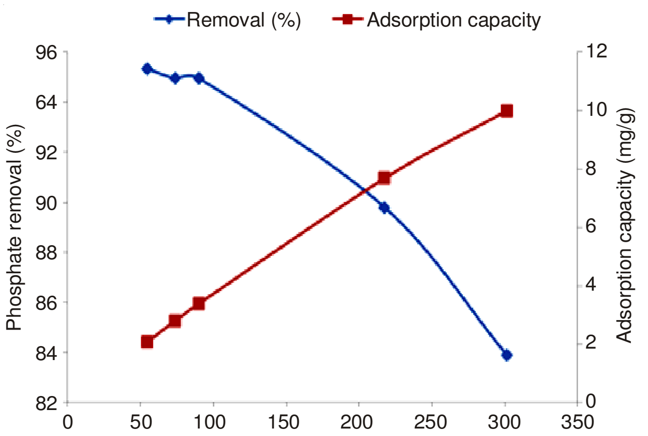

Fig. 5. Effect of initial concentration of phosphate on the adsorption capacity and percentage removal of phosphate (conditions: sorbent dosage = 0.5 g, pH = 12, shaking time = 24 h)

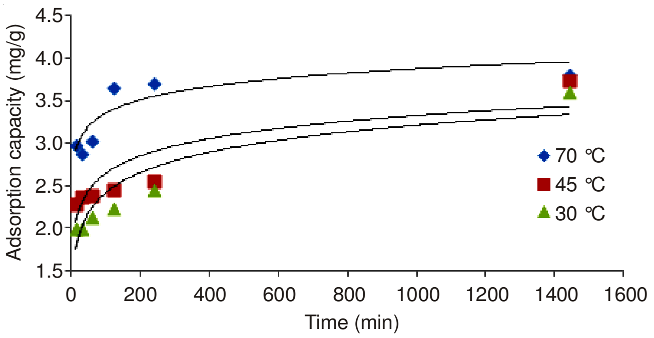

Fig. 6. Adsorption rate of phosphate by paper mill sludge (conditions: sorbent dosage = 0.5 g, initial concentration = 100 mg/L, pH = 12)

The kinetics of removal of phosphate is explicitly explained in the literature using pseudo first-order, second-order kinetics models[15,16], Elovich[17] and intraparticle diffusion mode[l18]. The mechanism for the removal of phosphate may involve the following four steps[19]: (1) migration of the sorbate from the bulk of the solution to the surface of the sample; (2) diffusion of the sorbate through the boundary layer to the surface of the sorbent; (3) adsorption of the sorbate at an active site on the surface of the sample; (4) intraparticle diffusion of the sorbate into interior pores of the sorbent particles. The boundary layer resistance will be affected by the rate of adsorption with an increase in the contact time, which will reduce the resistance and increase the mobility of the sorbate during adsorption. Since the uptake of sorbates at the active sites of samples is a rapid process, the rate of adsorption is governed mainly by either the rate of liquid phase mass transfer or the rate of intraparticle mass transfer. Hence in this work, the sorption rates were analyzed using a pseudo first-order model (eqn. 3), a pseudo second-order model (eqn. 4), Elovich model (eqn. 5) and intraparticle diffusion kinetic model (eqn. 6) as following:

$$\log (Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303} \qquad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1t}{Q_e} \qquad (4)$$

$$Q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln t \qquad (5)$$

$$Q_t = k_3 t^{0.5} + Q_0 \qquad (6)$$

where Q_e, Q(t) and Q_0 (mg/g) are, respectively, the amounts of sorption at equilibrium, the time t and the saturated state and k_1 (1/min), k_2 (g/mg min)) and k_3 (mg/(min$^{1/2}$ g)) are the rate constants for pseudo first-order, pseudo second-order and intraparticle diffusion, respectively α (mg/g min^{-1}) represent initial sorption rate while β (g/mg) is related to the extended of surface coverage and activation energy. The resulting sorption rate constants are listed in (Table-1). The correlation coefficients data for pseudo second-order model (Fig. 8) fits better than first-order kinetic model (Fig. 7) and Elovich model (Fig. 9) as shown in Table-1 for the all studied temperature with R_2 value > 0.99. The calculated Q_e values (Table-1) were similar with the experimental values which indicate that the sorption system follows the second-order kinetic model and further confirms that the adsorption process is based on chemisorptions. The resulting phosphate sorption rate constants (k_2) for the pseudo second-order model at various temperature are clearly different, following the increasing order from 6.18, 8.17 and 30.22 for 30 , 45 and 70 °C, respectively and this indicates that the adsorption process is endothermic. It can be explained by the availability of more active sites of adsorbent at higher temperatures.

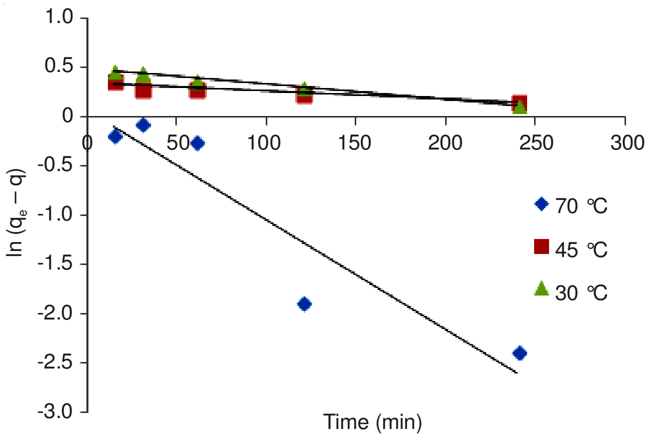

Fig. 7. First-order kinetic plot for sorption of phosphate by paper mill sludge

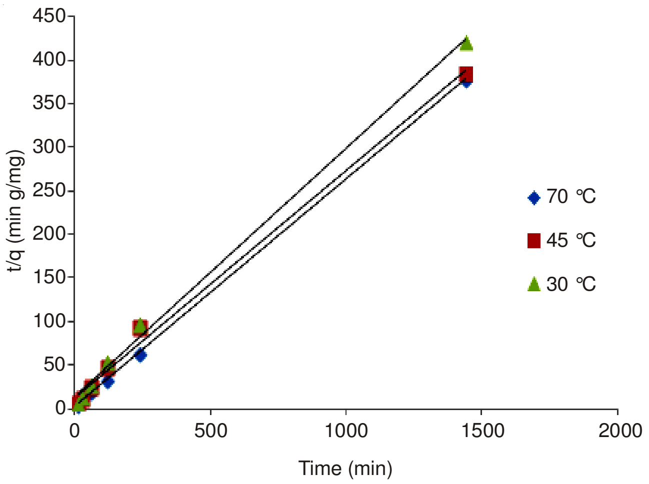

Fig. 8. Second-order kinetic plot for sorption of phosphate by paper mill sludge

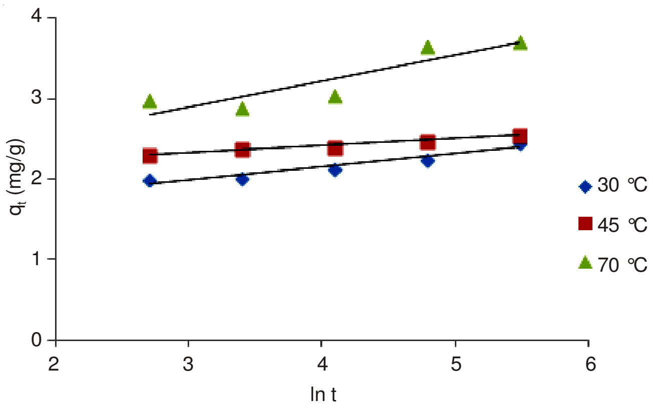

Fig. 9. Elovich kinetic plot for sorption of phosphate by paper mill sludge

Pseudo first-order, pseudo second-order models and Elovich models cannot identify the diffusion mechanism. In order to understand the mechanism of adsorption process and to determine the rate controlling step which is mainly depends on either surface or pore diffusion, intraparticle diffusion model were used[18]. Weber and Morris model is adopted in this study, since this is a widely used intraparticle diffusion model. A plot of Q_t *vs.* $t^{1/2}$ (square root of time) should be straight line if the sorption process follows intraparticle diffusion meanwhile if these lines pass through the origin then intraparticle diffusion would be the sole controlling step. When the plots do not pass through the origin indicates some degree of boundary layer control and proves that intrapacticle diffusion is not only rate limiting step while other processes might control the rate of adsorption, all of which may be operating simultaneously[20]. Fig. 10 represents a plot of linear form of intraparticle diffusion model. The result shows that the intercept did not pass through origin and correlation coefficient values (R_2) less than 0.99 (Table-1), suggesting that intraparticle diffusion was involved in the sorption process, but it was not the rate controlling step.

The rate constant, k depends strongly on temperature, T. It is due to the increase in collisions which result in number of molecules having energy that exceeds the activation energy. Consequently, this will lead to rapid increase in k value. The k (T) data for many reactions can fit in the Arrhenius equation as below;

$$\ln k = \ln A - \frac{E_a}{RT} \tag{7}$$

slope -Ea/R and intercepts ln A (Fig. 11). The magnitude of activation energy gives an idea about the type of adsorption whether it is physical or chemical[21]. According to the Arrhenius equation, low activation energy shows a fast reaction as obtained in this study ($E_a = 37.01$ J/mol). The positive activation energy indicates that the sorption of phosphate by paper mill sludge was a chemical adsorption.

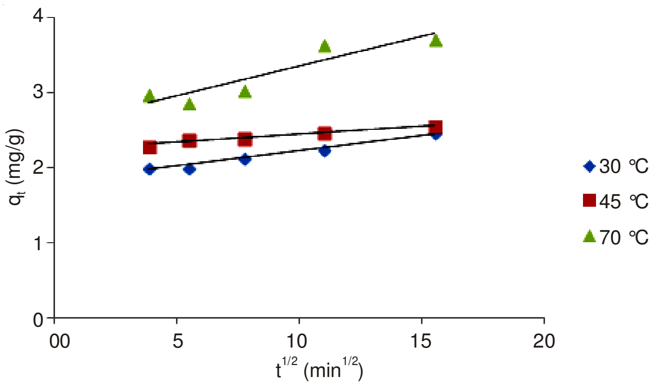

Fig. 10. Intraparticle diffusion plot for sorption of phosphate by paper mill sludge

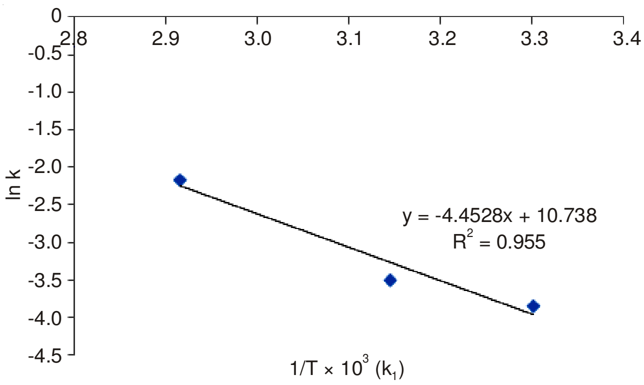

Fig. 11. Arrhenius plot for adsorption of phosphate by paper mill sludge

Adsorption isotherm of phosphate by paper mill sludge: The sorption isotherm of phosphate by paper mill sludge was measured by shaking it for 24 h at different initial concentrations at pH 12 at room temperature. In this study, the isotherm data were analyzed using four different kinds of isotherm models namely Langmuir, Freundlich, D-R (Dubinin-Radushkevich) and Temkin.

Langmuir isotherm model: The Langmuir isotherm suggests that sorption takes place on a homogeneous surface to obtain maximum adsorption capacity. No further adsorption process will occur if the site is occupied by a solute. The linear form of the Langmuir isotherm equation can be represented by the following equation[22]:

TABLE-1
KINETIC PARAMETER FOR ADSORPTION OF PHOSPHATE ONTO PAPER MILL SLUDGE AT VARIOUS TEMPERATURES

Temp.	Q_e (Exp)	First order			Second order		
°C	mg/g	k1 × 10-3	Q_e (mg/g)	R^2	k_2 × 10-3	Q_e (mg/g)	R^2
70	3.81	11	1.08	0.874	30.22	3.85	0.999
45	3.74	2	1.4	0.969	8.17	3.77	0.998
30	3.61	1	1.64	0.991	6.18	3.51	0.996
		Intraparticle diffusion			Elovich		
		k_3	Q_o (mg/g)	R^2	α	β	R^2
70		0.078	2.573	0.838	5.988	1244.36	0.908
45		0.021	2.239	0.953	11.236	9.71E+08	0.957
30		0.041	1.816	0.982	3.096	129.51	0.79

$$\frac{1}{q_e} = \frac{1}{bO_m} + \frac{C_e}{Q_m} \quad (8)$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, C_o (mg/L) is the initial adsorbate concentration, q_e (mg/g) is the adsorption capacity at equilibrium, Q_m (mg/g) and b (L/mg) are Langmuir constant related to maximum adsorption capacity and rate of adsorption, respectively obtained from the slope and intercept of the plot of C_e/q_e and C_e (Fig. 12). Furthermore, dimensionless separation factor (R_L) can be calculated to determine the adsorption process is favorable or unfavorable as shown in Table-2 using the following equation;

$$R_L = \frac{1}{1 + bC_o} \quad (9)$$

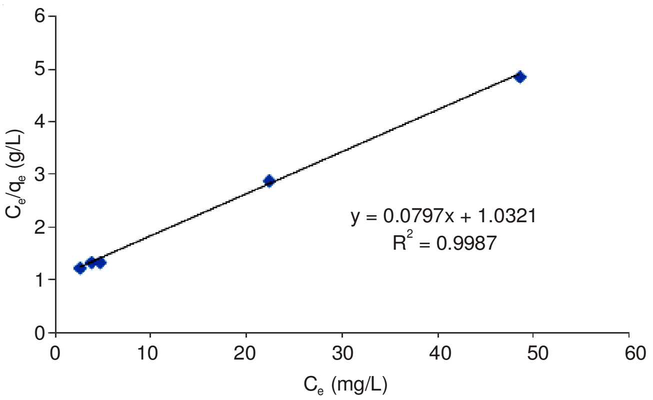

Fig. 12. Langmuir plot for solution of phosphate by paper mill sludge at room temperature

TABLE-2
PROCESS NATURE OF SEPARATION FACTOR

R_L value	Types of process
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Freundlinch isotherm model: The Freundlich isotherm assume heterogeneous system with different energy of active sites and reversible adsorption, which is not restricted to monolayer formations[23]. The Freundlich constant can be obtained from a plot of log q_e *vs.* log C_e (Fig. 13). The linear form of Freundlich isotherm as shown below;

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

where K_F ((mg/g) (L/mg)$^{1/n}$) indicates the relative adsorption capacity of the adsorbent related to bond energy and n is the heterogeneity factor representing the deviation from linearity of adsorption. Larger value of K_F indicates the greater adsorption capacity while n values indicate the favorability of the adsorption process. If n is above unity, then the adsorption process is favorable.

Dubinin Raduskevich (D-R) isotherm model: The D-R isotherm analysis widely used in order to determine high degree of rectangularity[24]. The linear form of D-R isotherm equation is as follows:

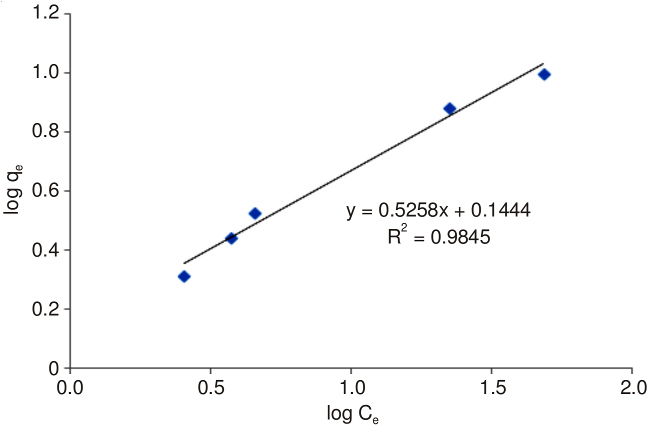

Fig. 13. Freundlich plot for solution of phosphate by paper mill sludge at room temperature

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (11)$$

where β (mol^2/kJ^2) represent adsorption energy constant obtained from slope of straight-line plot of ln q_e *vs.* ε^2 (Fig. 14) and ε, the polanyi potential, can be calculated using following equation;

$$\varepsilon = RT \ln [1 + 1/C_e] \quad (12)$$

where R is the universal gas constant in kJ/(mol K) and T is the temperature in Kelvin. The mean free energy, E (kJ/mol) (Table-4) can be obtained by the following equation;

$$E \text{ (kJ/mol)} = (2\beta^{-0.5}) \quad (13)$$

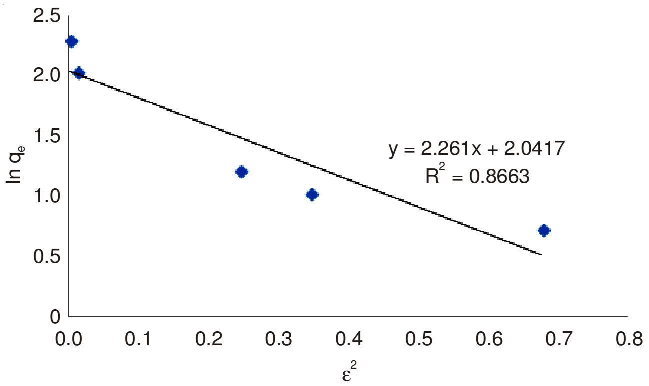

Fig. 14. D-R plot for solution of phosphate by paper mill sludge at room temperature

Temkin isotherm model: Another model for the analysis of indirect adsorbent/adsorbate interactions on adsorption isotherms is Temkin model[25]. Apart from that, this isotherm assumes that the heat of adsorption of all the molecules in the layer would decreases linearly with coverage and the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The linear form of Temkin isotherm equation is as follows:

$$q_e = \beta \ln K_T + \beta \ln C_e \quad (14)$$

where $\beta = RT/b_T$. A plot of q_e *vs.* ln C_e (Fig. 15), constant K_T and b_T can be found from intercept and slope. K_T (L/mg) represent Temkin constant related to the equilibrium binding energy while b_T (J/mol) is Temkin constant related to the heat of adsorption as shown in Table-4.

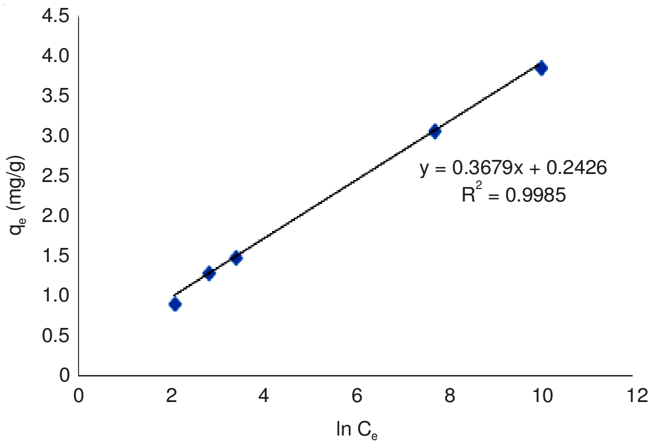

Fig. 15. Temkin plot for solution of phosphate by paper mill sludge at room temperature

TABLE-3
R_L VALUE AT DIFFERENT INITIAL CONCENTRATION OF PHOSPHATE

No	Initial Phosphate concentration (mg/L)	R_L value
1	60	0.8364
2	80	0.7769
3	100	0.7414
4	200	0.369
5	300	0.2111

Referring to Table-4, Langmuir isotherm model fitted well with the highest $R^2 = 0.9987$ compared to the other three isotherm models. The maximum capacity at equilibrium, Q_m was 12.65 mg/g while b which denotes adsorption energy was 0.077 L/mg. The high correlation coefficient confirmed that monolayer adsorption of phosphate onto the paper mill sludge surface. The R_L values which were in the range of 0.83 and 0.21 as shown in Table-3 indicated that the adsorption process were favorable under studied condition. Temkin and Freundlich isotherm models also showed relatively good agreement with the $R^2 = 0.9985$ and $R^2 = 0.9845$, respectively.

The value of K_T and b_T of the Temkin isotherm was reported as 1.934 L/mg and 6.734 kJ/mol which explains equilibrium binding energy and the heat of adsorption, respectively. Meanwhile Freundlich constant for adsorption capacity, K_F was 1.393 mg/g. The n_f value (indicator for adsorption intensity) calculated from the Freundlich model was 1.905 which in the range of $1 < n < 10$, indicating favorable adsorption. This adsorptive behaviour implied that the adsorption also took place on a heterogeneous surface. Hence, it can be concluded that adsorption of phosphate by paper mill sludge followed multisorption process where both monolayer and bilayer adsorption present simultaneously in the surfaces of the sorbent but the former adsorption more predominant.

The applicability of the isotherm models to the adsorption behaviours can be judged by using the correlation coefficient (R^2) values. The R^2 values of Freundlich and Temkin isotherms were higher than the Dubinin-Radushkevich isotherm ($R^2 = 0.8663$) but lower compared to Langmuir model. The adsorption equilibrium data fitted the isotherm models in the order of: Langmuir > Temkin > Freundlich> Dubinin-Radushkevich.

TABLE-4
ISOTHERM CONSTANTS AND REGRESSION DATA FOR ADSORPTION OF PHOSPHATE ON PAPER MILL SLUDGE

No.	Isotherm model	Isotherm constant		R^2
1	Langmuir	Q_m (mg/g)	12.65	0.9987
		b (L/mg)	0.077	
2	Freundlich	K_f((mg/g) (L/mg) 1/n)	1.393	0.9845
		n_f	1.905	
3	Temkin	K_T (L/mg)	1.934	0.9985
		b_T (kJ/mol)	6.734	
4	Dubinin-Radushkevich	Q_m (mg/g)	7.704	0.8663
		k (mol^2kJ^2)	2.261	
		E (kJ/mol)	0.470	

Comparison of maximum adsorption capacity (Q_m) of phosphate for some low cost adsorbent: Finally, the performance of paper mill sludge was compared with some other low cost adsorbent as shown in Table-5. The obtained binding capacity clearly indicated that paper mill sludge is an effective adsorbent for phosphate removal from water.

TABLE-5
REPORTED ADSORPTION CAPACITIES (Q_m) OF PHOSPHATE FOR SOME LOW-COST ADSORBENTS

No	Adsorbent	Q_m (mg/g)	Ref.
1	Geothite	0.286	26
2	Natural zeolite	6.42	27
3	Na-Natural zeolite	2.15	28
4	Synthetic iron oxide coated sand	2.19	29
5	Coated crushed brick	1.75	30
6	Naturally iron oxide coated sand	0.88	30
7	Iron-hydroxide eggshell	14.49	6
8	Iron oxide tailing	8.21	30
9	Paper mill sludge	12.65	Present study

Conclusion

The raw paper mill sludge has the potential to be used as a low cost adsorbent for removal of phosphate from aqueous solutions effectively at pH 12. The pseudo second-order model fits better than the pseudo first-order model for adsorption kinetic data and indicates the adsorption process is based on chemisorptions. The adsorption capacity for phosphate was increased with increasing temperature and indicates that the process was endothermic. The calculated E_a is 37.01 J/mol further suggests that the sorption of phosphate by paper mill sludge was based on chemical adsorption. Intraparticle diffusion was involved in the adsorption process but it is not a rate determining step. The equilibrium data were fitted well to Langmuir isotherm with maximum adsorption capacity of 12.65 mg/g.

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