NUR IZZATY BINTI MOHD 2018 MSc

DEVELOPMENT OF NON-IONIC SILICONE SURFACTANT-BASED EXTRACTION METHODS OF TRIAZINE HERBICIDES IN MILK AND WATER SAMPLES

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DEVELOPMENT OF NON-IONIC SILICONE SURFACTANT-BASED EXTRACTION METHODS OF TRIAZINE HERBICIDES IN MILK AND WATER SAMPLES

by

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LIST OF ABBREVIATIONS

A	moles of triazine solubilized
AC MNPs	activated charcoal coated with magnetic nanoparticles
AC	activated charcoal
AC-OFX MNPs	OFX 0309 on activated charcoal coated with magnetic nanoparticles
AC-OFX	activated charcoal with OFX 0309
BET	Brunauer-Emmett-Teller
C0	initial triazines concentration (mol/L)
Ce	equilibrium concentration of triazines in the aqueous phase (mol/L)
CMC	critical micelle concentration
C_o	triazine concentration in the initial sample-surfactant mixture
CPC	Cetylpyridinium chloride
CPE	cloud point extraction
CPT	cloud point temperature
Cs	surfactant concentration (mol/L)
C_S	triazine concentration in the surfactant rich phase volume
CTAB	Cetyltrimethylammonium bromide
Cw	triazine compounds concentration in aqueous phase (mol/L)
EPA	United States Environmental Protection Agency
EU	European Union
FT-IR	Fourier transform infrared spectroscopy (FT-IR)
GC-MS	Gas chromatography – mass spectrometry

HPLC-DAD	High performance liquid chromatography with diode array detector
ILs	Ionic liquids
K	Kelvin
LLE	liquid-liquid extraction
LOD	limit of detection
Log K_{ow}	the octanol/water (o/w) partition coefficient
LOQ	limit of quantification
m	Langmuir isotherm constant
MNPs	magnetic nanoparticles
MSPE	magnetic solid phase extraction
n	Langmuir isotherm constant (L/mol)
nd	Not detected
PANI	polyaniline
pK_a,	acid dissociation constant (K_a) of a solution
PLE	pressurized liquid extraction
Qd	amount of solute
*q*e	moles of triazines solubilized per mole of surfactant (mol/mol)
Qo	feed amount of solute
R_s	surfactant rich phase
R_v	phase volume ratio
R_w	aqueous phase
SDS	Sodium dodecyl sulphate
SEM	Scanning electronic microscope

SFE	supercritical fluid extraction
SPE	solid phase extraction
SPME	solid phase microextraction
T	temperature (°C)
TCA	trichloroacetic acid
TEM	Transmittance electron microscope
TGA	Thermogravimetric Analysis
v/v%	volume per volume percent
Vd	volume of dilute phase (L)
Vo	volume of solution (L)
VOCs	volatile organic compounds
Vs	volume of triazines concentration in surfactant rich phase (L)
VSM	Vibrating sample magnetometer
Vw	volume of triazines concentration in aqueous phase (L)
w/w%	weight per volume percent
X	moles of surfactant used (mol)
XRD	X-ray Diffraction
$\Delta G°$	delta Gibbs free energy
$\Delta H°$	delta enthalpy of solubilization
$\Delta S°$	delta entropy of solubilization

PENGEMBANGAN KAEDAH PENGEKSTRAKAN BERASASKAN SURFAKTAN SILIKON BUKAN IONIK RACUN PEROSAK JENIS TRIAZIN DALAM SAMPEL SUSU DAN AIR

ABSTRAK

Pengekstrakan titik awan (CPE) - kaedah spektrofotometri telah dikembangkan untuk pemisahan atrazin dan propazin menggunakan surfaktan silikon bukan ionik, poliether polisiloksina, sebagai pendekatan baru pengekstrak racun perosak jenis triazin dalam CPE. Surfaktan jenis ini dipilih sebagai pelarut pengekstrak hijau kerana struktur dan sifatnya. Terdapat dua jenis poliether polisiloksina (OFX 0309 dan DC 193C) yang dikaji dalam CPE untuk mengkaji keberkesanan surfaktan sebagai pengekstrak terhadap racun perosak jenis triazin. Pemulihan kinerja CPE dapat diperhatikan pada keadaan berikut; CPE-OFX 0309; 1.0 mL 0.4 v/v % surfaktant, sampel pada pH 5, 2.0 M kepekatan Na_2SO_4, masa pengeraman selama 15 minit pada suhu 50 °C dan isipadu sampel 1mL berkepekatan 10 mg/L manakala bagi CPE-DC 193C; keadaan yang sama diaplikasikan kecuali kepekatan garam yang diaplikasikan (1.5 M kepekatan Na_2SO_4). Menggunakan pemboleh ubah yang telah dikaji, CPE telah diaplikasikan dalam sampel susu dan air. Model Langmuir didapati sesuai dengan penguraian larutan racun perosak jenis triazin ke dalam surfaktan OFX 0309 dan DC193C. Oleh itu, model Langmuir telah digunakan untuk menjelaskan keterlarutan antara surfaktan dan racun perosak jenis triazin. Pemboleh ubah termodinamik telah ditentukan seperti tenaga bebas Gibbs (ΔG^o) yang meningkat dengan suhu, nilai entalpi (ΔH^o) dan nilai entropi (ΔS^o) yang meningkat dengan hidrofobik surfaktan. Hasil termodinamik menunjukkan bahawa keterlarutan racun perosak jenis triazin yang diserap ke dalam kedua-dua surfaktan adalah dilaksanakan, spontan dan endotermik. Berdasarkan kinerja surfaktan OFX 0309 dalam kaedah CPE yang dikembangkan, surfaktan OFX 0309 digunakan untuk memodifikasi permukaan arang aktif (AC) sebelum disalut dengan permukaan magnet (AC-OFX MNPs) sebagai bahan penyerap. OFX 0309 telah dipilih kerana sifatnya yang mempunyai rantai polisiloksina yang fleksibel tanpa struktur gegelang serta struktur micelles padat yang memberikan pengekstrakan yang baik terhadap racun perosak jenis triazin. Penjerap AC-OFX MNPs yang disintesis telah digunakan dalam pengekstrakan fasa pepejal magnet (MSPE). Dengan menggunakan sifat magnet penjerap AC-OFX MNPs, pengekstrakan dengan kecekapan pengekstrakan yang baik telah diterokai. Beberapa pemboleh ubah seperti 20 w/v% kepekatan surfaktan digunakan untuk mengubahsuai permukaan karbon aktif, 15 mg kuantiti bahan penyerap, sampel pH 5, 4 minit masa pengekstrakan, 300 µL isipadu larutan penyaherapan, 80 saat masa penyahserapan menggunakan campuran pelarut organic acetonitrile:methanol dan 15 mL isipadu sampel telah dioptimumkan dalam kaedah MPSE. Menggunakan pemboleh ubah yang telah dikaji, penjerap AC-OFX MNPs ini telah diaplikasikan dalam sampel susu dan air untuk mengkaji keberkesanannya menggunkan kaedah MSPE keatas pengekstrakan racun perosak jenis triazin ditambah dengan kromatografi cecair prestasi tinggi dengan pengesan array dioda (HPLC-DAD).

DEVELOPMENT OF NON-IONIC SILICONE SURFACTANT-BASED EXTRACTION METHODS OF TRIAZINE HERBICIDES IN MILK AND WATER SAMPLES

ABSTRACT

Cloud point extraction (CPE) – spectrophotometric method had been developed for separation of atrazine and propazine using non-ionic silicone surfactant, polysiloxane polyether, as a new approach of triazine compounds extractor in the CPE. This type of surfactants was chosen as a green extraction solvent because of its structure and properties. There were two types of polysiloxane polyether (OFX 0309 and DC 193C) were studied in the CPE to investigate their effectiveness as extractor toward triazine compounds. Performance recovery of CPE can be observed when the following conditions was applied; CPE-OFX 0309, 1.0 mL 0.4 v/v % surfactant concentration, solution pH at 5, 2.0 M of Na_2SO_4, incubation time for 15 minute at 50 °C dan sample volume of 1mL at concentration of 10 mg/L while for CPE-DC 193C; the same conditions was applied except for concentration of salt used (1.5 M of Na_2SO_4). Using the optimized parameters, CPE was applied in milk and water samples. Langmuir model was found to fit well with the solubilization of the triazine compounds into the OFX 0309 and DC193C surfactant. Thus, Langmuir isotherm has been used to explain the solubilization study between surfactant and triazine compounds. The thermodynamic parameters were determined such as Gibbs free energy (ΔG^o) which increases with temperature, value of enthalpy (ΔH^o) and value of entropy (ΔS^o) which increase with the surfactant hydrophobicity. The thermodynamic results indicated that the solubilization of the triazine compounds solubilized into the both surfactants were feasible, spontaneous and endothermic. Based

on the performance of OFX 0309 in the developed of CPE method, the OFX 0309 surfactant was used to modify the surface of activated charcoal (AC) before coated with magnetic surfaces (AC-OFX MNPs) as adsorbent material. The OFX 0309 surfactant was chosen due to its properties that have flexible polysiloxane chain without any aromatic structure with compact micelles structure which provided good recoveries toward the triazine compounds. The synthesized material of AC-OFX MNPs was employed in magnetic solid phase extraction (MSPE). Due to magnetic properties of the AC-OFX MNPs material, the extraction with good extraction recovery was explored. Several parameters such as 20 w/v % of concentration surfactants used to modify the surface of AC, 15 mg of amount of sorbent, sample pH 5, 4 minute of extraction time, 300 μL of desorption solvent, 80 seconds of desorption time with using a mixture of acetonitrile: methanol and 15 mL of sample volume were optimized in the MSPE method. Using the optimized parameters, the newly synthesize AC-OFX MNPs was applied in milk and water samples to determine the recovery of MSPE method towards triazine herbicides coupled with high performance liquid chromatography with diode array detector (HPLC-DAD).

CHAPTER 1

INTRODUCTION

1.1 General background of research

Triazine herbicides have been the most excessively applied herbicides over 40 years in preventing the existence of broadleaf weeds in desired crops. Although the use of triazine herbicides is banned, the use of the herbicides has been increasing due to the worldwide requirement for the higher agricultural activities. The most common used triazine compounds are atrazine followed by propazine and prometryn. The main triazine compounds are derived from s–triazine, a six–member heterocycle with symmetrically located atoms in which positions 2, 4, and 6 are substituted. Due to the stereochemical stability of *s*–triazines, the triazine compounds are strongly exist and resist in environmental for several months and sometimes years (approximate half–life in soil for 146 days, in water for 742 days) (Sheets, 1970). Triazine compounds can be transformed into degradation products which even more toxic and persistent in the environment compared to its parent compounds (Rodríguez-González et al., 2017). The use of triazine compounds had attracted the researcher due to their mobility and solubility in water. The triazines are persistently sorb onto environment and easily migrate through the soil going into the ground water and surface water (Safari et al., 2015). Other than that, the existence and resistance of triazines in environment makes it transferable to animals and food chain (Teju et al., 2017). These triazines can be contaminating the milk by the feed or water consumed by the cow. Then, the milk will be consumed by human thus, provides harm towards human health as one of nutritional food for humans is milk. Previous study also had recorded that exposure of triazine compounds towards human had contributed towards development of ovarian cancer (Sebata et al., 2013). In European Union (EU), contents residues of atrazine and propazine in milk and cream are not higher than 50 μg/L (Gao et al., 2010) and the United States Environmental Protection Agency (EPA) has set the maximum allowable level of only atrazine at 50 μg/L in water (Sass et al., 2013). Other than that, the Food and Agriculture Organization of the United Nation and World Health Organization stated that maximal residue limits of milk established at 900 μg/L (Chang et al., 2016). Because of their low concentration existence in environment, analytical methods to monitoring the use of triazine compounds are required (Khammas et al., 2016).

The most common extraction technique to extract herbicides and organic pollutants were liquid–liquid extraction (LLE) and solid–phase extraction (SPE) (Barker, 2000). However, LLE procedure required large amounts of volatile organic compounds (VOCs) that are potentially toxic and are very time–consuming procedure (Ghasemi et al., 2016). The use of organic compounds in the analytical methods may affect human health as it can be easily absorbed through human respiratory and skin touch as the organic compounds are easily evaporated. Excessive exposure to organic solvents may induce long term nervous system disease. Other than that, the SPE procedure reduced the use of organic solvent than LLE but it can be relatively costly (Sarafraz-Yazdi et al., 2010). The SPE procedure also required the evaporation step of the final organic extract into a small volume to achieve high enrichment of the analytes (Płotka-Wasylka et al., 2016). Due to these multiples disadvantages, solid phase micro extraction (SPME) was introduced. The main advantages of SPME extraction technique are simplicity of operation and the used of low organic hazardous solvents. However, the SPME can be costly and/or time–consuming (Jiménez-Soto et al., 2012). With the current explore of analytical technologies, the principles and advantages of cloud point extraction (CPE) and magnetic solid phase extraction (MSPE) had been discovered by the researcher.

General concept of "green chemistry" are the procedures to reduce or eliminate the use or generation of toxic substances that may affect human health and the environment (Bezerra et al., 2005). In the CPE, it uses small amounts of non–toxic surfactants compared to toxic organic solvents, thus, it follows the principles of "green chemistry" (Ghouas et al., 2015). The CPE are dependable on the temperature and concentration of surfactant to solubilize the analyte into a micelle for phase separation. The CPE method is based on the unique properties of solubilization and clouding ability of surfactant micellar system (phase separation). At low surfactant concentration above the critical micelle concentration (CMC), micellar solution of surfactants can exist as homogeneous isotropic liquid phases. Phase separation can be generated by varying the temperature in this concentration range. At a certain temperature known as cloud point temperature (CPT), the micellar phase separates into two phases, both contain surfactant but with differ of total surfactant concentration (Duran et al., 2011). The first phase is surfactant rich phase, which contains the extracted hydrophobic organic compounds originally present in the sample subjected to the phase separation procedure. The second phase is aqueous phase which mostly consist of water. The surfactant aggregate (a micelle) orients its hydrocarbon tails towards the center to create a non–polar core. Isolated hydrophobic organic compounds present in the aqueous sample solution are favorably solubilized into the hydrophobic core of micelles (de Prá Urio et al., 2016). The organic compounds present was isolated from the sample solution and solubilized into the micelles in the bulk solution which then are further enriched by the phase separation behavior of the surfactant solution. The CPE method is being developed since it require less use of organic solvents, require very small amount of nonflammable and nonvolatile surfactant which make it an environmental friendly method with high extraction efficiency (Noorashikin et al., 2013).

Surfactants are amphiphilic molecules, having both polar and non–polar groups that exhibit important interfacial properties between phases and can be used in many industrial separation processes (Vaisman et al., 2006). The hydrophilic region of the surfactant (polar head group) and hydrophobic region (non–polar tail group) of the surfactant act to reduce the surface tension of a liquid. The solubility of the surfactant in both organic solvents and water was contributed by the head–tail group that usually consist of one or more hydrocarbon chain (Li et al., 2012). Surfactant can be classified into anionic, cation, zwitterion and non–ionic group. Non–ionic surfactant is the surfactant that does not have any positive or negative charged on their head group in solution and the surfactant do not ionize in aqueous solution (Paria et al., 2004). Non–ionic silicone surfactant with hydrophilic moieties not only share many common features with non–ionic surfactants but also possess the properties of the non–ionic surfactant. Due to this, the non–ionic silicone surfactant is known as an alternative material to replace the use of volatile organic compounds (VOCs) as organic extractor. The non–ionic silicone surfactant also offered several advantages such as non–toxic, odourless, colourless, and non–irritating and the fact that they do not evaporate easily. In addition, non–ionic silicone surfactant also well–known as a growing class of raw materials used in the production of cosmetic and industrial industries (Norseyrihan et al., 2016). Moreover, the US FDA (Food and Drug Administration, United State) had permitted this non–ionic silicone surfactant for internal consumption (Ellis, 2002).

Till recently, non–ionic surfactants (mainly polyoxyethylenenated alkyl phenols, from PONPE 7.5 and Triton series such as Triton X–100 and Triton X–114) are the most commonly employed extractor for organic compounds analysis in the CPE (Alibrahim, 2014, Demirhan et al., 2012). In most cases, Triton X–114 as the extractor in the CPE was chosen due to its relatively non–toxic reagent and low CPT. The used of the Triton X–114 was also favorable because it ease the phase separation of surfactant rich phase and aqueous phase by producing high density surfactant rich phase (Yang et al., 2017). However, its aromatic chromophore structure has strong UV absorbance signals which become obstacles in the UV spectrophotometry detector. The non–ionic silicone surfactants are superior as an extraction medium since they do not possess an aromatic ring and thus have virtually no absorbance in the UV region which facilitates subsequent analyte analysis. Therefore, a non–ionic silicone surfactant, polysiloxane polyether, OFX 0309 and DC 193C) were 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 phase and also low in density; thus, enhancing the extraction efficiency (Soroceanu et al., 2015).

In part I, a simple of the CPE method coupled with UV spectrophotometry was developed for determination of triazine compounds in water and milk samples using non–ionic silicone surfactant. Several crucial parameters were optimized and investigated such as types, concentration and volume of surfactant, pH, type, concentration and volume of salt, temperature, incubation time, water content, analyte concentration, sample volume and phase volume ratio. The two CPE methods were investigated and developed which of CPE–OFX 0309 and CPE–DC 193C. From the experimental data, the isotherm and thermodynamic study were developed to investigate the solubilization performance of these two types non–ionic silicone surfactants toward triazine compounds. The change in thermodynamics such as enthalpy (ΔH^o), entropy (ΔS^o), and Gibbs free energy (ΔG^o) were reported to find out the nature solubilization of triazine compounds towards the non–ionic silicone surfactants.

Nowadays, MSPE is a modification of solid phase extraction that used the magnetite properties to ease the extraction technique with high extraction efficiency. In MSPE, the used of magnetic nanoparticles (MNPs) as an adsorbent can be easily dispersed in sample solution and recollected using external magnetic field placed outside of the sample vial (Chen et al., 2016). Thus, the extraction step reduced time consume and minimized the use of organic solvents. In MSPE technique, the surface area of the adsorbent and sample solution is large enough for a faster mass transfer of analytes (Yu et al., 2016). Based on the performance of non–ionic silicone surfactant (OFX 0309 and DC 193C) studied in the CPE toward triazine compounds, an attempt was made to develop an efficient adsorbent material based on non–ionic silicone surfactant for the extraction of triazine compounds in water and milk samples. The OFX 0309 surfactant was further studied due to its excellent performance towards triazine compounds in the CPE method. In part II, the MSPE method was developed by applying the new synthesized adsorbent based on OFX 0309 surfactant modified on activated charcoal surface (AC) coated with magnetic nanoparticles (AC–OFX MNPs) coupled with high performance liquid chromatography with diode array detector (HPLC–DAD) for determination of triazine compounds in water and milk samples.

An adsorbent such as MNPs are used since the MNPs are easily produced, less costly and have high magnetic saturation that help in extraction process. Modifying the surface of the MNPs are the key to improve stability of the MNPs towards analytes through the physical or chemical adsorption of organic compounds (Banazadeh et al., 2016). The AC was used due to their large surface area and excellent adsorption capacity

(Gürses et al., 2016). In SPE and SPME, the AC have been successfully used as adsorbent for removal of organic pollutants (Guo et al., 2017, Kaipper et al., 2001). However, few problems were observed such as filtration problem, dispersion problem, create turbidity and high cost technique (Kakavandi et al., 2013). To overcome this problem, the AC coated with MNPs (AC MNPs), had been introduced. However, in the previous studies, the performance of AC MNPs towards the extraction efficiency performance of organic pollutants were reported in average of 70% (Xie et al., 2013). Based on the study, high amount of AC MNPs was used to achieved good recoveries in the extraction procedure. Therefore, many researchers have been focused on improving the adsorption capacity of AC to specific pollutants by modifying its microscopic structure and surface function groups. Since some of triazine herbicides are non–polar and polar, they can be combined with amphiphilic structure of surfactant with a hydrophobic tail and hydrophilic head, surfactant have been applied to modify the characteristics of a solid surface activated charcoal. Thus, the non–ionic silicone surfactant was used to modify the AC surface before coated with MNPs to enhance the extraction performance towards the triazine compounds. The OFX 0309 surfactant was first modified onto the AC surface and the material was coated with MNPs to provide higher binding sites towards the triazine compounds. The introduction of magnetic properties to the AC–OFX MNPs would combine the high adsorption capacity of AC and surfactant with the separation convenience of magnetic materials. Based on this, a method of MSPE coupled with HPLC–DAD was develop based on non–ionic silicone surfactant of OFX 0309 modified on AC surface coated with MNPs as an adsorbent in MSPE for the analysis of triazine compounds in water and milk samples.

1.2 Scope of research

This research was investigated the performance of non–ionic silicone surfactant through two different extraction techniques, CPE and MSPE for the analysis study of triazine herbicides. In the first part (Part I), the method of CPE was developed using two types of non–ionic silicone surfactants; CPE–OFX 0309 and CPE–DC 193C for determination of triazine compounds such as atrazine and propazine in water and milk samples using UV spectrophotometry. The solubilization study of both non–ionic silicone surfactant towards atrazine and propazine were studied in detail using isotherm and thermodynamics study. Based on the performance study of non–ionic silicone surfactant, the OFX 0309 surfactant was selected to be studied in further as an adsorbent material in MSPE method for the determination of triazine compounds in water and milk samples using HPLC–DAD (Part II). The adsorbent material was synthesized using OFX 0309 surfactant modifying the surface of AC coated with MNPs. The adsorbent material was then characterized using fourier transform infrared (FT–IR) spectroscopy, vibrating sample magnetometer (VSM), scanning electron microscope (SEM), transmission electron microscope (TEM), Brunauer–Emmett–Teller (BET), thermogravimetric analysis (TGA) and X–ray diffractometer (XRD). Finally, the AC–OFX MNPs material was used as adsorbent in MSPE. The MSPE method was developed using AC–OFX MNPs as an adsorbent material for determination of triazine herbicides such as atrazine, propazine and prometryn in water and milk samples using HPLC–DAD. In Part I, atrazine and propazine are further study to investigate their performance with non–ionic silicone surfactant in CPE. They are chosen due to their different hydrophobicity although there are in the same triazine group. Meanwhile in Part II, prometryn is the analyte that existed in different group of triazine, having different hydrophobicity and properties than atrazine and propazine. Because of this, prometryn is added along with atrazine and propazine in MSPE method.

1.3 Research objectives

Main objective:

To develop extraction method of cloud point extraction (CPE) and magnetic solid phase extraction (MSPE) to investigation the performance of non–ionic silicone surfactant for triazine herbicides analysis in water and milk samples.

The following were the specific objectives of this present study:

1) To optimize and apply the CPE method based on non–ionic silicone surfactant of OFX 0309 and DC 193C towards atrazine and propazine using UV–spectrophotometry for determination of triazine herbicides in water and milk samples
2) To investigate the solubilization study of atrazine and propazine toward non–ionic silicone surfactant of OFX 0309 and DC 193C)
3) To synthesis and characterize new adsorbent material, OFX 0309 surfactant modified on activated charcoal surface coated with magnetic nanoparticles (AC–OFX MNPs) as adsorbent material in MSPE method.
4) To optimize and apply the MSPE method based on non–ionic silicone surfactant of OFX 0309 towards atrazine, propazine and prometryn using newly synthesized adsorbent material (AC–OFX MNPs) coupled with HPLC–DAD for determination of triazine herbicides in water and milk samples.

1.4 Outline of the thesis

Thesis was separated into five specific chapters. Chapter 1 gives the introduction of the research background and the research objectives. In Chapter 2, the literature review of the research is reviewed and organized in detailed. In Chapter 3, the methodology of the research was reported according to the specific objectives approach. The methodology was explained and clarified in detail into part I and part II. In part I, detailed methodology of the CPE procedure was explained while in the part II, the MSPE methodology was explained. In Chapter 4, the data for optimization and validation of CPE–UV spectrophotometry method were explained along with the data for solubilization study of the OFX 0309 and DC 193C surfactant towards atrazine and propazine (part I). In the part II, the characterization data of the adsorbents materials (MNPs, AC MNPs and AC–OFX MNPs) were presented followed by the data of optimization and validation of MSPE method coupled with HPLC–DAD. Finally, Chapter 5 discussed on the overall conclusion of the research and future recommendation suggested for this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Triazine herbicides

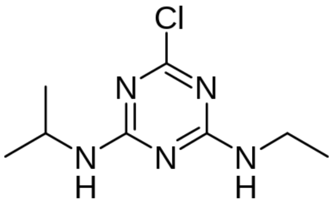
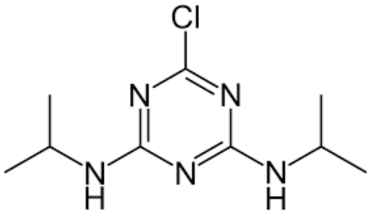
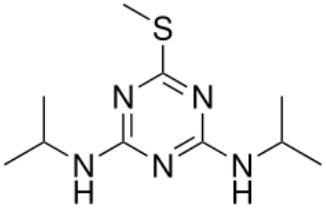
In agricultural industries, triazine compounds were the mostly used pesticides for 50 years. This is due to applicability of triazines to a variety of cultures as well as to pasture and corn fields. In the atmosphere, triazine compounds exists in both particulate and vapor phases due to its low vapor pressure and this influence their way of transported into environment. Thus, the triazine residues contaminate the ground and wastewaters, agricultural products and, consequently, in the direct and indirect pollution of food, food products and food chain (Yang et al., 2014). Commonly, triazine compounds can be transformed in the environment by biotic and abiotic process where their degradation products can be even more toxic and persistent than their parental compounds (Rodríguez-González et al., 2017). Triazine herbicides can persist for many months in some soils and seasonal carry–over can sometimes cause difficulties. The effectiveness of triazines, when applied to soils, is dependent on several variables, which include the soil structure, organic matter content, moisture content and particle size distribution causing their persistency (Dean et al., 1996). In a study done in 2004, it is shown that atrazine can persist for 105 days in river water at 20 ºC thus showing the longest half–lives among the other triazine compounds (Navarro et al., 2004). However, serious problems towards human and animals was created due to their slow degradation processes as they are classified as human carcinogen. The triazine compounds chemical properties are summarized in **Table 2.1**.

The atrazine have been included in the list of “priority hazardous substances” in Decision 2455/2001/EC that amends the Directive 2000/60/EC and the atrazine, propazine and prometryn are considered as a group to be endocrine–disrupting chemicals (EEA, 2001). In United States Environmental Protection Agency (EPA), maximum residue limits (MRLs) of triazines in milk are only established for atrazine 50 μg/L and the EPA has set the MRLs of atrazine in water at 50 μg/L (Sass et al., 2013). Other than that, the Food and Agriculture Organization of the United Nation and World Health Organization stated that MRLs of milk established at 900 μg/L (Chang et al., 2016). Because of these restrictions (exist in low concentration), analytical methods are required for monitoring the widespread distribution of triazine compounds (Khammas et al., 2016).

Several extraction techniques had been proposed to remove triazine compounds from sample solution. Among the conventional technique used is by using organic solvents to separate targeted triazine compounds from the samples. However, this technique required large use of solvent and that may increase the discard of organic to the environment, requiring additional clean up. Previous studies proved that, adsorption is an effective technique for the removal of organic compounds (Palma et al., 2007). The solubilization of triazine 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 process.

Among previous reported technique used were magnetic solid phase extraction (MSPE), aqueous two–phase system (ATPS) and cloud point extraction (CPE). According to Zhao et al., 2011, an absorbent with the use of magnetic properties had been successfully applied to remove triazine compounds in water samples by using MSPE technique. The synthesized absorbent possesses high adsorption capacity and gives extraction recovery up to the range of 89 – 96.2%. Other researchers also reported that ionic liquids (ILs) and surfactants can also act as extractor with good solubilization capacity (Darshak R Bhatt et al., 2015, Liu et al., 2014). Both ILs and surfactant provided hydrophobic micelles which contribute towards good solubilization ability and been proven to greatly reduced the use of organic solvents, making the technique more environmental friendly in removal of organic pollutants (Darshak R Bhatt et al., 2015). In **Table 2.2**, various determination technique for triazine compounds were summarized. The reported techniques have been reported to provide low LODs and LOQs in the applied extraction techniques.

Table 2.1: Physiochemical properties of studied triazine compounds.

Name	Chemical structure	Molecular formula	Molecular weight (g/mol)	p*K*$_a$	Log *K*$_{ow}$
Atrazine		$C_8H_{14}ClN_5$	215.69	1.75	2.7
Propazine		$C_9H_{16}ClN_5$	229.71	1.7	2.93
Prometryn		$C_{10}H_{19}N_5S$	241.36	4.1	3.51

p*K*$_{a,}$: the acid dissociation constant (*K*$_a$) of a solution.

Log *K*$_{ow}$: the octanol/water (o/w) partition coefficient.

Table 2.2: Summary of existing methodologies for detection of studied triazine compounds.

Tittle	**Samples**	**Method of extraction**	**Analysis**	**LODs (µg/L)**	**LOQs (µg/L)**	**% Recovery**	**Ref.**
Determination of triazine compounds in environmental water samples by HPLC using graphene –coated magnetic nanoparticles as adsorbent	Environmental water samples	MSPE	HPLC	0.02 – 0.04	0.07 – 0.12	89 – 96.2	(Zhao et al., 2011)
Determination of triazine compounds in milk by cloud point extraction and HPLC.	Milk	CPE	HPLC	6.79 – 1.19	22.6 – 37.3	70.5 – 96.9	(Liu et al., 2014)
Determination of triazine compounds in vegetables by ionic liquid foam floatation solid phase extraction high performance liquid chromatography	Vegetables	Ionic liquid foam floatation SPE	HPLC	1.36 – 2.76	4.53 – 9.51	78.6 – 104.4	(Zhang et al., 2014)
Aqueous two–phase extraction for determination of triazine compounds in milk by high performance liquid chromatography	Milk	Aqueous two – phase extraction	HPLC	2.1 – 2.8	6.9 – 9.4	86.3 – 120.6	(Yang et al., 2014)
Molecularly imprinted solid phase extraction in a syringe filter for determination of triazine compounds in Radix Paeoniae Alba by ultra–fast liquid chromatography	Radix Paeoniae Alba	MIP–SPE in a syringe filter	Ultra–fast liquid chromatography	0.09 – 0.39	0.30 – 1.31	92.4 – 107.3	(Li et al., 2016)

2.2 Cloud Point Extraction (CPE)

There are various extraction techniques used in extraction of triazine compounds such as liquid –liquid extraction (LLE). In LLE, large amount of VOCs, harmful solvents towards human and environment was required to separate the triazine compounds from the samples (Sarafraz-Yazdi et al., 2010). Thus, the used of organic solvents give disadvantages in terms of human health. Other disadvantages of LLE included the time – consuming process and the procedure level of difficulties. Due to this, CPE method was introduced in 1978. CPE act as alternative of LLE due to the following reasons; good capacity to solubilize solutes with different types and nature; ability to concentrate solutes with high recoveries; safety and cost benefits; required very small amount of the relatively non–flammable and non–volatile surfactant; easy disposal of the surfactant; and the inhibition by the surfactants of adsorption of non–polar analytes to glass surface (Nazar et al., 2011, Tabrizi, 2006). A comparison of various extraction technique for organic pollutants involving liquid–liquid interaction was summarized in **Table 2.3**. CPE method depends upon phase separation behavior exhibited due to the present of certain surfactant micelles. The hydrophobic groups of surfactants monomer tend to form aggregates called micelles at the concentration of surfactant known critical micelles concentration (CMC). The CMC of a surfactant depends on several factors such as the surfactant molecular structure and experimental conditions such as ionic strength and temperature. At appropriate alteration of the conditions, the sample solution becomes turbid at a temperature known as cloud point (CP) due to the insolubility of the surfactant in water. When the temperature reaches the cloud point, the solution containing the surfactant becomes turbid and separated into two phases: ‘surfactant rich phase’ and ‘aqueous phase’ (Filik et al., 2011).

Table 2.3: Comparison of various extraction technique for organic pollutants involving liquid –liquid interaction (Filik et al., 2011).

Extraction technique	Solvent type	Time	Advantages	Disadvantages
Liquid–liquid extraction (LLE)	Organic solvent	24 h	Analyte is partitioned between two immiscible solvents.	Large consumption of solvent and concentration of sample required after extraction.
Soxhlet	Organic solvent	6 – 24 h	Large amount of sample, filtration not required, not matrix dependent, and easy to operate.	Long extraction time, large consumption of organic solvent, preconcentration of sample required after extraction.
Supercritical fluid extraction (SFE)	Organic solvent	30 – 60 minute	Fast extraction, non–toxic, environmental friendly, small amount of solvent, filtration not required.	Limited sample size, extraction efficiency depends on matrix and analyte
Pressurized liquid extraction (PLE)	Organic solvent	10 – 60 minute	Fast technique, small solvent usage, no filtration needed and easy to use.	Extraction efficiency is more matrix dependent
Cloud point extraction (CPE)	Surfactant solution	10 – 20 minute	Fast extraction, surfactant is non–toxic, environmental friendly, small amount of solvent.	Required optimization of operating conditions

As shown in **Figure 2.1**, the CPE manipulates the temperature and concentration of surfactant to move the analyte into a micelle phase for separation (Zain et al., 2015). CPE is performed by adding surfactant solution to the sample at levels exceeding the CMC, allowing the formation of micelles. As the analytes dissolve and partition into the micelles, two immiscible phases formed. The position of the surfactant rich phase can be either at the top or bottom layer depending on the surfactant density. The surfactant rich phase consists of most targeted analytes in a small micellar volume while the aqueous phase consists of water surfactant monomer below the CMC and perhaps some targeted analytes. In the CPE, the surfactant aggregate (a micelle) orients its hydrocarbon tails towards the centre to create a non–polar core. The isolated hydrophobic compounds (a large number of bioactive compounds) present in the aqueous solution are favorably partitioned in the hydrophobic core of micelles (de Prá Urio et al., 2016).

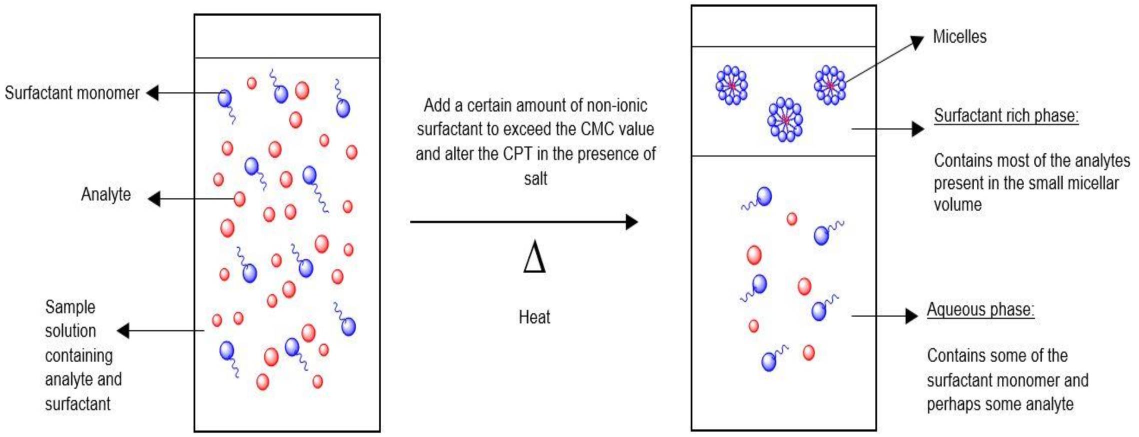


Figure 2.1: Illustration of CPE methods

2.3 Surfactant

The term surfactant is a blend of ‘‘Surface Active Agent’’. Surfactants are usually amphiphilic molecules, having both polar and non–polar groups that exhibit important interfacial properties between phases and can be used in many industrial separation processes (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, consist of between 8 and 18 atoms of carbon while X is the polar or ionic head group (Bezerra et al., 2005). The hydrophilic region of the surfactant (polar head group) and the hydrophobic region (non–polar tail group) of the surfactant act to lower the surface tension of a liquid. This head–tail group usually consist of one or more hydrocarbon chain which make surfactant soluble in both organic solvents and water (Li et al., 2012). Surfactant can be classified into anionic, cation, zwitterion and non –ionic families. According to **Figure 2.2**, the binding sites of each family of surfactant, were depending on the hydrophobicity of the micelles, amphoteric structure and the ionic compounds of micelles. Based on this, the interaction between the micelles and targeted analytes can be predicted to ease separation process. In a solution, low concentrations of surfactant molecules presented are mainly as monomers. When their concentration increases above a certain threshold, called the critical micellar concentration (CMC), surfactant monomers spontaneously accumulate to form colloidal –sized clusters, known as micelles that entrap the organic compounds (Paleologos et al., 2005).

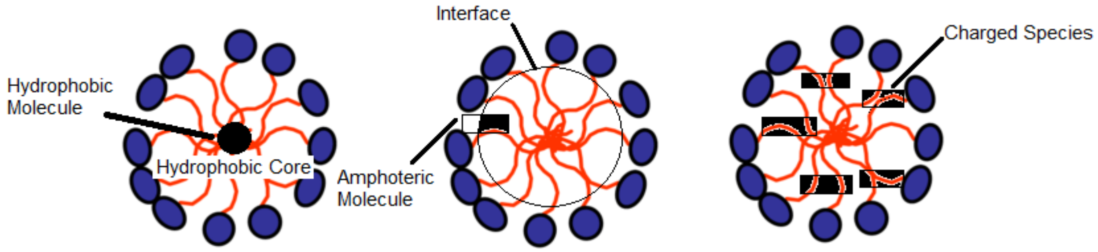


Figure 2.2: Illustration of binding sites of a micelle for hydrophobic, amphoteric and ionic compounds (Paleologos et al., 2005).

An anionic surfactant existed as a negatively charged head surfactant in the solution. The anionic surfactants have the advantages of being high and stable foaming agent. This causes the anionic surfactant to be widely used in production of shampoo and dish washing liquids. However, they have the disadvantage of being sensitive to minerals and the presence of minerals in water. The present of anionic surfactant along with the minerals will partially deactivated the present of the anionic charges causing the anionic charges surfactant to slightly lose its ability as anionic micelles. Among the subgroups of anionic surfactant are the ammonium soaps, alkali metal, amine soaps, divalent and trivalent metal soaps, alkyl sulphates and alkyl phosphate (Mishra et al., 2009).

A cationic surfactant is the surfactant that have positively charged head group in solution. A very large proportion of this class consists of nitrogen compounds such as fatty amine salts and quaternary ammoniums compounds, with one or several long chain compounds, which are derived from natural fatty acids (Azarmi et al., 2015). Cationic surfactant is commonly used as disinfectant and preservative. However, the charged surfactant will slow down the rate of water droplet merging since the charges will repel towards each other. Thus, lower the extraction efficiency. Other than that, cationic surfactant are known to be highly resistant towards biodegradation due to its lack of a primary degradation site in their molecules (Banno et al., 2013). This causing the cationic surfactant to be highly resist in environment.

Zwitterion, are surfactant molecule that exhibit both anionic and cationic charges on the same molecule structure, also known as amphoteric surfactant. Due to its amphiphilic properties, the surfactants tend to aggregate at gas–liquid and solid–liquid interface. An important property of the amphoteric surfactant are they highly dependent on the pH of the solution (Azarmi et al., 2015). Zwitterion surfactants also exhibit excellent dermatological properties and suitable to be used in personal care preparations.

These zwitterionic surfactants are mainly presented by acyl ethylenediamines and alkyl amino acids (Kume et al., 2008).

Non –ionic surfactant is the surfactant that does not have any positive or negative charged on their head group in solution. They do not ionize in aqueous solution. This surfactant are adsorbed physically rather than electrostatically or chemisorbed (Paria et al., 2004). Non–ionic surfactants are compatible with other molecule types, and are excellent candidates to enter complex mixtures, as found in many commercial products. They are much less sensitive to electrolytes, particularly divalent cations, than ionic surfactants, and can be used with highly saline or hard water (Doroshchuk et al., 2015). The non–ionic surfactants are mainly derived from the reaction of alcohols, alkylphenols and amines with ethylene oxide and/or propylene oxide (Kume et al., 2008). Thus, they exhibit a very low toxicity level and are used in pharmaceuticals, cosmetics, and food products (Heidarizadi et al., 2016). Non–ionic surfactants are found today in a large variety of domestic and industrial products, such as powdered or liquid formulations. The triton X−114 are the well–known non–ionic surfactant for micelle formation. Among the properties of non–ionic surfactant is they are normally compatible with all other types of surfactant. Their physicochemical properties of ethoxylated compounds make them are very temperature dependent surfactant and sugar based non–ionic surfactant mostly exhibit the normal temperature dependence (Doroshchuk et al., 2015).

2.3.1 Non–ionic silicone surfactant

Non–ionic silicone surfactant with hydrophilic moieties not only share many common features with conventional non–ionic surfactants but also possess properties of non –ionic surfactant. Silicone surfactants are equally surface active in water as well as in organic solvents and mineral such as oils and polyols. The non–ionic silicone surfactant lowering the surface tension of water to as low as 20 mN/m and remain as liquids even with very high molecular weights (Torchilin, 2001). 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 compounds on plant leaf's. They are also well–known as a growing class of raw materials used in the cosmetic, food, and pharmaceutical industries. Their biocompatibility and safety to human and environmentally friendly characteristics have been proven for a long time (Norseyrihan et al., 2016). Despite their extensive use in industrial, only a few investigations are available in the literature of these interesting amphiphilic copolymeric surfactants and they were summarized in **Table 2.4**. Studies also had reported that surfactant used for modification adsorbent is able to give good extraction recovery (Rajabi et al., 2016).

In the CPE technique, non–ionic silicone surfactant was applied, replacing the non –ionic surfactant used as extractor. Non–ionic silicone surfactant has more flexible polysiloxane chains without any aromatic structure and this overcome the disadvantages of other non–ionic surfactants. Other than that, non–ionic silicone surfactant can form more compact micelle structures which offer low water content in the surfactant rich phase and also low in density, thus, producing surfactant rich phase at the upper layer of a solution (Soroceanu et al., 2015). Previously, only few researchers had reported the use of non–ionic silicone surfactant such as DC 190C, DC 193C and OFX 0309 as extractor in the CPE. These types of surfactant are able to give satisfactory extraction recovery upon determination using instruments. In (Bingjia et al., 2007), DC 190C and DC 193C was studied for removal of polycyclic aromatic hydrocarbons (PAHs) and the recoveries achieved shows that

DC 190C have better removal efficiency than DC 193C. The performance of DC 193C were then studied by (Noorashikin et al., 2013) for extraction of parabens coupled with HPLC. In this study, the recovery was achieved in the range of 71.2 – 97.7% with 0.1 – 0.2 μg/L as the LODs range. Then, the performance of DC 193C was further studied in extraction of phenolic compounds and analyzed using UV spectrophotometry. The recoveries were achieved in range of 69 – 97%. Other non–ionic silicone surfactant that were studied were OFX 0309, for extraction of phenolic compound coupled with HPLC. The extraction offered good recoveries (90 – 99%) (Norseyrihan et al., 2016).

Table 2.4: Summary of applied surfactants in extraction/removal of organic pollutants.

Surfactants	**Application**	**Ref.**
Sodium dodecyl sulphate (SDS)	CPE of albumin	(Zhu et al., 2006)
Aliquat –336	CPE of Cyanobacterial Toxins	(Man et al., 2002)
	CPE of bisphenol A	(Yu et al., 2009)
Triton X –100	CPE of Sudan dyes	(Liu et al., 2007)
	CPE of sulphonamides	(Zhang et al., 2011)
	CPE of phenols	(Saravanan et al., 2014)
Triton X –114	CPE of phenol	(Katsoyannos et al., 2006)
	CPE of phthalate compounds	(Ling et al., 2007)
	CPE of triazine herbicides	(Liu et al., 2014)
	CPE of sym –triazine herbicides	(Doroshchuk et al., 2015)
	CPE of Azo dyes	(Ghasemi et al., 2016)
PEG –6000	CPE of prometryne	(Tan et al., 2013)
PONPE 7.5	CPE of lead compounds	(Luconi et al., 2000)
DC 190C	CPE of PAHs	(Bingjia et al., 2007)
DC 193C	CPE of paraben compounds	(Noorashikin et al., 2013)
	CPE of phenolic compounds	(Zain et al., 2014)
OFX 0309/Slygard 309	CPE of methylphenol	(Norseyrihan et al., 2016)

2.4 Magnetic Solid Phase Extraction (MSPE)

Conventional SPE technique was a technique that required large amount of organic solvents with extraction time up to 24 hours. Although good recoveries were obtained, the SPE procedure were not desirable due to the large use of organic solvents and time consuming. Then, to overcome the large used of organic solvents, solid phase microextraction (SPME) was introduced. Although SPME used only minimal amount of organic solvents, the procedure was time consuming. Due to the disadvantages of SPE and SPME, an improvised SPE method, magnetic solid phase extraction (MSPE) were introduced.

Magnetic solid phase extraction is a new extraction and preconcentrating procedure from large volumes of samples based on the use of magnetic adsorbents (Safarikova et al., 1999). The MSPE method is the improvised extraction method of SPE (Asgharinezhad et al., 2014) and the comparison study were summarized in **Table 2.5**. In MSPE, the magnetic properties of the adsorbent are the key in the extraction technique. In MSPE, the used of MNPs as sorbent can be easily dispersed in sample solution and recollected using external magnetic field outside the sample solution (Chen et al., 2016). Thus, less time required in the extraction step and this minimized the use of organic solvents. This technique can be visualized as a magnetic separation commonly used to separate magnetic phases from non–magnetic phases and avid the additional steps such as centrifugation, precipitation or filtration of samples (Ibarra et al., 2015). The use of MNPs allowed the easy isolation of compounds in the solution by attracting them using the external magnetic field, making it suitable upon dealing with aqueous samples. The suspended MNPs adsorbent will tagged along the targeted analytes and easily removed from large volume of samples.