SYNTHESIS OF HYBRID MATERIALS FUNCTIONALIZED WITH CYANO-IONIC LIQUID FOR THE EXTRACTION OF CHLOROPHENOLS AND POLYCYCLIC AROMATIC HYDROCARBONS

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ABSTRACT

In the present study two new cyano/ionic liquid functionalized hybrid materials were successfully synthesised based on immobilization of cyanopropyltriethoxysilane and 1-benzyl-3-(trimethoxysilylpropyl)imidazolium chloride ionic liquid (**BTMP-IM**) on the surface of titanium (IV) butoxide and Fe_3O_4 magnetic nanoparticle to enhance extraction capability toward aromatic moieties.The cyano/ionic liquid functionalized silica-titania mixed oxide (**Si-Ti@CN/IL**) was prepared via sol-gel method in acidic condition and used as an adsorbent for preconcentration/separation of chlorophenols in aqueous samples prior to High-performance liquid chromatography (HPLC). The **Si-Ti@CN/IL** was characterised by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), Brunauer-Emmett-Teller (BET), elemental analysis with CHNS and X-ray diffraction (XRD) to support the structure of this new hybrid material. The new **Si-Ti@CN/IL** adsorbent shows a good performance for extraction of selected chlorophenols (CPs) in aqueous samples with high recovery and low limit of detection (LOD = 0.83 – 0.95 $\mu g\ L^{-1}$) with linearity range from 10 – 100 $\mu g\ L^{-1}$, meanwhile, limit of quantification (LOQ) was between 2.77 to 3.17 $\mu g\ L^{-1}$. The application of **Si-Ti@CN/IL** for environmental samples was successfully studied on tap water, lake water and leachate from landfill site. The results obtained high recovery (73.39 – 105.54 %) with good precision (%RSD: 0.82 – 4.19). The cyano/ionic liquid functionalized Fe_3O_4 magnetic nanoparticle (**MNP@CN/IL**) was synthesised via basic co-precipitation and sol-gel methods and used as an adsorbent for preconcentration/separation of polycyclic aromatic hydrocarbons (PAHs) and chlorophenols (CPs) in aqueous and soil samples through magnetic solid phase extraction (MSPE) prior to HPLC. The **MNP@CN/IL** was characterized by FT-IR, XRD, transmission electron microscopy (TEM), elemental analysis with EDX as well as CHNS and TGA. The magnetic properties of the adsorbent was analysed by vibrating sample magnetometer (VSM). The **MNP@CN/IL** shows good performance with high recovery and low LOD (0.42 – 0.76 $\mu g\ L^{-1}$ for PAHs) and (0.64 – 1.06 $\mu g\ L^{-1}$ for CPs) with linearity range from 0.1 – 100 $\mu g\ L^{-1}$for PAHs and 3 – 100 $\mu g\ L^{-1}$ for CPs. Meanwhile the LOQ for PAHs and CPs were 1.39 – 2.55 $\mu g\ L^{-1}$ and 2.15 – 3.54 $\mu g\ L^{-1}$. The application of **MNP@CN/IL** for environmental samples was successfully studied on leachate and sludge from landfill site. The results obtained high recovery (83.75 – 115.33 % for PAHs) and (77.67 – 112.8 % for CPs) with acceptable precision (%RSD: 1.00 – 4.49 for PAHs; 0.92 – 4.89 for CPs).

ABSTRAK

Dua cyano/cecair ionik yang difungsikan bahan hibrid yang baru telah berjaya dihasilkan berdasarkan imobilisasi cyanopropiltriethoxisilane dan 1-benzil-3-(trimethoxisilylpropil) imidazolium klorida cecair ionik (**BTMP-IM**) pada permukaan titanium (IV) butoxide dan Fe_3O_4 magnetik berzarah nano untuk meningkatkan keupayaan pengekstrakan terhadap kumpulan aromatik. Cyano/cecair ionik yang difungsikan dengan campuran silika-titania oksida (**Si-Ti@CN/IL**) telah dihasilkan melalui kaedah sol-gel dalam keadaan berasid dan digunakan sebagai penjerap untuk pemekatan/pemisahan klorofenol dari sampel akues sebelum dianalisa oleh Kromatografi Cecair Berprestasi Tinggi (HPLC). Struktur **Si-Ti@CN/IL** dikenal pasti oleh Fourier spektroskopi inframerah (FTIR), analisis gravimetrik haba (TGA), mikroskopi pengimbas pelepasan elektron (FESEM), Brunauer-Emmett-Teller (BET), analisis unsur dengan CHNS dan pembelauan sinar-X (XRD) untuk mengenal pasti struktur bahan hibrid terbaru ini. **Si-Ti@CN/IL** menunjukkan pencapaian yang baik bagi pengekstrakan klorofenol yang terpilih di dalam sampel akues dengan kebolehdapatan semula yang tinggi dan had pengesanan yang rendah (LOD = 0.80 – 0.95 μg L^{-1}) dengan julat kelinearan dari 10 – 100 μg L^{-1} , manakala had kuantifikasi (LOQ) adalah di antara 2.77 kepada 3.1 μg L^{-1}. Penggunaan **Si-Ti@CN/IL** telah berjaya diaplikasi terhadap sampel alam sekitar iaitu air paip, air tasik, dan larut resapan dari tapak pelupusan. Keputusan yang diperolehi menunjukkan kebolehdapatan semula yang tinggi (73.39 – 105.54 %) dengan kepersisan yang bagus (% RSD: 0.82 – 4.19). Fe_3O_4 magnetik berzarah nano yang difungsikan oleh cyano/ cecair ionik (**MNP@CN/IL**) disintesis melalui kaedah pemendakan bersama dan kaedah sol-gel dan digunakan sebagai penjerap untuk pemekatan/pemisahan poli hidrokarbon aromatik (PAHs) dan klorofenol (CPs) dari sampel air dan sampel tanah melalui kaedah pengekstrakan fasa pepejal bermagnetik (MSPE) sebelum dianalisa oleh HPLC. Struktur **MNP@CN/IL** dikenal pasti dengan FESEM, XRD, mikroskop penghantaran elektron (TEM), analisis unsur dengan EDX serta CHNS dan TGA. Sifat magnetik bagi penjerap ini telah dianalisis oleh magnetometer sampel bergetar (VSM). **MNP@CN/IL** menunjukkan pencapaian yang baik bagi pengekstrakan poli hidrokarbon aromatik dan klorofenol yang terpilih di dalam sampel alam sekitar dengan kebolehdapatan semula yang tinggi dan had pengesanan yang rendah (0.42 – 0.76 μg L^{-1} untuk PAHs) dan (0.64 – 1.06 μg L^{-1} untuk CPs) dengan julat kelinearan dari 0.1 – 100 μg L^{-1} untuk PAHs dan 3 – 100 μg L^{-1} untuk CPs, manakala had kuantifikasi LOQ adalah (1.39 – 2.55 μg L^{-1} untuk PAHs) dan (2.15 – 3.54 μg L^{-1} untuk CPs). Penggunaan **MNP@CN/IL** telah berjaya diaplikasi terhadap sampel alam sekitar (larut resapan dan enapcemar dari tapak pelupusan). Keputusan menunjukkan kebolehdapatan semula yang tinggi (83.75 – 115.33 % untuk PAHs) dan (77.67 – 112.8 % untuk CPs) dengan kepersisan yang boleh diterima (% RSD 1.00 – 4.49 untuk PAHs, 0.92 – 4.89 untuk CPs).

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LIST OF ABBREVIATIONS

BaP	Benzo(a)pyrene
BET	Brunauer-Emmett-Teller
BTMP-IM	1-benzyl-3-(trimethoxysilylpropyl) imidazolium chloride
CPs	Chlorophenols
CRY	Chrysene
DCM	Dichloromethan
FESEM	Field Emission Scanning Electron Microscopy
FLO	Flourene
FLU	Fluoranthene
FTIR	Fourier Transform Infrared Spectroscopy
HPLC	High Pressure Liquid Chromatography
ILs	Ionic Liquids
LOD	Limit of Detection
LOQ	Limit of Quantification
MNP	Magnetic nanoparticles
MNP@CN	Cyano functionalized magnetic nanoparticles
MNP@CN/IL	Cyano-ionic liquid functionalized magnetic nanoparticles
MSPE	Magnetic Solid Phase Extraction
PAHs	Polycyclic Aromatic Hydrocarbons
PCP	pentachlorophenols
PYR	Pyrene
RSDs	Relative Standard Deviation
Si-Ti	Silica-titania mixed oxide
Si-Ti@CN	Silica-titania mixed oxide with cyano

Si-Ti@CN/IL	Silica-titania mixed oxide with cyano-ionic liquid
Si-Ti@IL	Silica-titania mixed oxide with ionic liquid
SPE	Solid Phase Extraction
TEOS	tetraethoxysilane
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
VSM	Vibrating Sample Magnetometer
XRD	X-ray diffraction
2-CP	2-chlorophenols
2,3,4,6-TTCP	2,3,4,6-tetrachlorophenols
2,4-DCP	2,4-dichlorophenols
2,4,6-TCP	2,4,6-trichlorophenols
3-CP	3-chlorophenols
%R	Percent Recovery

CHAPTER 1: INTRODUCTION

1.1 Background of study

Organic pollutants including chlorophenols (CPs) and polycyclic aromatic hydrocarbons (PAHs) have become a crucial environmental and public health problem which may cause histopathological alterations, genotoxicity, mutagenicity, and carcinogenicity to humans (Aeenehvand, *et al.*, 2016; Hoseini, *et al.*, 2016; Yarahmadi, *et al.*, 2016). Due to serious public health issues and environmental damages that PAHs and CPs may cause, monitoring and determination of them in the environmental samples is necessary. The chromatographic analysis such as high performance liquid chromatography (HPLC) has used widely in monitoring of organic contaminations. However, environmental samples due to trace amount of analytes and highly complex matric effects seem to be incompatible with the available chromatographic systems without sample preparation *i.e.*, preconcentration, extraction, matric simplification, filtration and clean up (Hyotylainen, 2009). The most challenging problems with sample preparation are their time consuming and rebellious process and possibility of any error in analysis through loss of analytes or interfering impurities into the sample. In this regard, selecting an appropriate method for sample preparation plays a key role to get an accurate and reliable result in analysis step (Ramos, 2012). The current emphasis of researchers is on developing a faster, simple, sensitive, reliable, economically feasible and environmental friendly, especially solvent free sample preconcentration method which can take place before instrumental determination (Fang, *et al.*, 2010). The available sample preparation methods to determine organic pollutants in environmental samples are liquid–liquid extraction and solid phase extraction (Chirila, *et al.*, 2006).

One of the most used sample preparation methods is solid phase extraction (SPE). The wide usage of SPE is due to its highly separation capacity, flexibility, easy automation and low cost (Mirzajani and Kardani, 2016; Pebdani, *et al.*, 2016; Sajid and Basheer, 2016). Also, magnetic solid phase extraction (MSPE) as a new mode of SPE, has received great attention in trace analysis. The separation based on magnetic force avoids additional centrifugation, filtration or column passing operation demands (Amjadi, *et al.*, 2015; Azizi, *et al.*, 2016; Dezfoolinezhad, *et al.*, 2016; Mollahosseini, *et al.*, 2015; Zolfigol, *et al.*, 2016). MSPE has several advantages *i.e.*, easy reusability, simple method, high enrichment factor and fast operation and high separation efficiency. Different functionalized materials have been synthesised and employed as an adsorbent in SPE and MSPE methods (Huo and Yan, 2012; Mehdinia, *et al.*, 2011; Opeolu, *et al.*, 2010; Raoov, *et al.*, 2014; Sadanala and Chung, 2013; Song, *et al.*, 2011; Wu, *et al.*, 2012; Zhao, *et al.*, 2008). The most important point about SPE is the adsorbent which can control the selectivity, affinity and capacity of method. But conventional adsorbents has narrow range of selectivity of various analytes, therefore, different attempts have been made to modify SPE conventional adsorbents to increase their selectivity and there is still need new innovative and efficient adsorbent (Vidal, *et al.*, 2012b). In this respect, cyano based materials deserve particular attention due to the polarizable nature of the materials which are considered as highly efficient adsorbents for the extraction of polar analytes from water samples (Miskam, *et al.*, 2013). The cyano group have unshared electron pair of nitrile nitrogen which can easily forms intermolecular hydrogen bonds with the hydrogen of donor molecules/target analytes such as phenols, ketones, alcohols, esters and molecules bearing π–electrons. However, conventionally prepared cyano coating without chemical bonding to any substrate are not stable at room temperature (Kulkarni, *et al.*, 2006). The chemical attachment of cyanopropylsiloxanes onto solid surface solves this problem (Kulkarni, *et al.*, 2006;

Miskam, *et al.*, 2013; Wan Ibrahim, *et al.*, 2011). As CPs and PAHs having aromatic core and it is reported that compounds having benzene ring are good extractant agent for the extraction of them by virtue of π–π interaction (Rodríguez, *et al.*, 2000). In this regard, recently a new class of ionic liquids (ILs) whether the introduction of a benzene ring into the cationic part of ionic liquid or imidazolium-based ILs adsorbents deserve particular attention as for the detoxification of compounds with aromatic moieties from contaminated waters (Bo, *et al.*, 2014; Fan, *et al.*, 2014; Holbrey, *et al.*, 2003; Martinez and Iverson, 2012). However, the application of ILs still shows some limitations *i.e.*, the low mass transfer, the long equilibrium time and difficulty in phases separation (Galan Cano, *et al.*, 2013). In addition, the solubility of ILs in water often limits their frequent uses in separation study. These drawbacks can be abridging by the immobilisation of ILs onto polymers and solid supports as SPE and MSPE materials (Vidal, *et al.*, 2012b). Due to the unusual dual nature of ILs, they can act as low polarity phase in front of non-polar analytes and high polarity in front of analytes bearing strong proton donor groups, through multiple interactions *i.e.*, electrostatic, hydrophobic and π–π (Han and Row, 2010).

In this study we have reported the synthesis of a new SPE adsorbent (**Si-Ti@CN/IL**) and MSPE adsorbent (**MNP@CN/IL**) which are the combination of cyano group and ionic liquid and their performance as adsorbents towards selected aromatic moieties. The main consideration of these new materials is the presence of benzene group in the cationic part of the ionic liquid, with imparting π–π interaction between the adsorbent and aromatic moieties in the analytes, in addition, the presence of unshared electron pair of cyano groups in cyanopropyltriethoxysilane, which is our site of interest to attract analytes through hydrogen bonds. The combination of these two functional groups will increase the affinity and capacity towards selected aromatic moieties.

1.2 Objectives of the research

The objectives of this study are as follow:

(i) To synthesis and characterize cyano/ionic liquid functionalized silica-titania (**Si-Ti@CN/IL**).

(ii) To develop and apply **Si-Ti@CN/IL** as solid phase extraction (SPE) adsorbent for the extraction of selected Chlorophenols (CPs) in water samples.

(iii) To synthesis and characterize cyano/ionic liquid functionalized Fe_3O_4 magnetic nanoparticle (**MNP@CN/IL**).

(iv) To develop and apply **MNP@CN/IL** as magnetic solid phase extraction (MSPE) adsorbent for the extraction of selected polycyclic aromatic hydrocarbons (PAHs) and chlorophenols (CPs) in water and soil samples.

1.3 Scope of study

The scope of this research was to synthesis adsorbents by combination of two functional groups *i.e.*, cyano group and ionic liquid to increase the affinity and capacity towards selected aromatic moieties. To confirm the successful synthesis of new adsorbents, different characterization techniques has been employed *i.e.*, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), elemental analysis, field emission scanning electron microscopy (FESEM), Brunauer-Emmett-Teller (BET),transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). Then, the synthesised **Si-Ti@CN/IL** and **MNP@CN/IL** were applied as new adsorbents for the extraction of selected chlorophenols and polycyclic aromatic hydrocarbons from water and soil samples.

1.4 Outline of the thesis

The present thesis is divided into five chapters. The Chapter 1 consists of a brief introduction on the research background, the objectives of the research and scope of study. The compilation of literature review, organic-inorganic hybrid materials, their synthesis, functionalization and their application in separation process has been presented in Chapter 2. Chapter 3 gives an overview of the synthesis and characterization of cyano/ionic liquid functionalized silica-titania mixed oxide (**Si-Ti@CN/IL**), the optimization of solid phase extraction method for selected chlorophenols using **Si-Ti@CN/IL** prior to HPLC and the application of developed method on different water samples is discussed. In Chapter 4 the synthesis and related characterization of cyano/ionic liquid functionalized Fe_3O_4 magnetic nanoparticles (**MNP@CN/IL**), the optimization of magnetic solid phase extraction method and the determination of selected polycyclic aromatic hydrocarbons and chlorophenols using **MNP@CN/IL** prior to HPLC and its application on water and soil samples is presented. At the end, an overall conclusion and recommendations for future works is provided in Chapter 5.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Aromatic compounds, *i.e.*, CPs and PAHs are found as common pollutants in environmental samples *i.e.*, water and soil, air due to their wide industrial use (Czaplicka, 2004; Lundstedt, *et al.*, 2007). Many of these aromatic pollutants are known as serious public health hazardous substances due to their toxic, mutagenic and carcinogenic effects, and some are listed as hazardous pollutants by US environmental protection agency (USEPA) because of their harmful potential to human health such as chrysene, benzo[a]pyrene and some as restricted-use like pentachlorophenol (Crini, 2005; Mercier, *et al.*, 2011). Another problems with samples contain CPs and PAHs is trace amount of analysis and highly complex matric effects of environmental samples *i.e.*, water and soil (Ramos, 2012). To overcome these problems, sample pretreatment methods can be very helpful to preconcentrate the analytes and remove or limit the interferences in samples. However, sample pretreatment can be an essential and laborious step and improper selection of technique can influence the result of the study through either losing of the analytes or interfering of any impurities into the samples. It is therefore important to select a suitable pretreatment technique to avoid any upcoming issues such as high cost, consuming time, and quantitative and qualitative errors in final results (Liu, *et al.*, 2011; Wierucka and Biziuk, 2014). In this matter, liquid-liquid extraction (LLE) and solid phase extraction (SPE) are two well-known traditional sample pretreatment techniques which are employed to extract and preconcentrate various analytes from environmental samples. There is a growing tendency to use SPE rather than LLE method. This is because of problems that rise with LLE procedure *i.e.*, utilizing large volume of toxic organic solvents, time consuming clean-up process, foam formation and difficulty with automation of LLE. Taking into account that environmental friendly (green) chemistry techniques such as SPE for sample pretreatment that reduce the volume of solvent usage in the process and in follow reduction of hazardous organic wastes is getting more popular, in recent researches (Armenta, *et al.*, 2008). Amongst the available treatment methods, the adsorption by solid adsorbents is the most popular one, (Figure 2.1). This is because of the advantages of adsorption over others treatments, *i.e.*, ease of operation, low cost, simple design, effectiveness and efficient (Crini, 2005). Adsorption is a most efficient used equilibrium treatment which includes a surface attraction of solute molecules from aqueous phase to solid surface of adsorbent through physical or chemical binding (Hyotylainen, 2009; Ramos, 2012), (Table 2.1). Absorption treatment is highly dependent on the properties and surface morphology of the adsorbent which is used (Hyotylainen, 2009). Adsorbent is solid materials that collect solutes on its surface. Adsorbents are classified into two groups of natural and synthetic, each of these adsorbents has its own limitation (Rashed, 2013).

Table 2.1: Modified adsorbents of SPE/ MSPE for separation of CPs & PAHs in environmental water samples

Adsorbent	Method	Sample	Ref.
GO(graphine oxide)	SPE-HPLC	CPs in tap/river water	(Liu, *et al.*, 2011)
HS-SDME	SPE-HPLC	CPs in tap/river water	(Sharma, *et al.*, 2011)
TiO_2- graphine	SPE-electrochemical sensor	CPs in lake/river/sea water	(Bai, *et al.*, 2014)
Fe_3O_4@p(DEVP-co-EDMA)	MSPE-HPLC	CPs in tap/lake/drinking water	(Li, *et al.*, 2012)
3D-G@ Fe_3O_4	MSPE-HPLC	CPs in tap/river/sea water	(Liu, Wang, *et al.*, 2014)
MNP-IL	MSPE-HPLC	CPs in tap/river/spring water	(Yang, *et al.*, 2011)
MNP-C18	MSPE-HPLC-	PAHs in tap water	(Liu, *et al.*, 2009)
Fe_3O_4@AuNPs	MSPE-HPLC	PAHs in tap/lake/waste water	(Li, *et al.*, 2014)
Fe_3O_4-IL	MSPE-GCMS	PAHs in tap/river/well/reservoir water	(Galan Cano, *et al.*, 2013)

In the past decades, synthetic adsorbents have been employed more and more due to their high surface area, strength, surface modification and pore size distribution, and ease of regeneration. Currently, organic-inorganic hybrid materials have been highly used as adsorbent in separation methods due to their advanced properties; thermal stability and strength of inorganic materials combined with functional variation of organic materials which leads to a robust binding affinity towards target organic pollutants (Samiey, *et al.*, 2014).

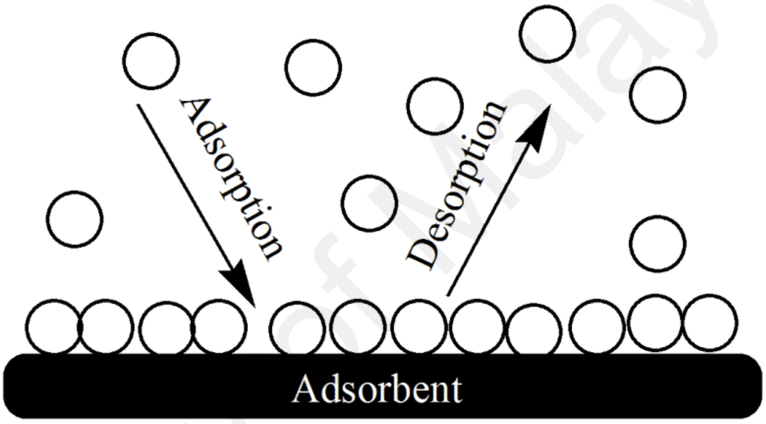


Figure 2.1: Schematic illustration of the adsorption-desorption processes.

2.2 Organic-inorganic hybrid materials

Organic-inorganic hybrid materials have made of two or more different organic and inorganic compounds in one polymeric matric. In recent years, researchers have given more attention to hybrid materials due to advanced properties and synergetic effect of two compounds in one matric in compare to their individual starting materials (Aghapoor, *et al.*, 2015; Alothman, 2012; Chahkandi, *et al.*, 2014; Davarpanah, *et al.*, 2013; Lee, *et al.*, 2012; Parin and Sagar, 2015; S. Wang, *et al.*, 2013; Wright and Uddin, 2012; Zhu and Row, 2012). Based on the connection between organic and inorganic compounds, the hybrid materials fall into three categories *i.e.*, structurally hybridized materials, chemically bound hybridized materials and functionally hybridized materials (Lee, *et al.*, 2012; Parin and Sagar, 2015). Structurally hybridized materials are designed under physical interaction between compounds at macroscopic level. The combination usually undergo ambient or elevated temperature without containing new chemical species, like the coagulation of poly-ferric chloride and poly-dimethyldiallyammonium chloride (Gao, *et al.*, 2008). Chemically bond hybridized materials are produced through strong chemical bonds between compounds at molecular level where a new chemical group introduced into the molecular chain of materials, like chemical species distribution of poly-aluminumsilicate chloride and poly-aluminum chloride (Gao, *et al.*, 2002). Functionally hybridized materials with either structurally or chemically bond that combine two or more functional materials in one matric which results in new functions or super functions such as functionalization of magnetic iron oxide with n-methylimidazole (Yang, *et al.*, 2011).

2.2.1 Nanoparticles

Organic-inorganic nano hybrid materials often are produced by assembly of organic matrices on inorganic nanoparticles (Jeon and Baek, 2010). This class of hybrid materials often show improved performance in contrast with their microparticle form. This is due to their excellent integration and improved interface between nanoparticles and organic matrices (Peng, *et al.*, 2006; Perrier, *et al.*, 2005; Taniguchi, *et al.*, 2008).

Nanoparticles are generally defined as solids less than 100 nm at least in one dimension. Most often these particles have spherical diameters on the order of 10 nm or less. It is understood that the behaviour of particles in nano scale is different from macro size. When the particles change size from macro to nano scale, the surface area and surface energy increase. Therefore, nano scale particles provide different physical, chemical and biological properties from the same materials in macro size. Nano scale particles process a large fraction of the atoms at or near the surface per unit of volume (Behari, 2010; Willard, *et al.*, 2004).

2.2.2 Mixed metal oxides

Mixed metal oxides nanoparticles are oxygen-containing of two or more kinds of metal cations in which vary by a strict stoichiometry (Kang, *et al.*, 2014; Patil, *et al.*, 2014). Mixed metal oxides are produced in the form of either powder or single crystals. So, they are classified as aluminates, chromates, fluorites, silicates, titanates and ferrites in the form of crystalline or amorphous according to their chemical structure (Patil, *et al.*, 2014). Mixed oxides are important class of compounds due to their thermal and chemical stability. These compounds are widely used in different industrial applications *i.e.*, ceramics, electronics, magnetic, adsorbent and catalysis. Different attempt has focused on developing of mixed metal oxides (Kang, *et al.*, 2014). The mixed metal oxides have been highly used in organic conversion applications. This is because of their ease of handling, less corrosion in reactor and plant, low cost, reusability and recyclability. The mixed metal oxides are usually prepared by solid state chemical reaction, microemulsion, sol–gel and precipitation methods. Precipitation and sol–gel are considered to be the most used methods due to the simplicity, good homogeneity and high surface area (Manoj, *et al.*, 2012).

2.2.2.1 Titania-Silica based hybrid materials

Silica-based adsorbents have been extensively employed as adsorbent for the separation and extraction of various kinds of toxic chemicals in environmental samples (Brasil, *et al.*, 2005; De Moraes, *et al.*, 2005a; De Moraes, *et al.*, 2005b). The silica based materials does not swells or shrinks like polymer resin (Airoldi and De Farias, 2000) and unmodified natural materials (Brasil, *et al.*, 2006). More over silica materials show good thermal stability (Airoldi and De Farias, 2000). However, there is a main draw back in term of narrow pH range stability towards silica materials usage (Miskam, *et al.*, 2013). Titania based materials (Li, *et al.*, 2007; Nawrocki, *et al.*, 2004a; Nawrocki, *et al.*, 2004b) are well known for pH stability and they display stronger Lewis basic and acidic activity regarding to the Ti^{4+} sites which act as an electron-pair acceptor. The rich hydroxyl surface of titania with strong Brønsted acidity offers anion-exchange properties at acidic pH and cation-exchange properties at alkaline pH. More over the superior mechanical strength and physical properties of titania desire more attention to being used as support material in different applications (Li, *et al.*, 2007).

Titania-silica nanoparticle mixed oxides have received great attention in application with organic substrates because of their good accessibility, high dispersion and high thermal and mechanical stability (Husing, *et al.*, 2002). The titania-silica materials have been extensively employed as an adsorbent for separation of various chemical contaminants (Brigante and Schulz, 2011; Inada, *et al.*, 2013; Rasalingam, *et al.*, 2013). However, the synthesis of titania-silica still is challenging due to difficulty to control the homogeneity and porosity of materials especially with high loading of titanium (Zhang, *et al.*, 2005). Variety attempts have been made to develop titania-silica materials synthesis procedures *i.e.*, microemulsion, impregnation, precipitation, chemical vapour deposition and sol-gel method. The most conventional synthesis method is the one that can have better control on hydrolysis and condensation of titania atoms due to faster hydrolysis of titania in compare with silica (Gervais, *et al.*, 2001; Zhang, *et al.*, 2005).

2.2.2.2 Magnetic nanoparticles

The magnetic nanoparticles (MNPs) are a class of nanoparticle with magnetic properties. MNPs consist of two metal oxides such as iron (Chen, *et al.*, 2008; Laurent, *et al.*, 2008), cobalt (El-Okr, *et al.*, 2011; Kraus, *et al.*, 2009), nickel (Cheng, *et al.*, 2005; Kraus, *et al.*, 2009) and platinum (Abu-Reziq, *et al.*, 2007; Park and Cheon, 2001). This group of nanoparticles have sufficient surface stabilisation in absence of external magnetic field, and indicate strong magnetic properties in presence of magnetic field. Therefore, they are able to be re-dispersed and reused (Willard, *et al.*, 2004). The magnetic properties of MNPs make them suitable across wide range of applications like cell sorting (Di Corato, *et al.*, 2011; Yoon, *et al.*, 2006), in medical treatment, cancer treatment, hyper thermal agents (Laurent, *et al.*, 2011; Xu, *et al.*, 2012), and drug delivery (Dobson, 2006; Veiseh, *et al.*, 2010), in chemistry as catalyst or catalyst support (Migowski and Dupont, 2007; Yoon, *et al.*, 2003), in biomedical process as MRI contrast agent (Moffat, *et al.*, 2003; Oghabian and Farahbakhsh, 2010) and in waste water treatment as extraction medium (Cheng, *et al.*, 2012; Huang and Hu, 2008).

The most often used magnetic iron oxides nanoparticles is magnetite (Fe_3O_4). However, due to possible oxidation and aggregation which cause the loss of magnetic property, pure iron oxide is not suitable for separation. To overcome this problem, the surface of the magnetic core is coated with inorganic materials such as silica, silicones, surfactants or organic materials like ionic liquids (Gee, *et al.*, 2003; Herve, *et al.*, 2008; Jeong, *et al.*, 2004; Pareta, *et al.*, 2008).

A variety of methods have been investigated for synthesis of magnetic nanoparticles with proper particle size, shape, crystal structure and poly-disparity (Hyeon, 2003) *i.e.* thermal decomposition reaction (Park, *et al.*, 2004), gamma irradiation (Lee, *et al.*, 2014), electrochemical (Hill, *et al.*, 2015), reverse micelle (Sharifi, *et al.*, 2012), sol-gel techniques (Eshaghi and Esmaeili-Shahri, 2014; He, *et al.*, 2014; Iqbal and Asgher, 2013; Liu, *et al.*, 2013) and precipitation (Khalafi Nezhad, *et al.*, 2015; Shanmuga, *et al.*, 2015). But just limited numbers of these methods are applicable in industrial sectors. This is because of their high cost and safety problem that arise from them (Hasany, *et al.*, 2012; Xu, *et al.*, 2014).

2.3 Synthesis of organic-inorganic hybrid materials

There are different methods to prepare hybrid materials which are based on the type of hybrid materials (Wright and Uddin, 2012). This method either can be a physical blending under room or elevated temperature or chemical bonding such as copolymerization and chemical grafting (Lee, *et al.*, 2012). In this section some of common methods of synthesizing the titania-silica and iron oxide magnetic nanoparticles are reviewed.

2.3.1 Microemulsion

Microemulsion is isotropic, macroscopically homogeneous and thermodynamically stable liquid solution system of water (polar phase), oil (non-polar phase), and surfactant (Maqsood Ahmad, *et al.*, 2012). The surfactant molecules form an interfacial layer to separate the polar and the non-polar phases. This may forms direct micelles with polar-head out as droplets of oil dispersed in water phase (oil/water microemulsion), inverted micelles with hydrocarbon tail out as droplets dispersed in oil phase (water/oil microemulsion) or sponge structure (bicontinuous microemulsion) in water and oil continues phase (Aubery, *et al.*, 2013). Different variables may affect the properties and structure of nanoparticles synthesized by microemulsion method e.g., solvent, aqueous phase content, concentration, surfactant type. However, there is still uncertainty about the correlation between the size of microemulsion droplets and the synthesized nanoparticles. Moreover, there are not sufficient systematic studies to investigate the relationship between the dynamic behaviour of the microemulsion and the kinetics of nanoparticle, while this might be a critical variable influencing the nanoparticle formation (Maqsood Ahmad, *et al.*, 2012).

2.3.2 Chemical vapour deposition

Chemical vapour deposition of coating is the chemical reactions of homogeneous gas phase reactants in a thermally activated surface to form a stable solid material. Chemical vapour deposition can provide excellent control at atomic or nanometer scale level on formation of crystal structure, surface morphology and orientation of resultant products. Therefore, it can produce different materials in the range of single layer, multilayer, composite and amorphous at low temperatures. The chemical vapour deposition is a versatile method for the deposition of thin films and coating *i.e.*, semiconductors, dielectrics, ceramic fibres, matrix composites and metallic films. However the drawbacks of chemical vapour deposition is limited its application, the used of volatile and toxic chemical precursors and flammable gases is illuminated the chemical vapour deposition as less environmentally friendly method. The chemical vapour deposition tends to be very expensive because it requires sophisticated reactor and vacuums in the process. Also it has some difficulty to control the stoichiometry of multi-source precursors due to variety in evaporate or sputter rates for each element (Choy, 2003).

2.3.3 Precipitation

Precipitation is one of the oldest but simplest techniques to prepare mixed metal oxide nanoparticles from desired cations in solvent which usually is water. Addition of a precipitation agent to the mixture helps to uniformly growth of the produced nuclei and obtaining an insoluble solid. The synthesised mixed oxide nanoparticles from this technique have irregular morphology with broad particle size distribution. However, the particle size and the morphology can be controlled by optimizing the synthesis parameters such as pH, temperature, time, type and concentration of precipitation agent and the amount of metal precursors. Washing and drying procedures may have drastic impact on mechanical properties and degree of aggregation (Hasany, *et al.*, 2012; Willard, *et al.*, 2004). Especially, the precipitation approach is utilized to synthesis ferrite magnetic nanoparticles with controlled size and magnetic property (Ayyappan, *et al.*, 2009; Gnanaprakash, *et al.*, 2006).

2.3.4 Sol-gel

The sol-gel process is a chemical combination method that mainly is based on hydroxylation and polymerization reactions. The sol-gel is widely used for the preparation of organic-inorganic hybrid materials (Cattoen, *et al.*, 2014; S. Wang, *et al.*, 2013). Sol-gel method are able to form novel materials in variety formats such as monoliths, porous structure, dense powders and thin films or fibres, relatively, under mild condition. This has made sol-gel as a versatile tool in optical, thermal, electronic, chemical and biomedical fields (Kabir, *et al.*, 2013). In analytical chemistry, sol-gel method provides great potential of producing novel adsorbents. Although, sol-gel method has been used for long time, but its application in analytical field is just back to two decades. Rising number of publications on preparation of new adsorbents through sol-gel method and its application presents great success in contribution of sol-gel method. There are many papers which have studies the preparation of adsorbents for different mode of SPE such as solid phase micro extraction (Kabir, *et al.*, 2013; Kumar, *et al.*, 2008), solid phase extraction (Fang, *et al.*, 2005; He, *et al.*, 2007), capillary micro extraction (Kabir, *et al.*, 2004; Kataoka, *et al.*, 2009), stir bar sorptive extraction (Hu, *et al.*, 2007; Nogueira, 2012) and magnetic solid phase extraction (Asgharinezhad, *et al.*, 2014; Dobson, 2006).

A sol is stable colloidal suspension particles with diameters of 1-100 nm in a solvent. A gel is a continuous solid network with three dimensional porous structures which encloses a liquid phase. The sol-gel process generally includes hydrolysis of at least one precursor which usually is a metal alkoxide under controlled acidic or basic condition with water at room temperature to form metal hydroxide. During acidic hydrolysis, the oxygen atom of alkoxide group is protonated and under nucleophilic attack of the oxygen atom of a water molecule makes alcohol a better leaving group and leads to produce metal hydroxide. Meanwhile, the basic hydrolysis reaction occurs by nucleophilic attack of hydroxyl anion to metal atom of metal alkoxide under release of deprotonated metal alkoxide species. In general, the sol-gel process is carried out in low molecular weight organic solvents such as alcohol, as shown in following equation:

$$\mathrm{M-OR+HOH'\rightarrow M-OH'+ROH} \qquad (2.1)$$

The condensation and polymerization of precursors leads to increase the viscosity of the solution through preparation of an oxide polymeric or colloidal suspension particle as the sol. Generally, Van der Waals forces or hydrogen bonds are responsible about interaction between particles. Condensation reaction includes nucleophilic attack of either metal hydroxide or alkoxide to a protonated metal hydroxide species. The reaction leads to the $\mathrm{M{-}O{-}M'}$ bonds. This step can be occurred by releasing of either water or alcohol as by-products of reaction, as illustrated in following equations:

$$\mathrm{M-OH+RO-M'\rightarrow M-O-M'+ROH} \qquad (2.2)$$

$$\mathrm{M-OH+HO-M'\rightarrow M-O-M'+HOH} \qquad (2.3)$$

The reactions in both hydrolysis and condensation are SN2 type (Brinker and Scherer, 2013). Formation of continuous network through agglomeration of colloidal or polymeric particles is known as gelation. Covalent bonds have an important role in irreversible linking polymer chains. The overall gelation time strongly depends on the condition of process which is taking place on it, can be formed within a second to several months or even more. Drying step leads to removal of by-products, solvent and high shrinkage of the network (Lenza and Vasconcelos, 2002).

There are several advantages of sol-gel process which the most important are summarized as follows (Avnir, *et al.*, 2006; Carter and Norton, 2013; Milea, *et al.*, 2011):

- Generally, sol-gel preparation proceeds under low temperature, close to room temperature, thus minimize thermally volatilization of components. This makes it environmentally acceptable process.
- Low temperature processing of sol-gel permits hybridation of thermally unstable organic polymers with inorganic materials.
- High purity of products which is caused by using very high pure reactants.
- High degree of homogeneity of products.
- Controlling the kinetics of chemical reactions.
- Controlling the particle shape, size and other properties.
- Producing materials in different forms such as monolith, particles, very thin films and ultra-fine powder.

The typical starting materials in sol-gel process are at least one precursor, solvent, catalyst, water and other additives such as organic molecule. All the reactions involves in sol-gel process perform to produce a physicochemical bonded structure with better thermal, hydrolytic and pH stability (Milea, *et al.*, 2011; Willard, *et al.*, 2004). Some of these parameters are reviewed as follows:

(i) Solvent

In sol-gel system, solvent can play an effective role in the reactions rate. For instance, the use of methanol as a solvent into the system which methanol is a by-product of hydrolysis reaction might enhance the rate of hydrolysis (Milea*, et al.*, 2011; Segro*, et al.*, 2009). Solvent is performing a critical role in controlling the homogeneity of the system during sol-gel process. Controlling the homogeneity of product in processes that contain various metal alkoxide precursors might be difficult, due to the different reactions that caused between metal alkoxides (Milea, *et al.*, 2011). Transition metal alkoxides such as Ti have very fast hydrolysis reactions because of high charge density on the metal. This event may cause major problem in controlling of morphology and structure of final products. Solvents can be used to control reaction kinetics. For instance, a nonpolar, aprotic solvent can reduce the hydrolysis reaction through oligomerization. Water plays an important role in controlling the rate of hydrolysis and polycondensation in sol-gel process due to function of water as reaction medium. The amount and how the water is added indicate semi or complete hydrolysis. Meanwhile presence of a co-solvent such as alcohols helps to facilitate the hydrolysis process especially to dissolve the water immiscible alkoxides and improves the homogeneity (Milea*, et al.*, 2011; Segro*, et al.*, 2009).

(ii) Catalyses

Catalyst can speed up the rate of hydrolysis and condensation reactions during sol-gel processing. Two types of catalyst which might be used in sol-gel processing are acid and base. Under acidic condition, hydrolysis speeds up more efficiency than condensation reactions. In fact, after removing of first electrons from donating alkoxy group, protonation of metal is less favourable and following step will be slow down. This leads the formation of linear structure in the final product. On the other hand, basic catalyst makes highly condensed structure. This is the reason that in basic catalysts, the rate of condensation reaction is faster and the rate of hydrolysis reactions is relatively slower. The result from basic catalysis occur with highly branched networks (Milea, *et al.*, 2011).

(iii) Backbone of precursors

Commonly, alkoxide of silicon, titanium, aluminium, zirconium and germanium are used as sol-gel precursors. One of the well-known materials used as precursors is silicon alkoxides. This is because of the stability of Si-O bond and highly availability of them. However, other metal alkoxides may create higher thermal, chemical or pH stable sol-gels than silica based sol-gel such as Ti (Milea, *et al.*, 2011; Vioux, *et al.*, 2010; Vives and Meunier, 2008). Coordination number and partial positive charge of metal atoms in precursors affects the mechanism and rate of sol- gel reactions. Higher charge density metal such as transition metal alkoxide increases the hydrolysis reaction faster (Vioux, *et al.*, 2010). Length of the alkyl chain of alkoxide affects the hydrolysis rate. As the alkyl chain grow longer, hydrolysis and condensation reactions slow down. This caused by electronic and steric impact. Furthermore, substituted alkyl or aryl groups in precursors may reduce hydrolysis rates because of steric hindrance. Alkyl or aryl substituted precursors make open network by increasing the flexibility of sol-gel (Vioux, *et al.*, 2010).

2.3.5 Functionalization of cyanopropyltriethoxysilane onto inorganic materials

Cyanopropylsiloxanes are known as one of the most used material in exhibiting both polar and polarisable characteristics which is suitable at both low and high temperatures (Kulkarni, *et al.*, 2006). The cyano group in cyanopropylsiloxanes has a key role in electron attracting activity through dipole-dipole, dipole-induced dipole, and charge transfer interactions (Kulkarni, *et al.*, 2006). The cyano group with unshared electron pair in the nitrile nitrogen is responsible for hydrogen bonding with hydrogen donor molecules, such as phenols, alcohols, ketones, esters, and analytes bearing π-electrons (Kulkarni, *et al.*, 2006). The polar attraction of cyanopropyltriethoxysilane has generated great attention recently, and several studies have focused on it. Kulkarni (2006) has presented sol-gel coating containing highly polar cyanopropyltriethoxysilane and non-polar poly(dimethylsiloxane) for capillary micro-extraction (CME) of polycyclic aromatic hydrocarbons and fatty acids (Kulkarni, *et al.*, 2006). Wan Ibrahim (2011) have synthesized polydimethylsiloxane-cyanopropyltriethoxysilane (PDMS-CNPrTEOS) from hybrid coating of cyanopropyltriethoxysilane and polydimethylsiloxane (PDMS) and used as an adsorbent for stir bar sorptive extraction (SBSE) for extraction of non-steroidal anti-inflammatory drugs (Wan Ibrahim, *et al.*, 2011). Another hybrid material, methyltrimethoxysilane-cyanopropyltriethoxysilane (MTMOS-CNPrTEOS) was synthesised under sol-gel method by the same research group. This adsorbent has applied successfully on dispersive-micro-SPE (D-μ-SPE) for extraction of selected organophosphorus pesticides (OPPs) from water samples (Muhamad, *et al.*, 2014). Meanwhile, the study of the MTMOS-CNPrTEOS as an alternative adsorbent for SBSE method has shown good applicability of this material to extract non-steroidal anti-inflammatory drugs from urine samples (Wan Ibrahim, *et al.*, 2011). El-Nakat (2014) immobilized cyanopropyltriethoxysilane onto ammonium carboxylate to form a meso-structured and ladder organic-inorganic hybrid material through sol–gel process. The material exhibits a high chelating capability towards heavy metals cations from water media (El-Nakat, *et al.*, 2014). In a recent study by our research group, Miskam (2013) was studied the advantages of titania in pH stability and chemical strength with polar attraction of cyanopropyltriethoxysilane, introduced as a new sol-gel, titanium (IV) butoxide-cyanopropyltriethoxysilane (Ti-CNPrTEOS) hybrid, with high selectivity towards polar aromatic amines. The material was capable of removal of polar compounds (Miskam, *et al.*, 2013). Functionalization of magnetic nanoparticles (Fe_3O_4), graphene (G) with cyanopropyltriethoxysilane (Fe_3O_4@G–CNPrTEOS) was successfully studied in the magnetic solid phase extraction (MSPE) of polar and non-polar organophosphorus pesticides *i.e.*, phosphamidon, dimethoate, diazinon and chlorpyrifos in fresh cow's milk (Nodeh, *et al.*, 2016).

2.3.6 Functionalization of ionic liquids onto inorganic materials

Ionic liquids are a broad group of salts, which many of them are in liquid form bellow 100 ^{o}C or in some cases at room temperature, known as room temperature ionic liquids "RTILs" (Plechkova and Seddon, 2008). Ionic liquids have fascinating properties which depend on their entirely ionic chemical compositions. The ionic composition of ionic liquids consists of organic cation *i.e.*, imidazolium, pyridinium, ammonium, phosphonium, pyrolidinium and inorganic anion *i.e.*, chloride (Cl^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-). More newly synthesised RTILs contain organic anions such as trifluoromethylsulfonate $[CF_3SO_3]^-$, bis[(trifluoromethyl)sulfonyl]imide $[(CF_3SO_2)_2N]^-$ and trifluoroethanoate $[CF_3CO_2]^-$. The chemical structure of the most common cations and anions are illustrated in Figure 2.2. The asymmetric cations/anions of ionic liquids deplete the lattice energy and in follow the melting point of these materials (Buszewski and Studzinska, 2008; Heintz, 2005; Marsh, *et al.*, 2002; Somers, *et al.*, 2013; Sun and Armstrong, 2010).

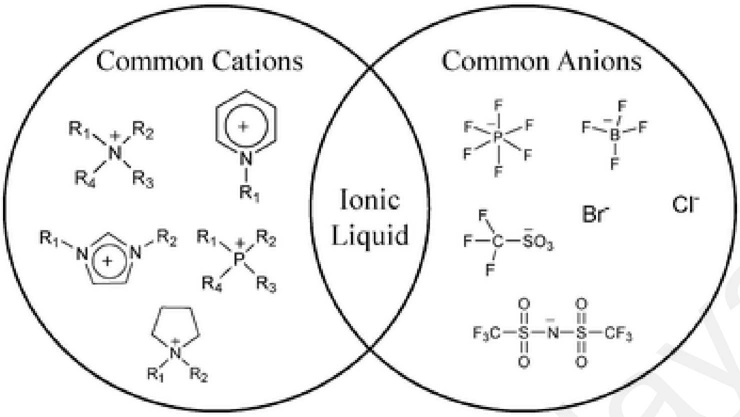


Figure 2.2: Common cations and anions of ionic liquids (Joshi and Anderson, 2012)

The interesting properties of ionic liquids are directed from the possibility to change their cation and anion combinations that give a vast range of unique properties. These include high thermal stabilities, wide range of viscosities, non-flammability, wide liquid ranges, electrolytic conductivity, adjustable miscibility, recyclability and reusability. The physicochemical characteristics of ionic liquids with numerous possibility of combination of different cations and anions to synthesis verity of ionic liquids make them interesting compounds to employ for selected applications. These vulnerable features of ionic liquids, with their easy method of preparation, have resulted wide use of them in both researches and industries (Berthod, *et al.*, 2008; Buszewski and Studzinska, 2008; Sun and Armstrong, 2010).

Ionic liquids are applied in different applications *i.e.*, analytical chemistry, electrochemistry, organic and inorganic chemistry. Due to their extremely low vapour pressure, they are utilized widely in green chemistry researches (Plechkova and Seddon, 2008; Renner, 2001). Moreover, there are many publications on the application of ionic liquids as non-molecular solvent for catalysis in clean technology (Pu, *et al.*, 2007; Welton, 2004), synthesis (Hallett and Welton, 2011), electrochemistry (Armand, *et al.*, 2009; Wei and Ivaska, 2008). More recently, ionic liquids have been employed as separating agent in analytical chemistry fields including separation and extraction (Berthod, *et al.*, 2008; Joshi and Anderson, 2012; Sun and Armstrong, 2010).

Among various ionic liquids, the imidazolium based ionic liquids have been used in many separation studies (Berthod, *et al.*, 2008; Vioux, *et al.*, 2010). This is because of their unusual characteristics. Many of these characteristics come from the acidic nature of the proton in C2 which is situated between two electronegative nitrogen atoms (Figure 2.3). The interaction of mentioned proton with anions extends hydrogen bonded structures and resulting supramolecular ions aggregates. This can improve the selectivity and activity of materials through ionic or radical intermediates or transition states (Consorti, *et al.*, 2005; Dupont and Suarez, 2006; Vioux, *et al.*, 2010). In addition, introducing any functional groups on imidazolium cations can improve capability of ionic liquids to utilize for the specific purposes (Lee, 2006). For instance, the presence of any π-π active functional group such as benzyl ring may provide π-π interaction potential with any extended π-electron or π-π systems (Stepnowski, *et al.*, 2006). Meanwhile, addition of alkoxysilyl groups to nitrogen atoms of imidazolium ring may help in solidification and coating of ionic liquid through formation of siloxane bond between ionic liquid and inorganic material (Anderson and Armstrong, 2003; Armand, *et al.*, 2009; Cazin, *et al.*, 2005).

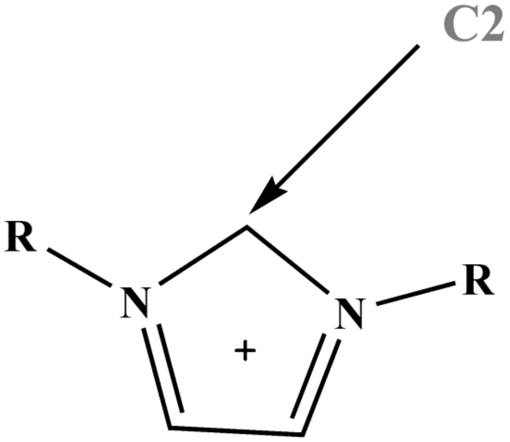


Figure 2.3: Scheme structure of imidazolium ring and location of C2.

The immobilization of imidazolium ionic liquids onto inorganic matrices such as silica-based materials forms a hybrid materials with combining fascinating properties of ionic liquid and physical/chemical stability of inorganic on one solid state (Wanigasekara, *et al.*, 2010). In such hybrid materials, the properties of ionic liquids have interacted or combined with those of other components (Le Bideau, *et al.*, 2011). The most popular way to synthesize these hybrid materials is through sol-gel method, as it is a simple method under extra-ordinary conditions to develop organic-inorganic hybrid materials at room temperature (Bagheri, *et al.*, 2005a; Reisfeld and Saraidarov, 2006). Synthesis of hybrid silica has been considered as the most used hybrid material for immobilization of ILs (Delahaye, *et al.*, 2011). Organic-inorganic hybrid silica can be formed from organotrialkoxysilyl precursors, such as tetraethoxysilane (TEOS). These hybrids generally have large surface areas; above 200 m^2g^{-1} and a broad pore size distribution (Adima, *et al.*, 2000). These material has been applied as stationary phase in extraction techniques such as solid phase extraction (SPE) (Fang, *et al.*, 2010; Tian, *et al.*, 2009a; Tian, *et al.*, 2009b; Vidal, *et al.*, 2012a), magnetic solid phase extraction (MSPE) (Bouri, *et al.*, 2012; Huo and Yan, 2012; Yang, *et al.*, 2011), and in separation method such as gas chromatography (GC) (Anderson and Armstrong, 2003; Poole and

Poole, 2011), liquid chromatography (LC) (Peng, *et al.*, 2007; Shu Juan, *et al.*, 2004) and capillary electro-chromatography (CEC) (Han, *et al.*, 2011; Wang, *et al.*, 2008).

Ionic liquids have brought novel structure and improved properties to inorganic nanomaterial fabrications with their unique flexibility and adaptability via chemical approaches such as high nucleation rate, affecting the shape of product by hydrogen bond interaction and provide nanoaqueous and polar alternatives for two phase systems (Li, *et al.*, 2008). Among inorganic materials, immobilizations of ionic liquids on magnetic nanoparticles have receiving increasing interest. There are some studies that reported the immobilization of ionic liquid on magnetic nanoparticles and the application of them in analytical chemistry as new adsorbents for sample pretreatment and separation (Galan Cano, *et al.*, 2013; Rajabi, *et al.*, 2015; Yang, *et al.*, 2011). Using nanomagnetic nanoparticles as surface support helps to reduce the quantity of ionic liquid. This is beneficial due to high cost of ionic liquids. Also, magnetic nanoparticles decrease the high viscosity and homogenous reaction of ionic liquids (Safari and Zarnegar, 2013). From another side, the modification of magnetic nanoparticles with ionic liquids can control the aggregation and redispersing of materials on the surface of medium (Abu-Reziq, *et al.*, 2007). Ionic liquid forms a protection shell around the MNP through electrostatic repulsion. The functionalized imidazolium-based ionic liquids even can stabilize MNP more efficiently due to interaction of the functional groups on their cationic part to the MNP (Janiak, 2014).

2.4 The application of hybrid materials in separation process

2.4.1 Solid phase extraction (SPE)

One of the common pretreatment methods for water samples is solid phase extraction (SPE). This is because solid phase extraction requires lower volume of organic solvent, ease of automation and possibility of integrating into on-line mode, also it is more efficient and has shorter extraction time compared to liquid liquid extraction (LLE) (Buszewski and Studzinska, 2012; Rodríguez, *et al.*, 2000). Besides, SPE is a cheaper method compared to solid phase micro extraction (SPME) (Buszewski and Studzinska, 2012; Xu, *et al.*, 2007). Moreover, selectivity and sensitivity of the technique in recovery of target analytes can be controlled by type of SPE adsorbent. Therefore, it should consider the physicochemical characteristics of the adsorbents, during method development of SPE (R. Liu, *et al.*, 2014). The commercial SPE adsorbents such as C-18 are suitable for limited numbers of analytes and there is limitation on reusability of the cartridges (Raoov, *et al.*, 2014). For this purpose, there is a trend towards developing, modification and functionalizing polymeric adsorbents.

The SPE technique is based on the partition coefficient of analyte between the mobile phase and the solid phase which is adsorbent. In this technique it is essential that the analytes have more affinity towards adsorbent than the mobile phase. In SPE procedure (Figure 2.4) the adsorbent is placed between two frits disks in a cartridge. The analyte solution passes through the cartridge by the force of vacuum. The basic steps of SPE technique are including: activation and conditioning the surface of adsorbent by passing suitable solvent through the cartridge. Then, loading the analyte solution through the cartridge and trapping/interfering the target analytes into the adsorbent. Finally, desorption of the interfering target analytes from adsorbent by the use of suitable diluted solvent and collect the remain analytes for analysis procedure (Buszewski and Studzinska, 2012).

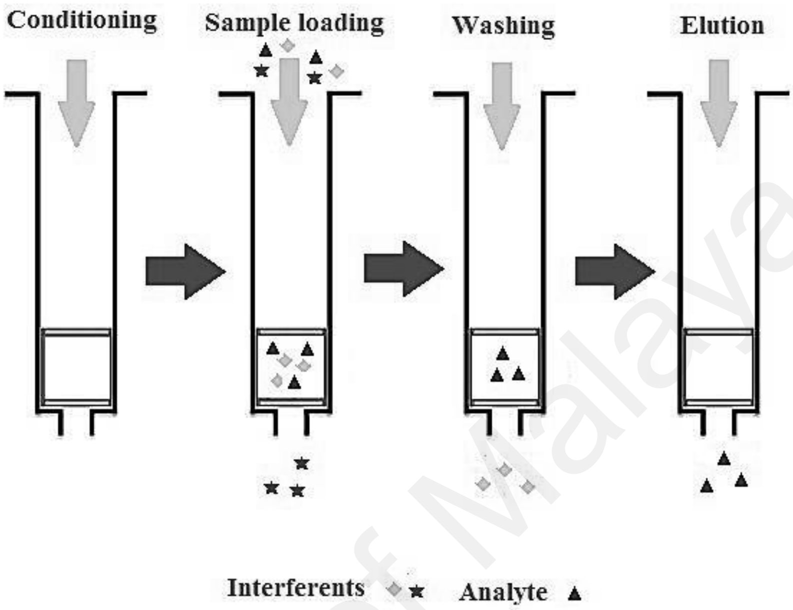


Figure 2.4: Classical solid phase extraction process.

2.4.2 Magnetic solid phase extraction (MSPE)

The utilization of magnetic adsorbents in solid phase extraction process (named as magnetic solid phase extraction (MSPE) has received great attention in recent years (Wierucka and Biziuk, 2014). The separation process in MSPE is taken place by direct contact of adsorbent with sample solution. This improves the adsorption selectivity of target analytes on the surface of adsorbent. The adsorbent is then removed from the solution by use of external magnetic field without any demand for additional process like centrifugation or filtration. Therefore, it reduces the processing time. Then, the analytes desorb from the surface of adsorbent by use of proper diluted solvent (Safarikova, *et al.*, 2005). The process of magnetic solid phase extraction is illustrated in Figure 2.5. Two primary parameters of MSPE is the adsorbent which can be selected by the polarity, solubility and the complex composition of the analytes, and a suitable type and amount of desorption solvent (Inada, *et al.*, 2013).

In recent years, interesting steps was taken in development of new magnetic nanoparticles by their surface functionalization with organic and inorganic materials including surfactants, silica, silicones and phosphonic acids (Behari, 2010; Govan and Gunko, 2014). Typically, to stabilize the magnetic core, the surface of the core is coated with silica layer. The surface of magnetic core is not able to bond with functional molecules, this is because of difference in particle size between magnetic nanoparticle in nanometer scale and target analytes in macro size (Wierucka and Biziuk, 2014). Coating a shell of silica can improve the sorption properties, thermal and mechanical stability of the magnetic nanoparticle. Also, silica shell can easily undergo additional functionalization via covalent bond with organo-silica groups (Govan and Gunko, 2014; Wierucka and Biziuk, 2014; Xu, *et al.*, 2014). The silica shell is immobilized onto the magnetic core as a result of basic sol-gel technique which is explained in Section 2.3.4.

The most noticeable disadvantages of the SPE are included: being a laborious and time consuming process, the limitation on range of the flow rate and the possibility of clogging the cartridges with unfiltered samples (Smith, *et al.*, 2001). The most interesting advantages of using MNPs as adsorbent in SPE is their high ratio of surface area to unit of volume and short diffusion route which offers higher sorption capacity, extraction efficiency, higher selectivity regarding target analytes, smaller amount of adsorbent, and shorter duration of extraction process in comparison with classical SPE. Due to these advantages, the magnetic nanoparticles are becoming an alternative to SPE adsorbents (Giakisikli and Anthemidis, 2013).

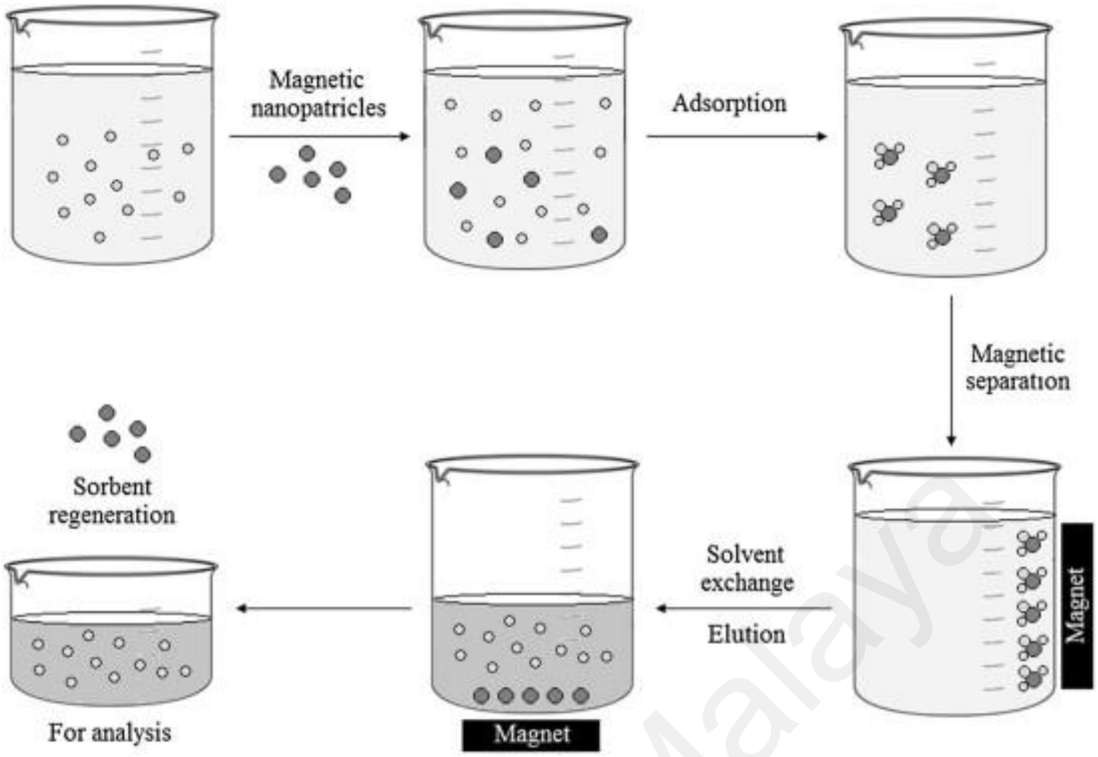


Figure 2.5: Magnetic solid phase extraction process (Wierucka and Biziuk, 2014).

2.5 Environmental pollutants

In 21^{st} century, one of the most critical issues that mankind has faced with is threaten and controlling the chemical pollutants which interred to the environment. Chlorophenols and polycyclic aromatic hydrocarbons are two groups of priority pollutants which can be easily found in environmental samples (Chen and Liao, 2006; Czaplicka, 2004). Following sections presents short literature on these two groups of pollutants.

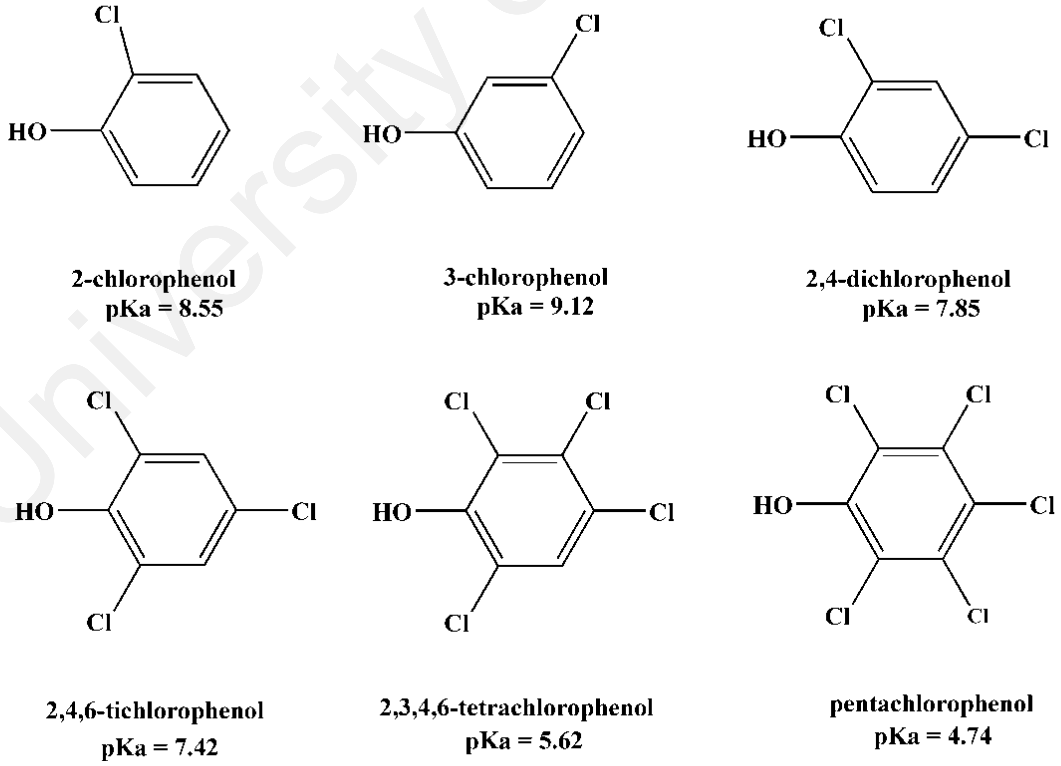
2.5.1 Chlorophenols (CPs)

Chlorophenols (CPs) are kind of organic compounds in which one or more number of hydrogen atoms on phenol is replaced by one or more numbers of chlorine atoms, (Figure 2.6). Most of chlorophenols are soluble in water and highly in alcohols (Olaniran and Igbinosa, 2011). The log octanol/water partition coefficient (K_{OW}) of CPs increase as the number of chlorines increases (Ivanciuc*, et al.*, 2006). It is noticed that the CPs can be found in variety type of environmental samples from surface and ground waters, bottom sediments, atmospheric air and soils (Al-Janabi*, et al.*, 2011; Sim*, et al.*, 2009; Sinkkonen and Paasivirta, 2000). The level of CPs concentration vary significantly and it is depend on the local sources and industrialization rate of the area (Czaplicka, 2004). For instance, the highest concentration of chlorophenols in river water was found of 2 − 2000 µg/L. In industrial sewages the highest concentration of chlorophenols may reach 0.1 − 10 mg/L for pentachlorophenol (Michalowicz and Duda, 2007).

Over the past century, CPs are well-known pollutant. The widespread usage of CPs make them one of the most noxious environmental wastes (Cui*, et al.*, 2016; Víctor-Ortega*, et al.*, 2016; Wu*, et al.*, 2016). CPs are considerably used as intermediates for drugs, plastics and dyes (Kamboh*, et al.*, 2011; Nodeh*, et al.*, 2015). The massive usage of CPs in pesticides, fertilizers, detergents, preservatives and dyeing manufacturing units is noticeable and considered as one of the major environment issue of modern era because these units release a huge quantity of CPs contaminated effluents to the natural streams (Kadmi*, et al.*, 2015; Kamboh*, et al.*, 2016; Kamboh*, et al.*, 2011; Nodeh*, et al.*, 2015; Wan Ibrahim*, et al.*, 2015). From an environmental aspect, the exposure of CPs contaminated effluents to the natural aqueous environment is of great concern (Elci, *et al.*, 2011; Gonzalez, *et al.*, 2010). The CPs can be easily transferred to drinking water and bring a chief threat to the human beings due to their acute toxicity, potential carcinogenicity and moderate bioaccumulation (Chung, *et al.*, 2013; Du, *et al.*, 2016). As a consequence, many CPs are listed by the US environmental protection agency (USEPA), and European community (EC). Japanese ministry of health, labour and welfare has stated the maximum contaminant level for phenols in drinking water is 5 μg L^{-1} (Raoov, *et al.*, 2014). However, exceeded concentration of CPs from available international standards *i.e.*, 4.596 mg L^{-1} of CPs in drinking water has been reported (Al-Janabi, *et al.*, 2011). Hence, for safer environment the precise determination and removal of CPs from aqueous environment is extremely essential (Igbinosa, *et al.*, 2013; Pera-Titus, *et al.*, 2004).

Literature survey declared that the most frequently used sample pretreatment method for CPs are solvent extraction (Arellano-Cardenas, *et al.*, 2008; Schellin and Popp, 2005), solid phase extraction (Guo, *et al.*, 2014; Liu, *et al.*, 2011), solid phase micro extraction (Bagheri, *et al.*, 2005b; Parham and Saeed, 2014; Xiulan, *et al.*, 2010), supercritical fluid extraction (Dunkle, *et al.*, 2014; Segovia-Martínez, *et al.*, 2010) and magnetic solid phase extraction (Cheng, *et al.*, 2012; Pan, *et al.*, 2014; Yamini, *et al.*, 2015).

Various adsorbents have been studied for removal of phenols such as chemically functionalized adsorbents with nonpolar reversed-phase silica e.g., C8 and C18. To minimize the ionization of analytes the pH of sample must adjusted to 2-3. It is necessary to condition the adsorbent with water miscible solvent before using water samples to avoid limitation of the mass transfer between water and adsorbent (Opeolu, *et al.*, 2010). Chemically modified polymeric adsorbents such as XAD have higher stability in acidic pH and higher capacity toward polar targets in compare to silica adsorbents (Jung, *et al.*, 2006). Carbon-based adsorbents have high efficiency for trace amount of analytes through π–π interactions, reversed-phase interaction and anion exchange behaviour of carbon. However, application of carbon adsorbents have some drawback *i.e.*, elution of phenols from carbon adsorbent is not easy, irreversible adsorption of some analytes which causes by quinone groups on the carbon surface and nonporous structure of carbon adsorbents may require higher pressures for water flow passage through cartridges (Liu, *et al.*, 2011). The studies of modification of magnetic nanoparticles with ionic liquids (Yang, *et al.*, 2011) and polymeric surfactants (Zheng, *et al.*, 2006) have shown that most of these adsorbents can only be applied on extraction of hydrophobic analytes through the hydrophobic interaction, while it may cause the blockage in the nonpolar samples with hydrophilic compounds.



2-chlorophenol
pKa = 8.55

3-chlorophenol
pKa = 9.12

2,4-dichlorophenol
pKa = 7.85

2,4,6-tichlorophenol
pKa = 7.42

2,3,4,6-tetrachlorophenol
pKa = 5.62

pentachlorophenol
pKa = 4.74

Figure 2.6: Structure of selected chlorophenols used in the study.

2.5.2 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a wide range of organic compounds which consist of two or more fused aromatic rings (Feng, *et al.*, 2015; Haritash and Kaushik, 2009). PAHs are hydrophobic in nature and relatively low aqueous solubility in water and highly solubility in organic solvents. The water solubility of PAHs depends on their molecular size and number of benzene rings and decreases by increasing the molecular size (Haritash and Kaushik, 2009). Most of PAHs have low vapour pressure and can be widely spread out in the air (Kim, *et al.*, 2013; Mercier, *et al.*, 2011; Skupinska, *et al.*, 2004). Another primary property of PAHs is their stability or persistence in the environment. This is because of their molecular structure and it has a direct relation with their number of benzene rings (Kanaly and Harayama, 2000; Lima, *et al.*, 2005).

PAHs are well known environmental long lasting pollutant which is mainly produced by incomplete combustion or pyrolysis of organic materials, especially through human activities such as combustion of fossil fuels in industrial and vehicle engines and incineration of wastes. PAHs are released to the environment through oil spills accidents and petroleum refining activities (Feng, *et al.*, 2015; Lundstedt, *et al.*, 2007; Taylor and Owens, 2009). The toxic potencies of PAHs compounds vary due to their molecular structures. The main reason to concern about them is because of their toxic, mutagenic and carcinogenic potential towards humans and animals (Chen and Liao, 2006; Colombo, *et al.*, 2006; Fang, *et al.*, 2004; Jiang, *et al.*, 2009; Lundstedt, *et al.*, 2007). The US Environmental Protection Agency (EPA) has classified some of PAHs including: benzo[a]pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene as Group

B2,due to their probability of carcinogenic risk to human health (USEPA, 2002). The level of PAHs concentration in drinking water by WHO varies between 1 ngL^{-1} and 11 μgL^{-1} (WHO, 2011). However, exceeded concentration of PAHs from available international standards *i.e.*, 2.847 mg L^{-1} in drinking water has been reported (Yang, *et al.*, 2010). Hence, for safer environment the precise determination and removal of PAHs from water body is extremely essential.

Due to low hydrophilic properties of PAHs, (Figure 2.7) their concentration is low in water samples. Therefore, it is necessary to run a proper preconcentration method regarding their trace amount in environmental samples. Different preconcentration methods have been employed such as solid phase extraction (Pan, *et al.*, 2011; Perez, *et al.*, 2014; Zhang, *et al.*, 2012), micro solid phase extraction (Ge and Lee, 2011; Zhang, *et al.*, 2012), cloud point extraction (Bingjia, *et al.*, 2007; Delgado, *et al.*, 2004), stir rod sorptive extraction (Barco-Bonilla, *et al.*, 2011; Luo, *et al.*, 2011), solid phase micro extraction (Doong, *et al.*, 2000; Mohammadi, *et al.*, 2005) and magnetic solid phase extraction (Bianchi, *et al.*, 2012; Cai, *et al.*, 2015; Han, *et al.*, 2012; Perez, *et al.*, 2014).

Due to the aromatic core of PAHs, some studies attempted to functionalize the magnetic core with phenyl groups as MSPE adsorbents which can selectively adsorb PAHs by generating π–π conjugative effect with aromatic core of PAHs molecules (Ying, *et al.*, 2013). For instance Bianchi (2012) functionalized the Fe_3O_4 magnetic nanoparticles with diphenyl and applied the prepared MSPE adsorbent for extraction of PAHs from biological samples. The results indicate the selectivity of adsorbent toward trace PAHs from complex samples. However, very low dispersibility of the modified MNPs-phenyl in water limits their contact with target analytes sufficiently (Bianchi, *et al.*, 2012). Wang (2013) has functionalized magnetic nanoparticles with polydopamine with good dispersibility and selectivity. But, the adsorbent due to the non-covalent modification does not have reliable stability (Y. Wang, *et al.*, 2013). Moreover, the hydrophobic modification of Fe_3O_4 with octadecyl moieties has been shown good adsorption and separation of PAHs from environmental samples. However, the low specificity to PAHs is drawback of these materials (Zhang, *et al.*, 2010). Therefore, the goal of new studies is to synthesis magnetic adsorbents with good stability, dispersibility and selective adsorption ability.

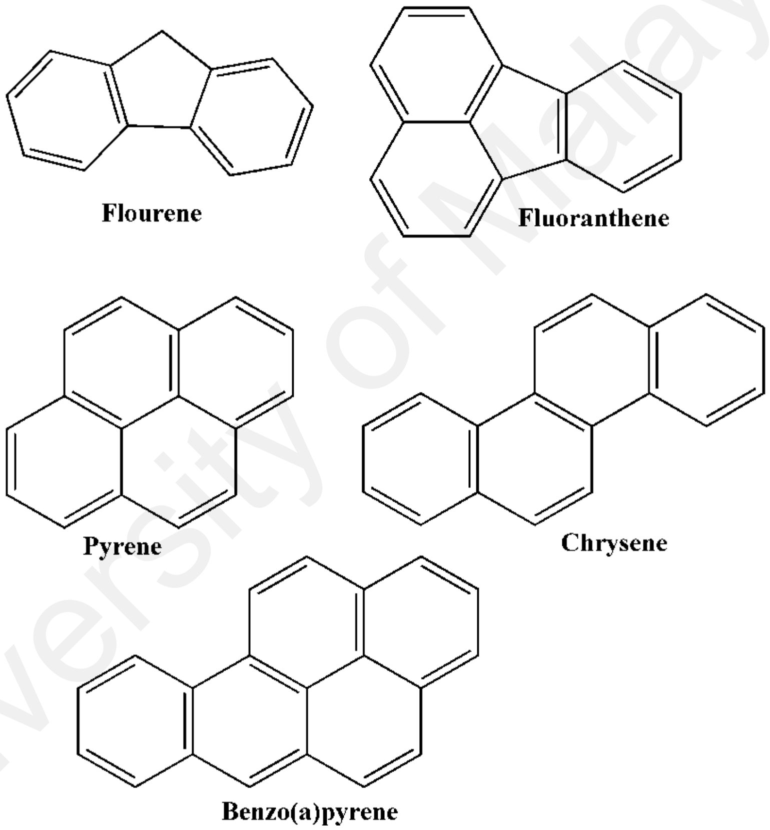


Figure 2.7: Structure of selected polycyclic aromatic hydrocarbons used in the study.

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CHAPTER 3: CYANO-IONIC LIQUID FUNCTIONALIZED SILICA-TITANIA MIXED OXIDE FOR SOLID PHASE EXTRACTION OF SELECTED CHLOROPHENOLS

3.1 Introduction

Isolation and enrichment of trace amount of target analytes is an important pretreatment step in working with environmental samples. Solid phase extraction (SPE) is one of the most common techniques of aqueous sample pretreatment. This is because of its short extraction time, low consumption of organic solvent, high enrichment factor and recovery. Also, the simplicity of procedure and the ease of automation are other interesting facts about SPE. (Gao, *et al.*, 2012; Janoszka, 2011; Pica, 2013; Portet-Koltalo, *et al.*, 2007). The most important factor in SPE method is the choice of adsorbent to obtain higher enrichment efficiency of analytes (Behbahani, *et al.*, 2014; Ghaedi, *et al.*, 2013; Mazdeh, *et al.*, 2016; Poole, 2003; Rezaei, *et al.*, 2013; Saljooqi, *et al.*, 2014; Samadi, *et al.*, 2012; Shamsipur, *et al.*, 2014; Sohrabi, *et al.*, 2013; Tabani, *et al.*, 2013; Taghizadeh, *et al.*, 2014). The goal of this research is to synthesis and characterize a newly synthesised SPE adsorbent, cyano-ionic liquid functionalized silica-titania mixed oxide (**Si-Ti@CN/IL**) through acidic condition sol-gel process. The silica-titania mixed oxide surface as an inorganic core of hybrid material was modified with cyanopropyltriethoxysilane and 1-benzyl-3-(trimethoxysilylpropyl)imidazolium chloride ionic liquid (**BTMP-IM**). The main consideration of this new material is the presence of benzyl groups and imidazole ring in the cationic part of the imidazolium-based ionic liquid, which capable of imparting π-π stacking interaction between aromatic moieties. Also, intermolecular hydrogen bonds with unshared electron pair of cyano groups on the surface of adsorbent with hydrogen bond acceptor sites of analytes.

This provides adsorbent with the selectivity towards wider range of organic pollutants with aromatic moieties.

The newly synthesised **Si-Ti@CN/IL** adsorbent was characterised by Fourier transform infrared (FT-IR) spectrometry, field emission scanning electron microscopy (FESEM), Brunauer-Emmett-Teller (BET), elemental analysis with CHNS thermal gravimetric analysis (TGA) and X-ray diffraction (XRD). An effective method of SPE has been developed by **Si-Ti@CN/IL** adsorbent for the determination of chlorophenols *i.e.*, 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP) and pentachlorophenol (PCP).

3.2 Experiment

3.2.1 Chemicals and reagents

Titanium (IV) butoxide ($Ti(OBu)_4$, HPLC grade Methanol, acetonitrile, ethyl acetate and n-hexane were purchased from (Merck, Germany). Cyanopropyltriethoxysilane, triethoxysilane (TEOS), 1-benzylimidazole, 3-(chloropropyl)-trimethoxysilane were obtained from (Sigma-Aldrich, Germany). Selected 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP) and pentachlorophenol (PCP) as shown in Figure 2.6 were from (Sigma-Aldrich, Germany). Tetrahydrofuran (THF), hydrochloric acid (HCl) and diethyl ether (Fisher-Scientific, UK), acetic acid 96 % from (Acros, USA). All chemicals and reagents were of analytical and chromatographic grades.

3.2.2 Instruments

IR spectra were recorded in ATR mode in the range of 400 – 4000 cm^{-1} using Perkin Elmer X1FTIR, USA. The surface morphology was analysed by Auriga field emission scanning electron microscopy (FESEM) instrument at 1.00 kV (Carl-Zeiss, Germany). The surface area and pore size were measured using Brunauer-Emmett-Teller (BET) by nitrogen adsorption-desorption isotherms at 77.350 K in Micromeritics ASAP2020, USA. The elemental analysis was conducted using (Perkin Elmer, USA) series II CHNS 2400. Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere in the range of 50 - 900 °C at a heating rate of 10 °C min^{-1} using (TGA7, Perkin-Elmer, USA). X-ray diffraction (XRD) was measured with a PANalytical Empyrean X-ray diffractometer (40 mA, 40 kV) using Cu Kα irradiation in the scanning range of 10 to 80°. The ultraviolet-visible spectrophotometry (UV-vis) analyses were performed on UV-vis spectrophotometer UV-1650 (Shimadzu). The SPE vacuum manifold (12-port) obtained from Thermo Fischer Scientific (Waltham, MA, USA). HPLC system (Shimadzu, Japan) consisted of LC-20AT pump, SPD-M20A diode array detector, SIL-20A HT autosampler and CTO-10AS VP column oven was used for Chlorophenols determination. The system was equipped with C-18 reverse column (250 x 4.6 mm) hypersil gold, particle size 5 μm (Thermo science, USA).

3.2.3 Chromatographic conditions

The chromatography analyses were performed using HPLC system. The column temperature was set at 40 ^{o}C. Mobile phase was at flow rate of 1 mL min^{-1}. The mobile phase consisted of purified water/methanol (20:80), both acidified to 1 % with acetic acid. Detection was carried out using UV-vis wavelength of 280 nm for all samples. The inject volume was constant on 20 µL.

3.3 Synthesis

3.3.1 Synthesis of 1-benzyl-3-(trimethoxysilylpropyl)imidazolium chloride

1-benzyl-3-(trimethoxysilylpropyl) imidazolium chloride (**BTMP-IM**), was synthesized as follow; 1-benzylimidazole (316 mg, 2 mmol) and 3-(chloropropyl)-trimethoxysilane (3.67 mL, 2 mmol) were added to a 50 mL two neck round-bottomed and reaction mixture was stirred under nitrogen atmosphere at 80 °C for 48 h. Then, the reaction mixture was cooled to room temperature and washed with 25 mL diethyl ether. The remaining of solvent was removed. Following the removal of diethyl ether by rotary evaporator the resulting viscous yellowish oil (yield % 97) was obtained and kept in the desiccator for 24 h. (Tyrrell, *et al.*, 2011) IR (cm^{-1}) (Figure 3.5A): 3299m, 3033w, 2942s, 2841m, 1561s, 1497s, 1230m, 1191s, 1072s, 1031s, 907w, 816s, 778s, 710s, 663s, 464s. ^{13}CNMR (400 MHz, $CHCl_3$) (Figure 3.1A): 138.1, 133.3, 129.6, 129.2, 121.9, 53.6, 52.0, 50.9, 50.7, 24.2, 6.1.^{1}HNMR (400 MHz, $CHCl_3$) (Figure 3.1B): 10.85-10.75 (s, 1H, Im-H), 7.49-7.40 (m, 3H, benzyl-H), 7.38-7.28 (m, 1H, Im-H), 7.27-7.20 (m, 2H, Im-H), 5.40-5.70 (s, 2H, benzyl-H), 4.25-4.32 (t, J = 7.6 Hz, 2H, alkyl-CH_2), 3.41-3.57 (s, 9H, O-CH_3), 1.12-1.20 (p, J = 6.8 Hz, 2H, alkyl-CH_2), 0.53-0.62 (t, J = 8.0 Hz, 2H, alkyl-CH_2).

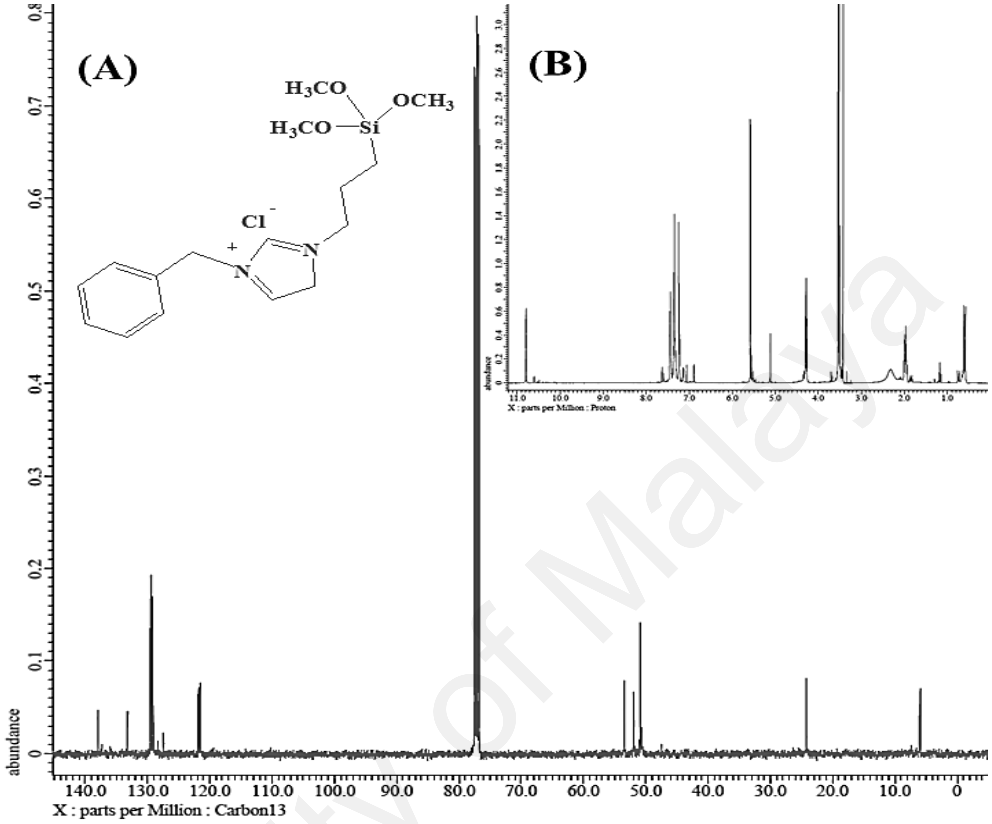


Figure 3.1: NMR spectrum of **BTMP-IM**: A) ^{13}CNMR and B) ^{1}HNMR.

3.3.2 Synthesis of silica-titania mixed oxide with cyano-ionic liquid (Si-Ti@CN/IL)

Silica-titania mixed oxide with cyano-ionic liquid (**Si-Ti@CN/IL**) as shown in Figure 3.2 was synthesized as follow; in first step for the preparation of silica-titania oxide cyano-functionalized backbone, titanium (IV) butoxide (3.27 mL, 9.6 mmol) and cyanopropyltriethoxysilane (2.31 mL, 9.6 mmol) in 5 mL of THF were stirred at room temperature for 30 min. Following the functionalization process, 1.71 g, 9.6 mmol of prepared ionic liquid *i.e.*, 1-benzyl-3-(trimethoxysilylpropyl) imidazolium chloride (**BTMP-IM**) were added to same reaction mixture (ratio cyanopropyltriethoxysilane: ionic liquid was 1 : 0.4) and it was further stirred for 30 min. Then, on the drop wise addition of 0.69 mL (1.2 M HCl aqueous solution) a clear and homogeneous hybrid wet gel was obtained. The resultant hybrid wet gel (**Si-Ti@CN/IL)** was dried in vacuumed oven at 80 ^oC for 48 h. The dried hybrid wet gel (**Si-Ti@CN/IL)** was grounded into fine powder with mortar and pestle, rinsed with 30 mL acetone as well as with surplus deionised water. The whitish precipitates of newly synthesized **Si-Ti@CN/IL** adsorbent were dried in oven at 100 ^oC for 24 h.

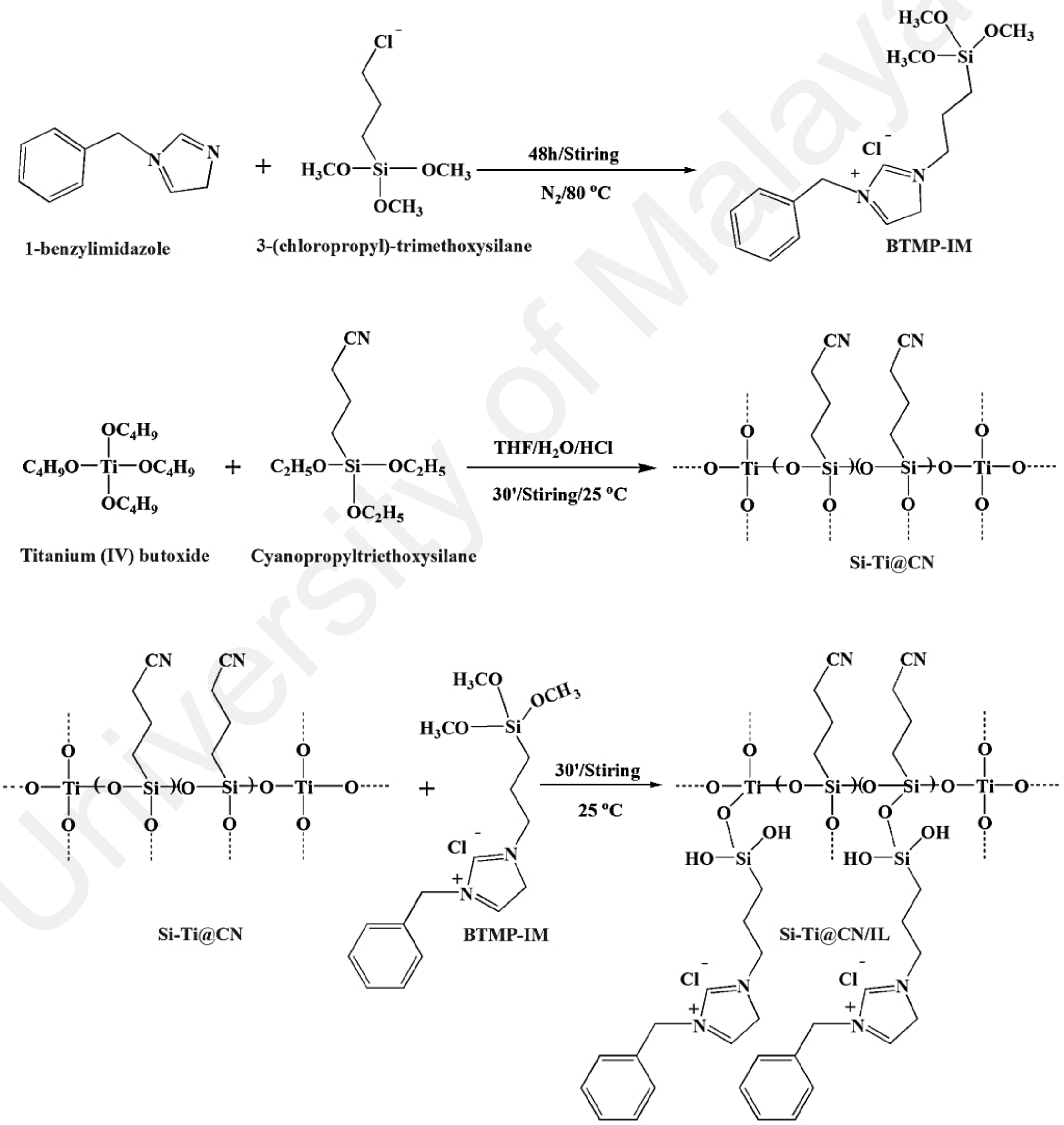


Figure 3.2: Synthesis pathway of **Si-Ti@CN/IL**.

For the synthesis of titania-silica oxide functionalised with cyano group (**Si-Ti@CN**) same procedure was as adopted as described for **Si-Ti@CN/IL**. But in **Si-Ti@CN** the adsorbent was not modified with 1-benzyl-3-(trimethoxysilylpropyl) imidazolium chloride (**BTMP-IM**). In **Si-Ti@IL** the Titanium (IV) butoxide (Ti(OBu)$_4$ was not modified with cyanopropyltriethoxysilane, while all the steps were followed. For the synthesis of titania-silica oxide (**Si-Ti**), same procedure was as adopted as described for **Si-Ti@CN/IL**. But in case of **Si-Ti**, the Titanium (IV) butoxide (Ti(OBu)$_4$ was modified with (9.60 mmol, 2.13 mL) triethoxysilane (TOES), while all the steps were followed. **Si-Ti**, **Si-Ti@CN** and **Si-Ti@IL** were synthesized as reference materials to evaluate the performance of cyano groups and ionic liquid for the extraction of cholorophenols, (Figure 3.3).

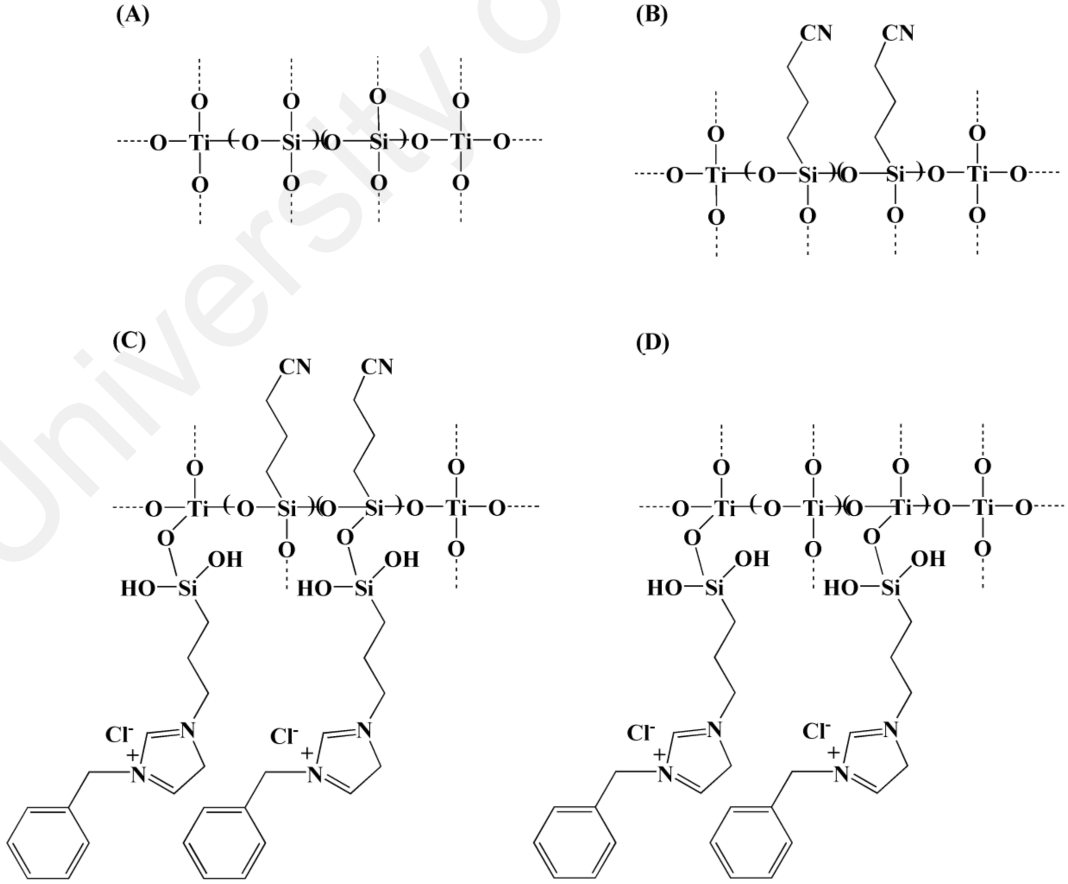


Figure 3.3: Structure of (A) **Si-Ti**, (B) **Si-Ti@CN**, (C) **Si-Ti@CN/IL**, (D) **Si-Ti@IL**.

3.3.3 Batch sorption study

In order to study the ability of the adsorbent to remove chlorophenols in wide range of polarity, 20 mg of adsorbent was equilibrated with 10 mL of 10 mgL^{-1} of several CPs including:(2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), and 2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP) in a sample vial. Each mixture was stirred mechanically for 2 h at room temperature. After that, the samples were filtered by nylon syringes with 13 mm in diameter and 0.22 μm in pore size. The residual concentration of the compound in the solutions was analysed by UV-vis spectrophotometer. The residual amount of chlorophenols was calculated from the following equation:

$$qe = \frac{V(Ci - Ce)}{m} \qquad (3.1)$$

where q_e is the adsorption capacity in mg.g^{-1}, C_i and C_e are the initial and equilibrium concentrations in mgL^{-1}, respectively, V is the volume of the solution in L and m is the mass of the adsorbent in g, respectively (Patnaik, 2010).

3.3.4 SPE procedure

100 mg of newly synthesized **Si-Ti@CN/IL** adsorbent were packed in a 3 mL SPE polypropylene cartridge fixing with upper and lower frits. The **Si-Ti@CN/IL** filled SPE cartridge was placed in the SPE vacuum manifold and 5 mL of methanol & 5 mL of water, respectively were used for the conditioning of **Si-Ti@CN/IL** filled SPE cartridges. For the optimization process, 10 mL of spiked sample (2 ppm mixed solution of selected chlorophenols) was loaded to the newly fabricated pre-conditioned

cartridges at a flow rate of 1 mL min^{-1}. During the SPE process, the packed adsorbent in the cartridges was not allowed to dry at any time. Following sample loading, the SPE cartridges were left to be dry under vacuum for 30 min. Then, the retained chlorophenols were eluted from the **Si-Ti@CN/IL** filled SPE cartridges by using 4 mL of methanol acidified with 1 % acetic acid. Finally, the eluted samples were evaporated under stream of nitrogen and re-dissolved with 0.5 mL of methanol acidified with 1 % acetic acid. The re-dissolved solution was injected to the HPLC for analysis. For the comparative study, all synthesized **Si-Ti@CN**, **Si-Ti@IL** and **Si-Ti** adsorbents were packed in 3 mL SPE cartridges and a mentioned SPE process was employed.

Various numbers of solvents were utilised as elution solvent, such as methanol, acetonitrile, tetrahydrofuran (THF) and n-hexane. The elution solvent volume was studied in the range of 1 – 20 mL. The sample loading volume was studied in the range of 1 – 25 mL with sample spiked 2 mg L^{-1} CPs mixture at pH 6. The sample pH was studied in the range of 2 – 10. The proper pH was adjusted with 0.01 M HCl and 0.01 M NaOH using pH meter model Ella Instrument. Effect of modifier was studied with addition of 1 % to 15 % of acetic acid.

3.3.5 Method validation

3.3.5.1 Comparative study

For the purpose of SPE performance comparison between newly synthesised **Si-Ti@CN/IL** and available median adsorbents including the homemade **Si-Ti**, **Si-Ti@CN** and **Ti@IL**, the same amount of 100 mg from each adsorbents were packed in 3 mL SPE cartridges. The percent recovery (% R) was determined from the following equation:

$$\%\mathrm{R} = \frac{[\mathrm{C}a \text{ final}]}{[\mathrm{C}s \text{ initial}]} \times 100\% \qquad (3.2)$$

where C_a final is the final concentration of analyte in the acceptor phase and C_s initial is the initial analyte concentration in sample (Patnaik, 2010).

3.3.5.2 Real sample analysis

To identify the matric effect of the optimised method, the different contaminated water samples *i.e.*, tap water, lake water and leachate were used. Tap water and lake water sample were collected from analytical chemistry laboratory and Varsity Lake, University of Malaya, Kuala Lumpur respectively, while leachate water samples were collected from landfill site, Jeram Kuala Selangor. The collected tap, lake and leachate water samples were filtered by 0.45 μm Millipore cellulose and 110 mm filter paper, respectively and then stored at 4 ^{o}C in glass bottle foiled with aluminium.

3.3.5.3 Linearity and precision

The linearity study was determined in seven different concentration levels. The repeatability as relative standard deviation (%RSD) and the precision of the developed method was evaluated by 5 variances with spiking level of 10 μg L^{-1} of CPs mixture in ultra-purified water. Standard deviation (SD) and RSD were determined by following equations:

$$SD = \sqrt{\frac{\sum(x-\bar{x})^2}{n-1}} \tag{3.3}$$

$$RSD = \frac{SD}{\bar{x}} \times 100\% \tag{3.4}$$

Where $\bar{x}$ is representing mean value, x is the result of every run, and n is the number of measurements (Patnaik, 2010).

3.3.5.4 Limit of detection (LOD) and Limit of quantification (LOQ)

The limit of detection (LOD) and the limit of quantification (LOQ) are two important factors in method validation that determined the lowest concentration of an analyte that can be reliably detected by an analytical procedure. The limit of detection and quantification were determined from the standard deviation of the blank ($\boldsymbol{\sigma}$) and slope of calibration curve (S) (Konieczka and Namiesnik, 2016) by using following equations:

$$LOD = 3(\frac{\sigma}{S}) \tag{3.5}$$

$$LOQ = 10\left(\frac{\sigma}{S}\right) \tag{3.6}$$

3.4 Results and discussion

3.4.1 Synthesis of adsorbent

The main goal of this study was to synthesis a new hybrid Cyano-IL based adsorbent, having aromatic core as well as cyano functional groups and exploration of its extraction properties towards the selected chlorophenols. To achieve the desired goal, 1-benzylimidazole was modified with 3-(chloropropyl)-trimethoxysilane. Combination of the titanium (IV) butoxide and cyanopropyltriethoxysilane formed hybrid **Si-Ti@CN** which was chosen as precursor. In second step the ionic liquid (**BTMP-IM**) was attached to the precursor in presence of acidified water. The morphology and structure of the **Si-Ti@CN/IL** adsorbent was fully characterized by means of Fourier transformed infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FESEM), BET, XRD and TGA analysis.

Since, it is reported that under the harsh chemical conditions (high/low pH conditions) sol–gel titania is more stable as compared to the sol–gel silica, the presence of titanium in structure of adsorbent improves its chemical stability and strength as well as the pH stability which is very important for effective extraction under high or low pH conditions (Segro, *et al.*, 2009). $Ti(OBu)_4$ was chosen as the source of titanium since $Ti(OBu)_4$ has comparatively slow reaction with water and does not require special care and handling precautions (Aegerter and Mennig, 2004). Water acted as a hydrolyser through the catalytic activity of HCl (Figure 3.4). To synthesis the desired adsorbent, the starting materials undergo several reactions in the acid catalytic sol-gel process. The acidic catalytic hydrolysis of $Ti(OBu)_4$ is expected to be the first reaction, then it is followed by hydrolysis of cyanopropyltriethoxysilane and IL. Using a strong acid catalyst such as HCl allows the control over hydrolysis and polycondensation stage by decreasing the reactivity of $Ti(OBu)_4$ to water. In such condition, to reduce the hydrolysis reaction, the alkoxy groups of $Ti(OBu)_4$ become protonated to make the local charge of titania more positive (Pinkse, *et al.*, 2004). In addition, protonated alkoxy groups limit the nucleophilic attack towards positively charged titania, which slower polycondensation process (Konishi, *et al.*, 2006). Therefore, HCl is not only utilized as an acid catalyst, but also as an electrolyte to stop agglomeration via electrostatic repulsion.

In addition, THF was used as a water-miscible solvent to dissolve water-immiscible metal alkoxide to obtain homogeneous hybrid sorbent. Relatively, the cation of IL attaches through the hydroxysilyl head of imidazolium group to the hydroxyl groups on the surface of silica and titania to form a hybrid material.

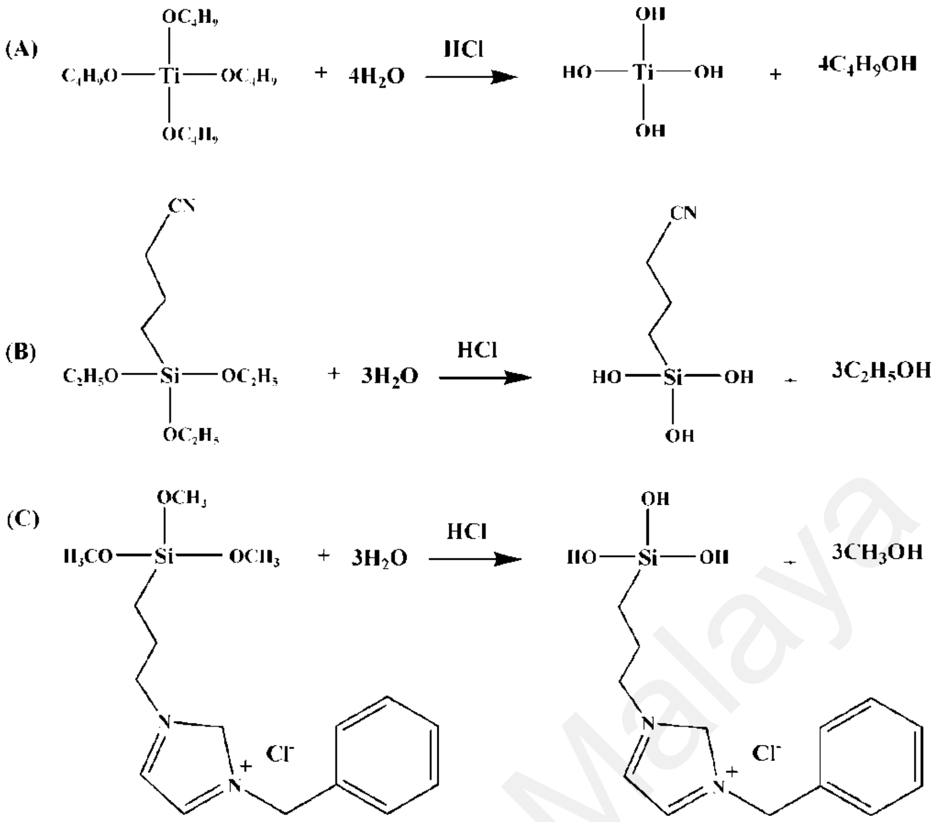


Figure3.4: Acidic hydrolysis reaction of (A) Ti(OBu)$_4$, (B) cyanopropyltriethoxysilane, (C) **BTMP-IM**.

3.4.2 Characterization

3.4.2.1 FTIR analysis

The FTIR spectral analysis for the confirmation of different functional group in newly synthesised materials is represented in Figure 3.5. In the FT-IR spectrum (Figure 3.5A) presence of C-H (aromatic), C=N, C=C, C-C, C-N and Si-O groups stretching at 3156, 1565, 1500, 1457, 1367 and 1039 cm^{-1} respectively is a qualitative evidence for the successful functionalization of 1-benzylimidazole with 3-(chloropropyl)-trimethoxysilane. Since, raw 1-benzylimidazole does not have any stretching vibration at around 1039 cm^{-1} (Si-O) but in FT-IR spectrum (Figure 3.5A) the presence a diagnostic sharp peak for Si-O confirmed the synthesis of **BTMP-IM**. Successful functionalization of Ti(OBu)$_4$ with cyanopropyltriethoxysilane or synthesis of **Si-Ti@CN** can be predict by the presence of characteristic peak for cyano group (C≡N) stretching (Figure 3.5B) at around 2253 cm^{-1}. Both synthesised materials *i.e.*, **BTMP-IM** as well as **Si-Ti@CN** showed some diagnostic absorption IR bands at specific frequencies. The **BTMP-IM** (Figure 3.5A) does not have any stretching vibration at around 2253 cm^{-1}, while **Si-Ti@CN** does not have any aromatic stretching band at around 1560 & 1500 cm^{-1}. But FT-IR spectral analysis (Figure 3.5C) due to the presence of characteristic peaks for cyano group (C≡N) as well as aromatic stretching band confirmed the formation of new hybrid Cyano-IL based adsorbent (**Si-Ti@CN/IL**). The C-H (aromatic), C≡N, C=N and C=C stretching in **Si-Ti@CN/IL** can be shown by the characteristic peaks at 3156, 2250, 1570 and 1533cm^{-1} respectively.

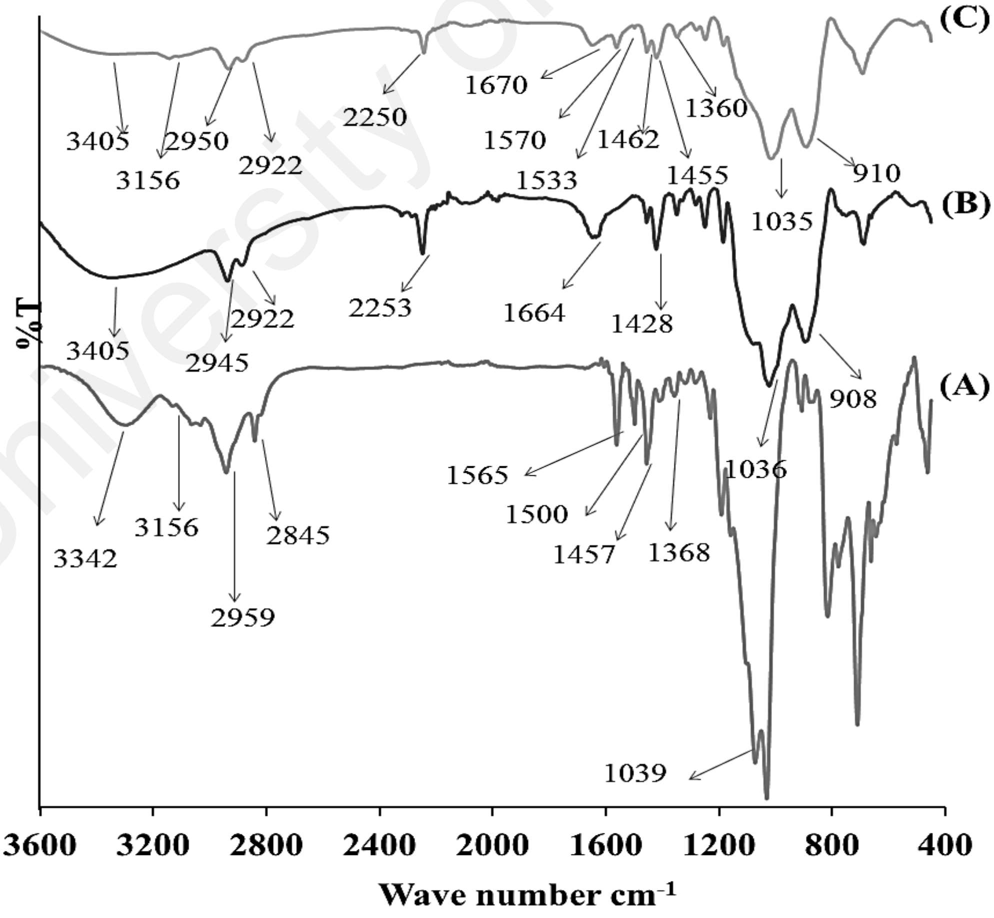


Figure 3.5: FTIR spectrum for (A) **BTMP-IM**, (B) **Si-TiCN** and (C) **Si-Ti@CN/IL**.

3.4.2.2 Surface morphology analysis

The morphological behaviour of **Si-Ti@CN** and **Si-Ti@CN/IL** was examined from FESEM results as presented in Figure 3.6. The FESEM image of **Si-Ti@CN** (Figure 3.6A) shows mesoporus compact particles with a rough morphology. Following the attachment of **BTMP-IM** as it was expected the mesopores were filled and aggregation of **BTMP-IM** on the surface of **Si-Ti@CN/IL**, therefore a smooth morphology with irregular shapes and sizes of particles (Figure 3.6B) can be clearly seen. So the deposition of foreign materiel *i.e.*, **BTMP-IM** on the surface of **Si-Ti@CN** confirmed the successful formation of new hybrid **Si-Ti@CN/IL** adsorbent.

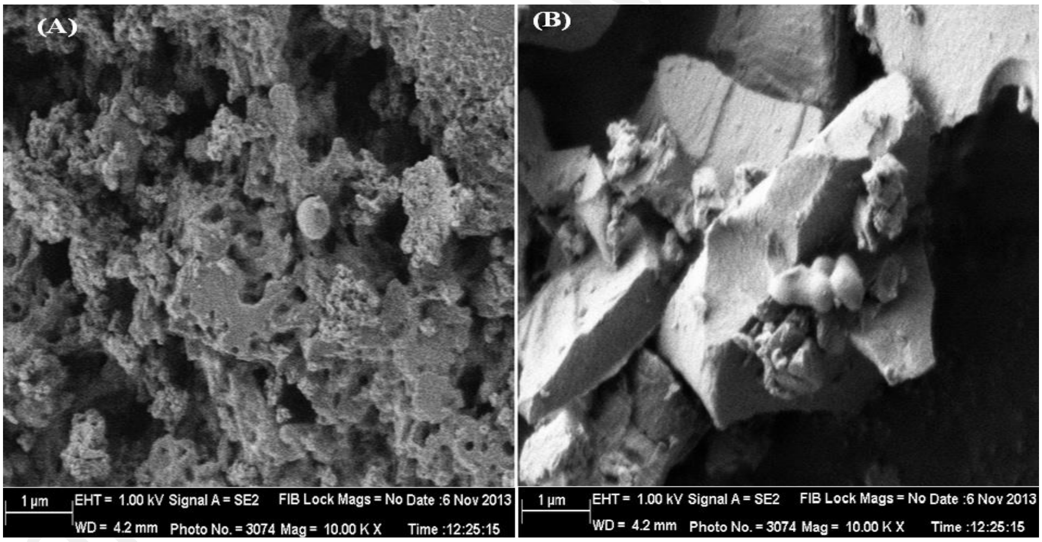


Figure 3.6: FESEM image of (A) **Si-Ti@CN** and (B) **Si-Ti@CN/IL**.

3.4.2.3 BET and elemental analysis

The N_2 adsorption/desorption isotherm for the **Si-Ti@CN/IL** (Figure 3.7B) exhibited a tendency to change the isotherm from type IV to I. This phenomenon in isotherm is typical in materials situated between mesopore to micropore sizes (Beaudet, *et al.*, 2002; Wahab, *et al.*, 2004). While the **Si-Ti@CN** (Figure 3.7A) shows isotherm type IV, indicating the formation of the typical mesopores structures (Miskam, *et al.*, 2013). The adsorption average pore diameter (D) of **Si-Ti@CN** and **Si-Ti@CN/IL** was determined by $4V/S_{BET}$ equation. In this equation, V stands for the adsorption total pore volume and S_{BET} stands for BET surface area of pores which obtained using the BET model. The average pore diameters related to both materials are consistent with the IUPAC definition of mesopores type, (Table 3.1). The average pore diameter, surface area and pore volume of **Si-Ti@CN/IL** showed a decrease in comparison with **Si-Ti@CN**. This might be due to pore coverage of IL in the surface of **Si-Ti@CN/IL**. Although the decrease of the surface area does not benefit the extraction efficiency, due to present of interaction sites on the surface of **Si-Ti@CN/IL**, the CPs extraction performance of adsorbent has shown an improvement.

The elemental analysis *i.e.*, CHNS results as represented in Table 3.1 also confirmed the successful attachment of **BTMP-IM** with **Si-Ti@CN**, it is obvious from the CHNS results that **Si-Ti@CN** contains 3.09% of N while **Si-Ti@CN/IL** contains 4.03%. The increase in N percentage is due to the attachment of **BTMP-IM**, knowing that the **Si-Ti@CN** contains one N atom situated in cyano group while **Si-Ti@CN/IL** contains one N atom from cyano group and two N atoms located in imidazolium ring. Therefore, in results of EDX it is expected to have higher N percentage.

Table 3.1: Physical properties of **Si-Ti@CN/IL** and **Si-Ti@CN**

Sample	S_{BET}(m^2/g)	V(cm^3/g)	D(nm)	Elemental composition (wt%)		
				C	H	N
Si-Ti@CN	13.54	0.04	11.7	17.03	3.08	3.09
Si-Ti@CN/IL	0.6	0.001	6.6	11.72	1.95	4.03

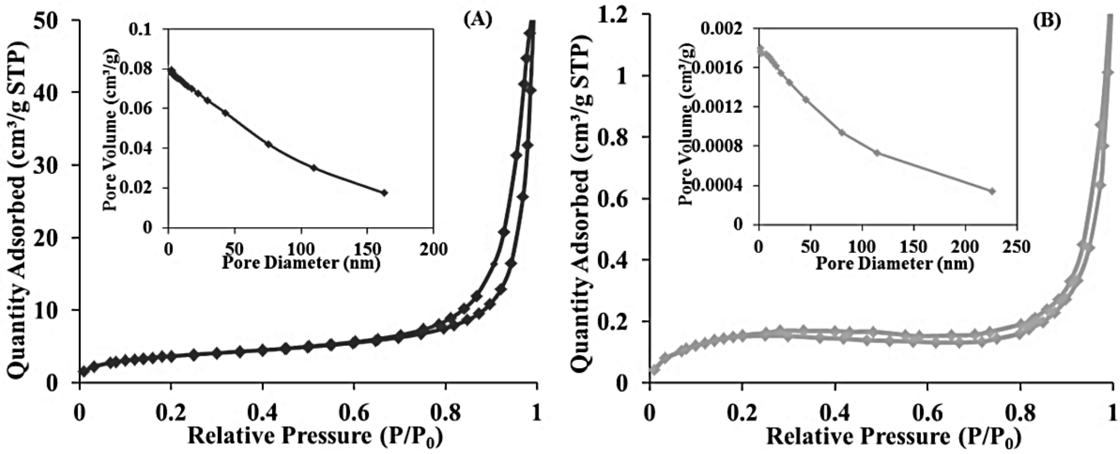


Figure 3.7: Adsorption-desorption isotherms of (A) **Si-Ti@CN** and (B) **Si-Ti@CN/IL**.

3.4.2.4 TGA analysis

The thermal stability of adsorbents was examined at the temperature range of 50 to 900 °C in nitrogen atmosphere (Figure 3.8A). **BTMP-IM** thermometric curve (Figure 3.8A) showed two main degradation steps, in first step about 10% weight loss from 50 – 150 °C was assigned to physically adsorbed water, in second step 70% weight loss from 150 – 600 °C was assigned to the combustion of organic material of benzyl imidazolium.

For both **Si-Ti@CN** and **Si-Ti@CN/IL** (Figure 3.8B&C) approximately 5% weight loss from 50 – 200 °C was attributed to the physically adsorbed waster. The 23% weight loss from 200-600 °C for **Si-Ti@CN** was assigned for the combustion of cyanopropyltriethoxysilane functionalities while in case of **Si-Ti@CN/IL** the weight loss from 200-600 °C was assigned for combustion of both benzyl imidazolium and cyanopropyltriethoxysilane. Since **Si** & **Ti** has high thermal stability, it was expected that immobilization of **BTMP-IM** on the inorganic surface of **Si & Ti** can improve the thermal stability of material compare to **BTMP-IM**.

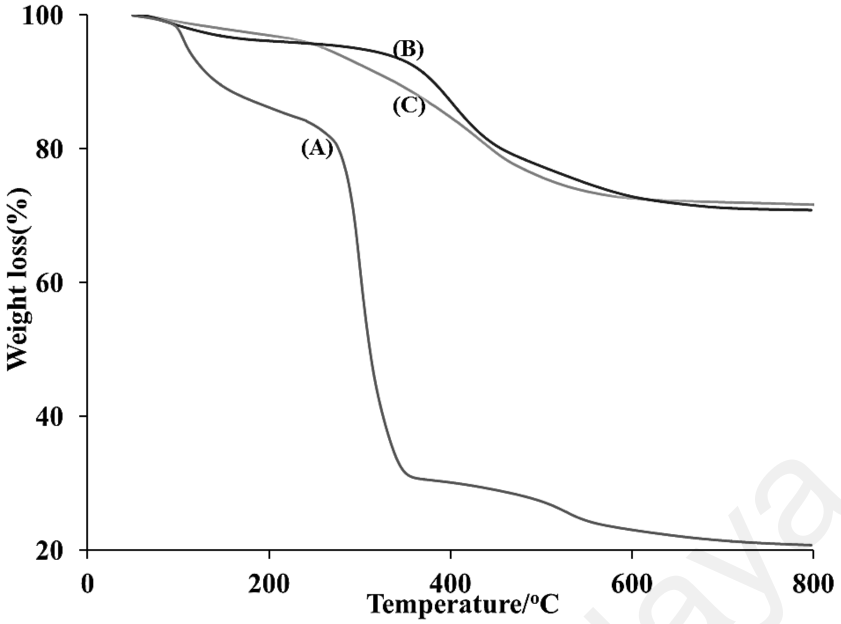


Figure 3.8: TGA profiles of (A) **BTMP-IM**, (B) **Si-Ti@CN** and (C) **Si-Ti@CN/IL**.

3.4.2.5 X-ray diffraction analysis

In order to find out further evidence for the formation of the new adsorbent, the pattern structure of materials was characterized through X-ray diffraction (XRD). Figure 3.9B shows the XRD pattern structure of **Si-Ti@CN** and **Si-Ti@CN/IL** in the range of 0 – 80 °. The presence of a peak in both patterns at 2θ near 25 degrees is merely indicates that the silica supported **Si-Ti@CN** and **Si-Ti@CN/IL** are amorphous in nature (Wahab, *et al.*, 2004). However, the absence of higher angle peaks in diffraction patterns exhibits no long-range ordering and amorphous structure. From this results can be concluded that the immobilization of cyanopropyltriethoxysilane and ionic liquid did not change the silica amorphous structure of the inorganic core.

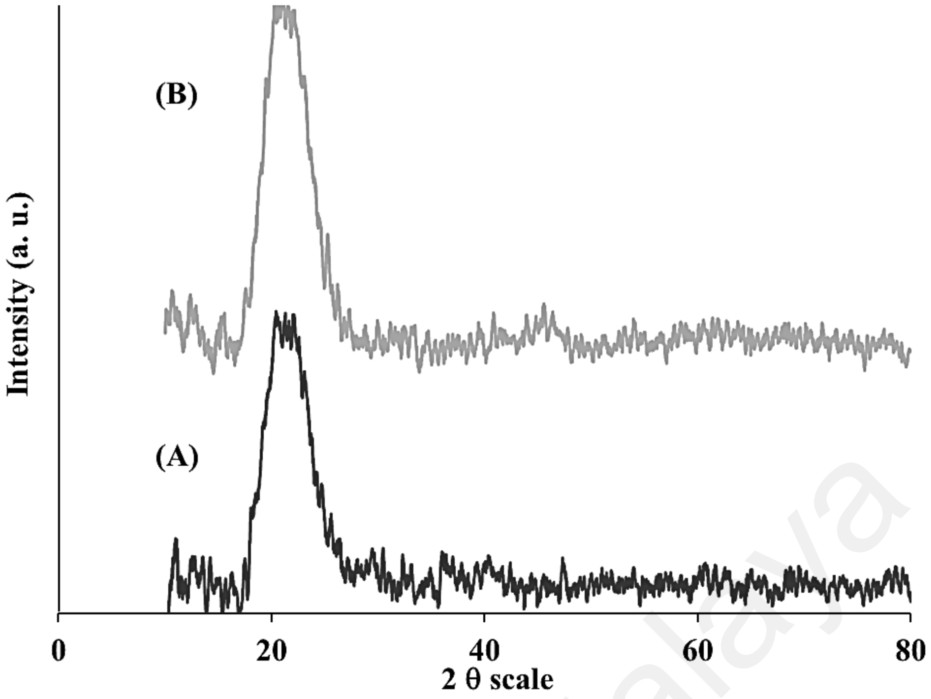


Figure 3.9: XRD analysis of (A) **Si-Ti@CN** and (B) **Si-Ti@CN/IL**.

3.4.3 Batch sorption analysis

The batch sorption method was applied to investigate the performance of cyano-ionic liquid functionalized Si-Ti material on the adsorption of several CPs in the wide range of polarity from hydrophobic to hydrophilic. From Table 3.2, it can be observed that the adsorption capacity of **Si-Ti@CN** was higher than **Si-Ti@IL** for polar CPs including 2-CP, 4-CP and 3-CP, due to higher availability of hydroxyl site of analytes to form hydrogen bonding through CN site. Meanwhile the adsorption capacity of **Si-Ti@IL** was higher than **Si-Ti@CN** for non-polar CPs due lack of H-bonding sites (CN) in **Si-Ti@IL** to interact with polar analytes. However, the adsorption capacity values enhanced for all compounds when **Si-Ti@CN/IL** was used as the adsorbent. It shows that both cyano group and ionic liquid (particularly the benzyl imidazolium group of IL's cation) in this material play a role for this new material that can be used as a potential adsorbent for chlorophenols. In addition, the selectivity of the adsorbent can be changed by changing the functional groups of cation in the ILs.

Table 3.2: Absorption capacity of selected CPs using **Si-Ti@CN**, **Si-Ti@IL** and **Si-Ti@CN/IL** in batch adsorption studies

	Adsorption Capacity (mg.g^{-1})					
	2-CP	**4-CP**	**3-CP**	**2,4-DCP**	**2,4,6-TCP**	**2,3,4,6-TTCP**
Si-Ti@CN	1.13	0.31	0.87	2.12	0.79	1.09
Si-Ti@IL	0.46	0.24	0.40	1.61	1.09	3.36
Si-Ti@C/IL	1.73	1.17	1.58	2.95	3.87	5.00

3.4.4 SPE optimization study

3.4.4.1 Elution solvent

Optimization or selection of appropriate elution solvent is a very crucial step in the SPE process in order to desorb the retained CPs. Four eluting solvents with different polarities *i.e.*, methanol, acetonitrile, tetrahydrofuran (THF), and n-hexane were used to get the quantitative desorption of retained chlorophenols. Since the selected elution solvent can be categorize into polar as well as non-polar, while selected CPs are polar in nature. Consequently, as expected results (Figure 3.10) showed that polar solvents have higher affinity towards chlorophenols due to the higher solvents strength compared to the non-polar solvents. The obtained results showed that compared to the other tested eluting solvent methanol is more efficient for desorption of targeted CPs from the surface of **Si-Ti@CN/IL** adsorbent. The high desorption in case of methanol might be due to the protic nature, since methanol is a highly protic solvent and it can easily form a hydrogen bond with the hydroxyl groups of adsorbent, while acetonitrile and tetrahydrofuran (THF) as aprotic polar solvents exhibit slightly less hydrogen bonding with hydroxyl groups of adsorbent compare to methanol (Liu, *et al.*, 2011).

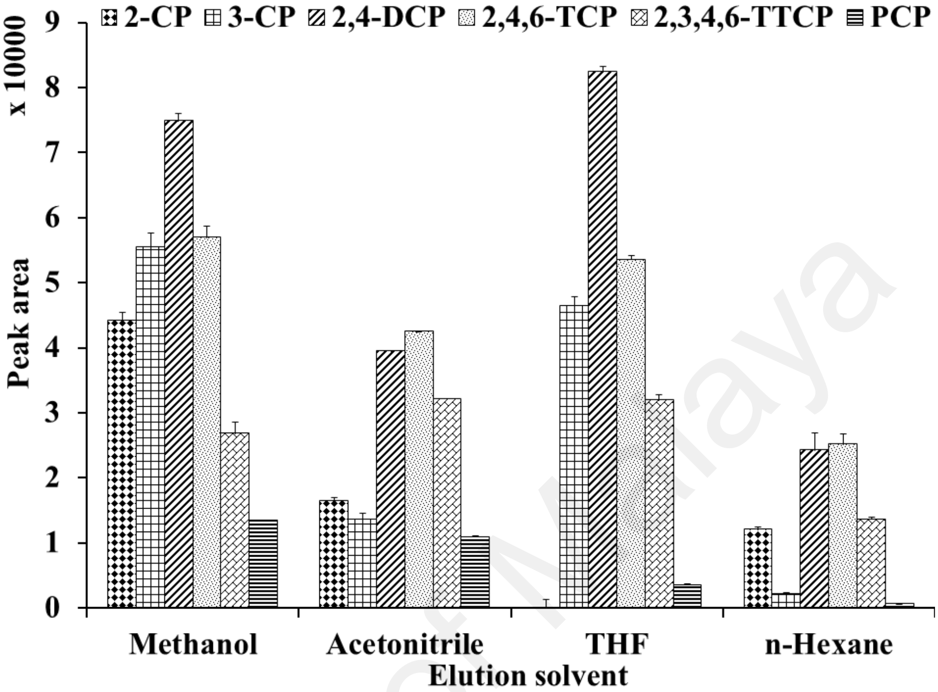


Figure 3.10: Effect of elution solvent on the extraction of CPs.

In order to optimize the minimum volume of elution solvent, 1 to 20 mL of eluent solvent was passed through the cartridge. As the eluent volume enhanced from 1 mL to 4 mL, the efficiency of CPs increased and best recovery for all CPs was achieved by using 4 mL of eluent solvent. Beyond the, 4 mL the peak area for analytes was reduced. Thus, 4 mL of methanol was chosen as the optimum eluent volume (Figure 3.11).

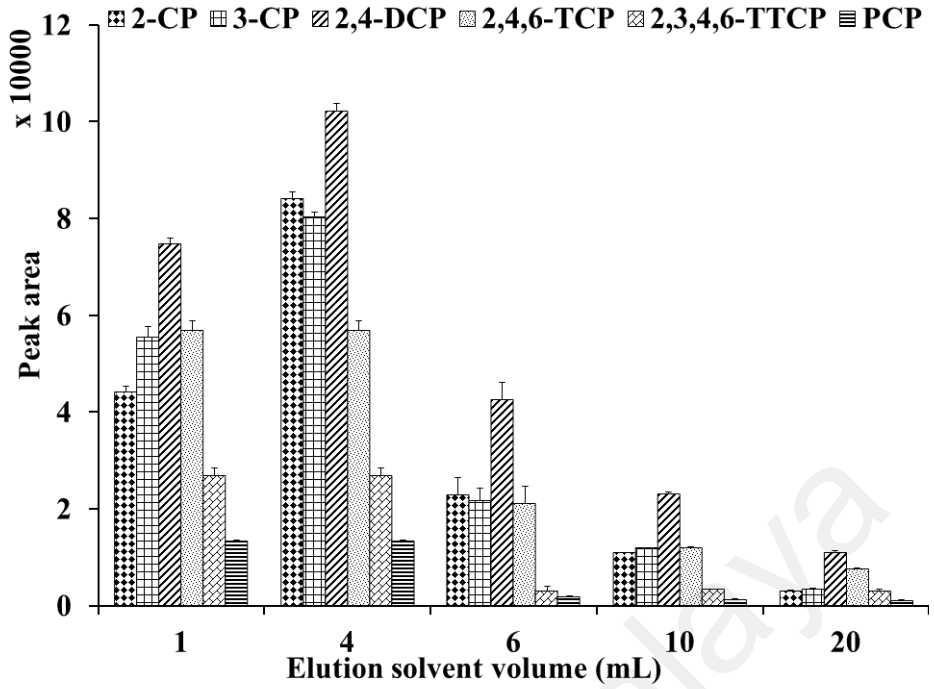


Figure 3.11: Effect of eluting solvent volume on the extraction of CPs.

3.4.4.2 Effect of sample loading volume

In order to investigate the maximum volume of sample which can be loaded into the adsorbent (the breakthrough volume) for quantitative extraction recovery, the volume of sample solution was varied from 1 – 25 mL and the SPE cartridges were loaded with different quantities (1, 5, 10, 15, 20, 25 mL) of 2 ppm mixed solution of selected CPs. As shown in Figure 3.12, the peak area improved by increasing the sample volume up to 10 mL for all the selected target analytes. Thus, 10 mL volume was selected for subsequent experiments.

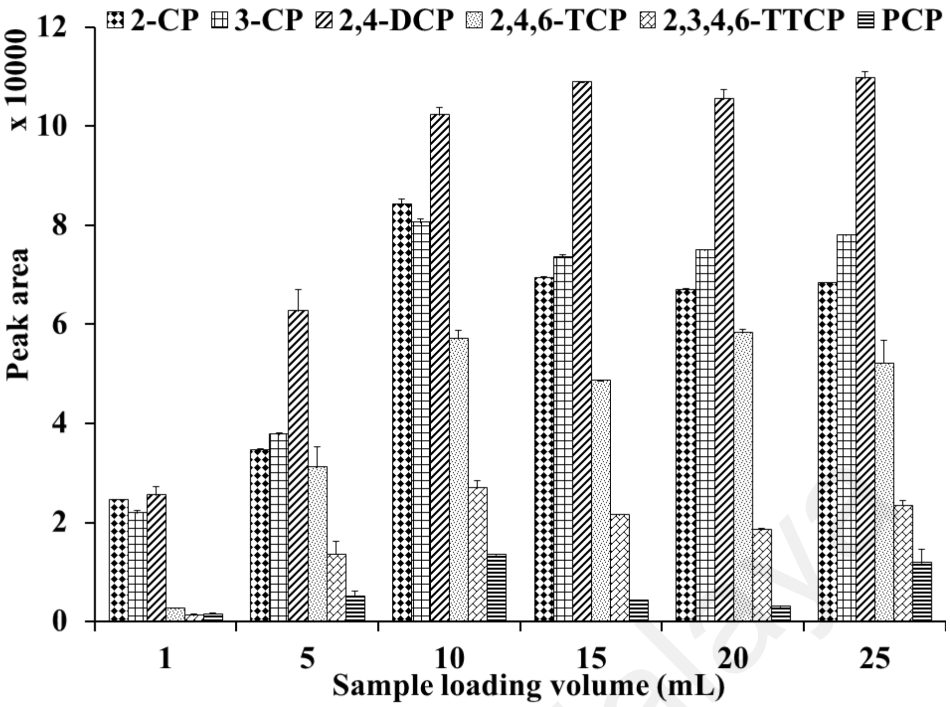


Figure 3.12: Effect of sample loading volume on the extraction of CPs.

3.4.4.3 Sample pH

The solution pH has momentous influence on the extraction performance, because by the variation of solution pH the extraction of target analytes can be significantly increased or decreased (Raoov, *et al.*, 2014). So herein the effect of solution pH on the extraction of selected CPs was investigated by varying the pH from 2 – 10 (Figure 3.13). Results indicated that strong acidic medium is more suitable for the extraction of selected CPs and maximum efficiency for all the selected CPs was obtained at pH 2. While by increasing the pH, it was observed that peak area was decreased. The highest peak area was for all CPs especially PCP and 2,3,4,6-TTCP at pH 2 can be explain on the basis of pK_a values of selected CPs that are in the range 4.74 – 9.12. It is notice that the chlorophenols are in their anionic form when the pH is higher than their pK_a, therefore to avoid ionization of CPs, it is necessary to keep pH lower than pK_a (Kulkarni, *et al.*, 2006; Rodríguez, *et al.*, 2000). Since, synthesised adsorbent

Si-Ti@CN/IL contains variety of anionic terminal functional group so at basic pH there may be strong repulsion forces between the anionic sites of both *i.e.*, adsorbent as well as target analytes. In addition, strong π–π interaction between benzyl group from imidazolium ring (ionic liquid) and phenolic compounds which appear in both high and low pH medium can increase the extraction (Raoov, *et al.*, 2014; Rodríguez, *et al.*, 2000).

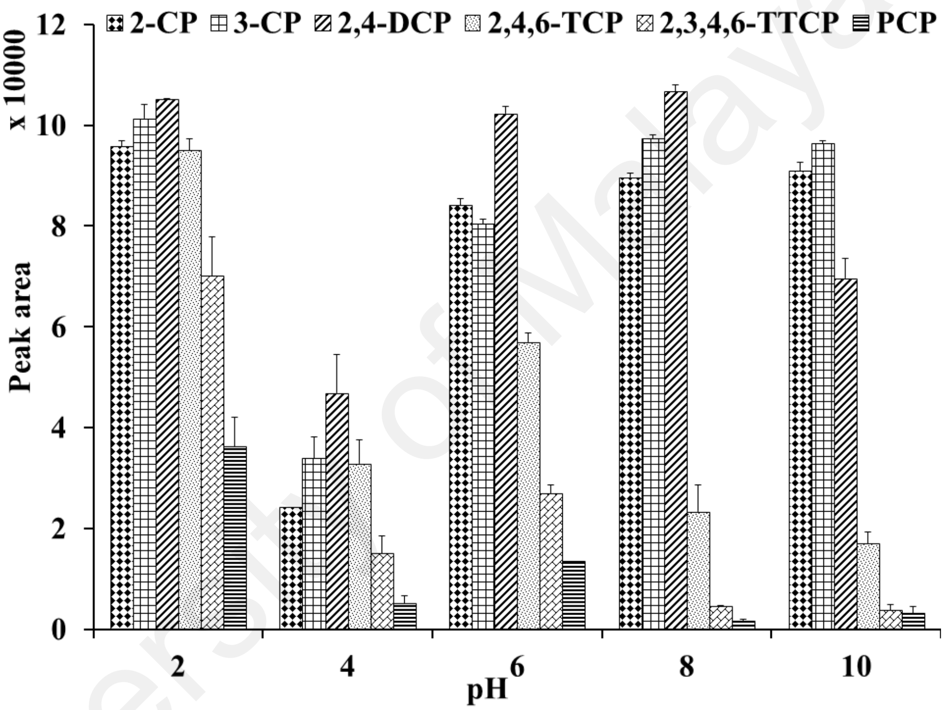


Figure 3.13: Effect of sample pH on the extraction of CPs.

3.4.4.4 The effect of modifier

To investigate the possible effect of modifier on desorption of targeted CPs, the acetic acid 1% – 15% was added to the eluting solvent. The highest recovery was observed with the addition of 1% acetic acid to methanol. As it is obvious from Figure 3.14 that further increase of the % of acetic acid above 1%, the recovery of target CPs significantly decreased except PCP. Thus, results confirmed that acetic acid as a modifier plays vital role during desorption of retained CPs from the surface of newly synthesised **Si-Ti@CN/IL** adsorbent. This is probably because of the high competition of acetic acid with retained CPs to form hydrogen bond with the functional groups of adsorbent. However, higher percentage of acetic acid would not benefit the elution step, (Feng, *et al.*, 2009) simply because of formation of hydrogen bond between acetic acid and methanol (Raoov, *et al.*, 2014). Therefore, the reaction between solvent and desorb retained CPs would be decreased. After each SPE run, the used SPE cartridges were rinsed thoroughly with methanol containing 1% acetic acid, followed by ultra-purified water to make sure that the analytes are removed from the adsorbent.

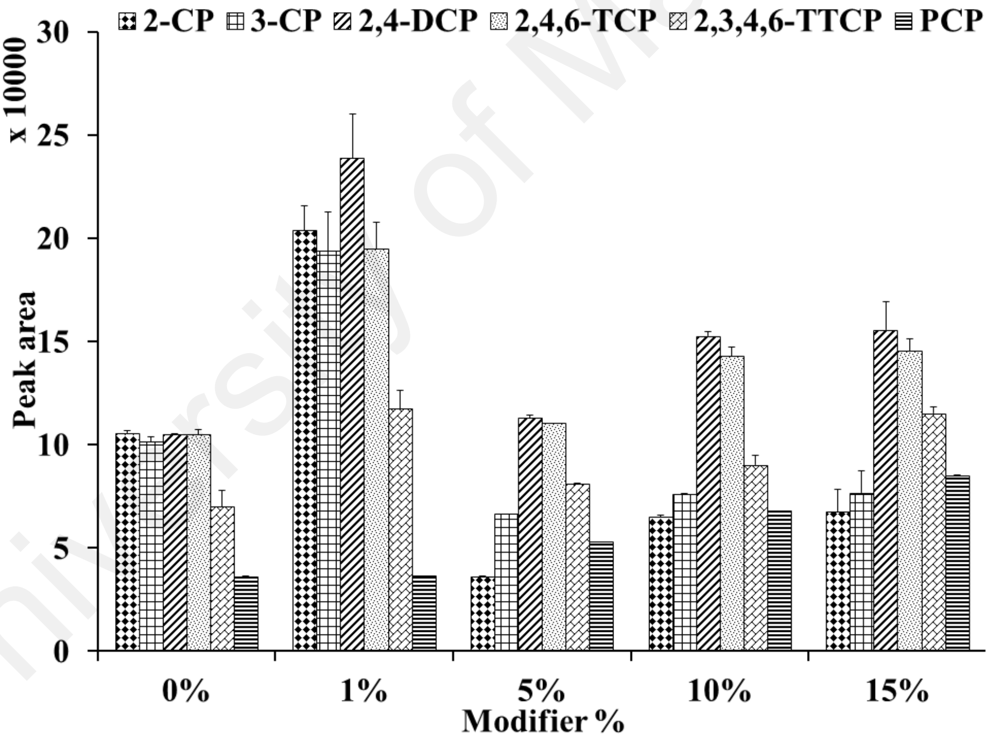


Figure 3.14: Effect of % modifier on SPE method.

3.4.5 Method validation

On the basis of acquired results for the extraction of CPs using **Si-Ti@CN/IL**, important parameters affecting the SPE were optimized as pH 2, 5 mL of methanol, followed by 5 mL of ultra-purified water as conditioning solvent, 10 mL sample volume and 4 mL of methanol containing 1 % acetic acid as the eluting solvent finally eluted samples evaporated over air stream vacuum and dispersed with 0.5 mL solvent. To validate the applicability of SPE methods of **Si-Ti@CN/IL**, the series of experiments were carried out to obtain the linearity, limit of detection (LOD) and limit of quantification (LOQ). SPE was carried out using the optimum extraction conditions. The linearity of the proposed method was investigated at seven various concentration levels of CPs in the range of 10 – 1000 μg L^{-1} for **Si-Ti@CN/IL**. Each concentration was repeated three times and the mean value of peak area was taken for the calibration curve. The results showed a good linearity for the extraction of target CPs with a coefficient of determination (r^2) ranging from 0.9968 – 0.9999.

The LOD and the LOQ for SPE extraction of CPs as given in Table 3.3 using **Si-Ti@CN/IL** adsorbent (0.83 – 0.95; 2.77 – 3.17 μg L^{-1}) were lower as compared to the compared to the **Si-Ti**, **Si-Ti@CN** and **Si-Ti@IL**). The lowest value of LOD and LOQ of **Si-Ti@CN/IL** compared to other tested adsorbents indicates the effect of cyano group as well as ionic liquid on increasing the sensitivity of the adsorbent. The intra-day precision of optimum method was obtained by performing 5 variances at a concentration of 10 μg L^{-1} with 100 mg of adsorbent. Inter-day precision was determined by 3 variances with the same concentration as inter-day batch, during 3 days. The optimum method demonstrated to be precise with RSDs of 2.31 – 4.71 % *(n*=5*)* for intra-day and 1.61 – 4.26 % *(n*=3*)* for inter-day batch (Table 3.3).

Table 3.3: Analytical figures of merits of **Si-Ti**, **Si-Ti@CN**, **Si-Ti@IL** and **Si-Ti@CN/IL** in SPE: repeatability (%RSDs, n=5), LOD (μg L^{-1}), and LOQ (μg L^{-1}) of CPs.

	Si-Ti			**Si-Ti@CN**			**Si-Ti@IL**			**Si-Ti@CN/IL**				
											RSDs			
Analyte	RSDs	LOD	LOQ	RSDs	LOD	LOQ	RSDs	LOD	LOQ	r^2	Intra (n = 5)	Inter (*n* = 3)	LOD	LOQ
2-CP	3.21	11.6	38.7	3.84	1.51	5.03	4.76	5.78	19.3	0.9990	2.31	1.61	0.85	2.82
3-CP	4.92	9.99	33.3	4.78	1.62	5.4	4.44	4.85	16.2	0.9968	3.98	3.68	0.84	2.79
2,4-DCP	1.36	10.5	34.9	4.08	1.38	4.6	3.6	6.48	21.6	0.9999	3.3	3.53	0.83	2.77
2,4,6-TCP	4.97	8.83	29.5	4.86	1.72	5.74	2.1	4.89	16.3	0.9999	4.71	4.16	0.93	3.1
2,3,4,6-TTCP	3.78	8.55	28.5	2.62	2.03	6.75	3.96	8.17	27.2	0.9999	4.17	4.23	0.95	3.17
PCP	3.65	8.71	29	2.25	1.71	5.7	2.66	3.31	11.0	0.9993	4.09	4.26	0.85	2.82

Linearity ranges: **Si-Ti**, **Si-Ti@CN** and **Si-Ti@IL** (100 - 5000 μg L^{-1}), and **Si-Ti@CN/IL** (10 – 1000 μg L^{-1}).

For the comparison of SPE performance similar amount (100 mg) of all the synthesized adsorbent *i.e.*, **Si-Ti**, **Si-Ti@CN Si-Ti@IL** and **Si-Ti@CN/IL** were packed in 3 mL SPE cartridges and optimum conditions were applied. The obtained results (Table 3.3, Figure 3.15) indicated that **Si-Ti@CN/IL** adsorbent has highest percent (76.57 – 106.67 %) with the relative standard deviation (%RSDs) of 2.31 – 4.71 % as compared to **Si-Ti** with recovery of (3.6 – 37.4 %) and %RSDs 1.36 – 4.97 , **Si-Ti@CN** with recovery of (21.5 – 59.9 %) and %RSDs 2.25 – 4.86 and **Si-Ti@IL** with recovery of (26.1 – 105.6) and %RSDs 2.10 – 4.76. This result justified the worth of **Si-Ti@CN/IL** as SPE adsorbent. Comparably 2-CP, 3-CP and 2,4-DCP have very low affinity for the **Si-Ti@CN** and **Si-Ti@IL**, while their percent recovery increased dramatically by using **Si-Ti@CN/IL**. The second concern is that the **Si-Ti@CN** has much lower affinity towards 2,4,6-TCP, 2,3,4,6-TTCP and PCP in comparison with **Si-Ti@CN/IL**. This is because of absence of π-π interaction sites of ionic liquid in the surface of **Si-Ti@CN** compare to **Si-Ti@CN/IL**. Meanwhile, the **Si-Ti@IL** by having π-π interaction sites of ionic liquid (benzyl ring and imidazolium ring) and H-bonding possibility through unshared electron pare of N of imidazolium ring has shown better results for all analytes except 3-CP compare to **Si-Ti@CN**, however the lack of cyano group and its highly possible hydrogen bonding still is the reason of lower percent recovery of 2-CP, 3-CP and 2,4-DCP compare to **Si-Ti@CN/IL.** Additionally, **Si-Ti** showed very poor capacity and affinity towards the selected CPs because of lack of interaction sites compare to other adsorbents, the only possible interaction might be hydrogen bonding through hydroxyl groups on the surface of adsorbent. So it is confirmed that combination of cyano group and ionic liquids on the surface of adsorbent enhance the affinity and capacity of the adsorbent for CPs.

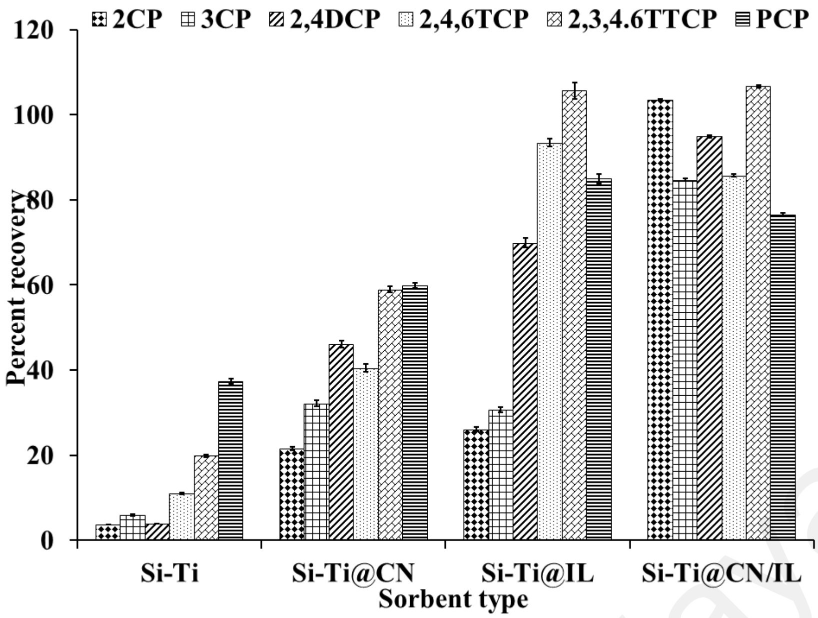


Figure 3.15: SPE performance of **Si-Ti@CN/IL** with **Si-Ti**, **Si-Ti@CN** and **Si-Ti@IL** for selected CPs.

The higher affinity of **Si-Ti@CN/IL** towards the CPs can be explained by the fact that the imidazole ring and benzyl group (cationic part of ionic liquid) are able to form a strong π–π interaction as well H-bonding with the aromatic core and hydroxyl groups respectively of the CPs. In addition the synthesised **Si-Ti@CN/IL** contains different anionic sites *i.e.*, O and N while selected CPs contains Cl and OH groups. At acidic pH, hydrogen (H) of hydroxyl (OH) groups of selected CPs shows binding abilities toward the anionic (O and N) sites of **Si-Ti@CN/IL**. While, the hydrogen (H) of hydroxyl (OH) group of **Si-Ti@CN/IL** shows binding abilities towards the Cl group of CPs (Figure 3.16). Consequently, in this scenario selected CPs are extracted through strong hydrogen bonding.

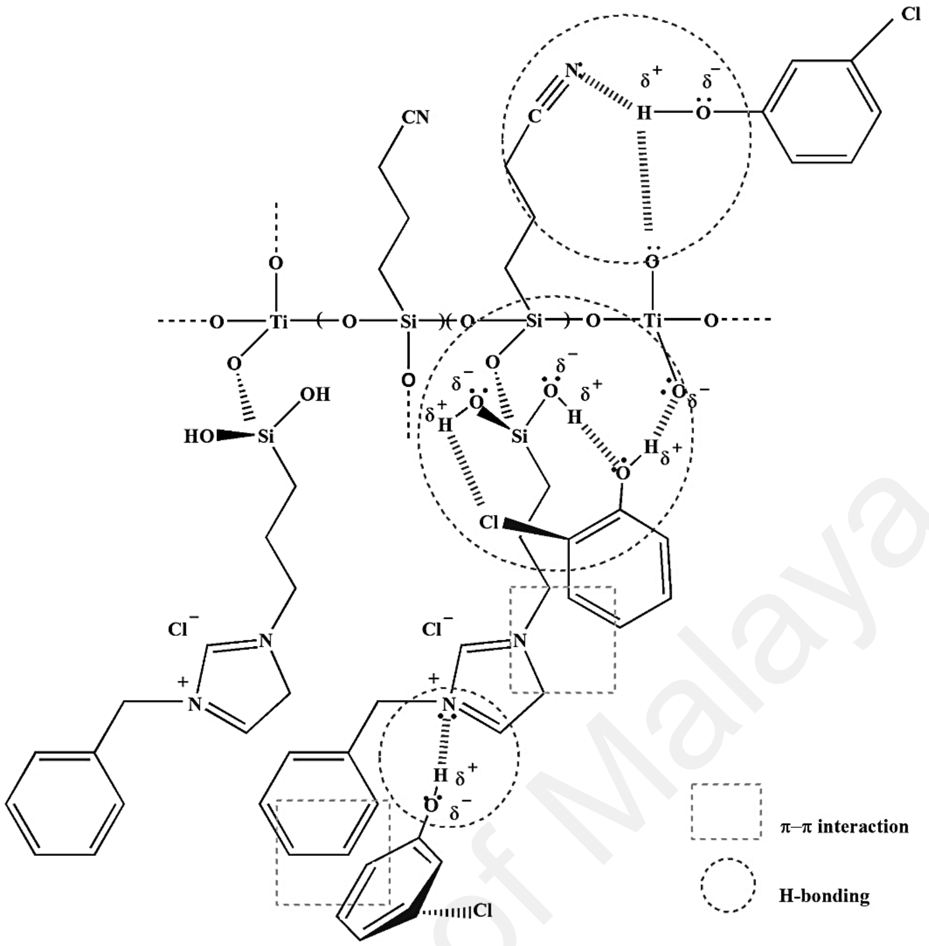


Figure 3.16: Proposed mechanism for the extraction of the CPs by **Si-Ti@CN/IL**.

3.4.6 Real samples analysis

The optimum SPE method using **Si-Ti@CN/IL** adsorbent was applied to the real environmental samples (tap water, lake water, and leachate from landfill site). To investigate the effect of the sample matric, the real samples were spiked with CPs at a concentration of 5 μg L^{-1} and 1000 μg L^{-1} under the optimum conditions described to obtain the accuracy of this method. Table 3.4 shows the recovery and repeatability for real samples. The recovery of leachate, lake water and tap water was in the range of 77.99 - 95.57%, 75.17 - 105.54 % and 73.87 - 101.17 % respectively. The RSDs of leachate, lake water and tap water was in the range of 1.07 - 3.40 %, 1.22-3.93 % and of 0.82 - 4.19 % respectively.

The high recovery percentage of analytes in environmental samples shows their high affinity towards **Si-Ti@CN/IL** and applicability of the adsorbent for environmental samples, respectively. The chromatogram illustrations of unspiked lake water with spiked with analytes is given in Figure 3.17.

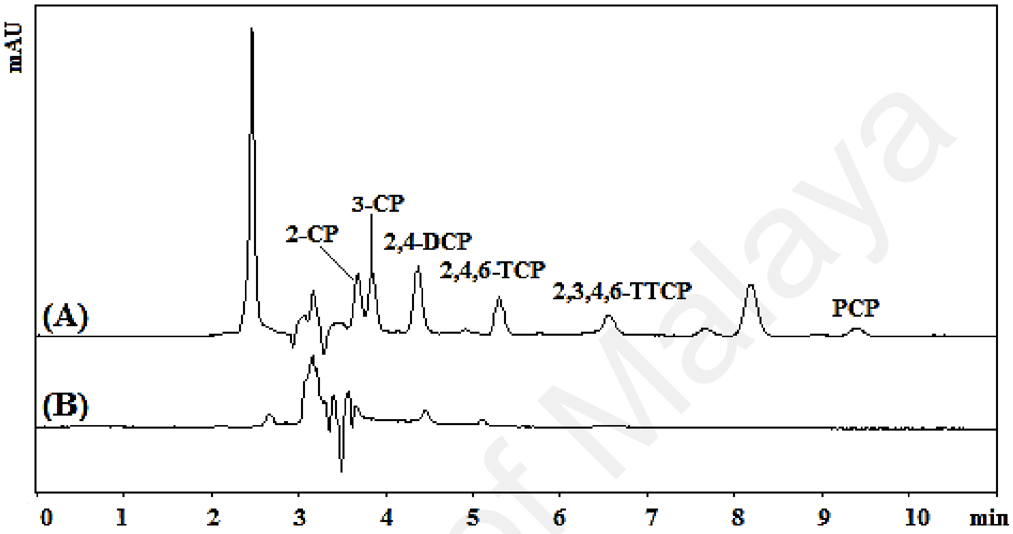


Figure 3.17: Chromatograms of lake water using **Si-Ti@CN/IL** as the SPE adsorbent; (A) lake water spiked with 5 µg L^{-1} CPs mixture and (B) unspiked lake water.

Table 3.4: Recovery and %RSDs (n=5) of CPs in the real water samples with a spiked concentration of 5 μg L^{-1} and 1000μg L^{-1}.

	Leachate		**Lake water**		**Tap water**	
Analyte	Recovery (RSDs)% 5 μg L^{-1}	Recovery (RSDs)% 1000 μg L^{-1}	Recovery (RSDs)% 5 μg L^{-1}	Recovery (RSDs)% 1000 μg L^{-1}	Recovery (RSDs)% 5 μg L^{-1}	Recovery (RSDs)% 1000 μg L^{-1}
2-CP	79.3 (1.91)	93.4 (2.27)	75.2 (2.28)	77.3 (1.97)	75.2 (2.27)	74.2 (1.99)
3-CP	95.6 (3.40)	90.1 (1.07)	83.9 (1.80)	93.8 (3.93)	82.4 (1.89)	97.4 (4.11)
2,4-DCP	90.1 (1.69)	92.5 (1.16)	105.5 (1.51)	89.0 (1.95)	96.6 (1.64)	88.6 (1.64)
2,4,6-TCP	89.1 (1.58)	78.6 (1.39)	79.8 (1.79)	86.5 (1.55)	77.1 (0.82)	87.0 (3.67)
2,3,4,6-TTCP	84.8 (3.34)	82.3 (2.45)	83.8 (2.40)	83.8 (1.36)	82.2 (2.30)	96.2 (4.19)
PCP	83.9 (2.05)	78.0 (1.32)	100.8 (1.22)	98.4 (1.43)	100.6 (1.62)	101.2 (3.91)

3.4.7 Comparison of Si-Ti@CN/IL with previously reported adsorbents

For the validation of the study, the obtained results were compared with previously reported adsorbents from literatures. Optimum SPE method by using polystyrene divinylbenzene as reverse phase adsorbent for separation of CPs from river and drinking water has shown lower percent recovery with higher LOD compare to present study (Al-Janabi, *et al.*, 2011; Opeolu, *et al.*, 2010). Also the commercial XAD-2 and XAD-4 as hydrophobic SPE adsorbents (Jung, *et al.*, 2006) were shown very low percent recovery for extraction of CPs from tap and river water samples. Solid phase extraction studies of multi-walled carbon nanotubes and magnetic 3-dimensional graphene as MSPE adsorbent (X. L. Liu, *et al.*, 2014) for separation of CPs, although showed good recovery but the LOD value is much higher than current study. The results of Table 3.5 reveals that the newly proposed SPE method based on **Si-Ti@CN/IL** is more reliable and efficient for the preconcentration/extraction of CPs from water sample with low LOD and RSD values with good percent recoveries acompared to the previously reported adsorbents.

Table 3.5: Comparison of %Recovery, %RSDs and LOD (μg L^{-1}) of the current study with other reported adsorbents.

Sample	Technique/Adsorbent	%Recovery	RSDs%	LOD	Ref.
River	SPE-HPLC/ PS-DVB	51.06–104.07	2.4–5.59	23–4596	(Al-Janabi, *et al.*, 2011)
Drinking water	SPE-HPLC/ PS-DVB	67.9–99.6	0.12–9.25	0.01–2.0	(Opeolu, *et al.*, 2010)
Tap-River-Sea	MSPE-HPLC /3D-G@Fe3O4	85.1–101.2	3.1–6.1	0.91–39.64	(Liu, Wang, *et al.*, 2014)
Tap-Stream	SPE-HPLC/ MWCNTs	82.9–97.2	6.8–7.4	5–10	(El-Sheikh, *et al.*, 2012)
Tap-River	SPE-HPLC/ XAD-2	8.01–79.9	0.16–4.69	–	(Jung, *et al.*, 2006)
Tap-River	SPE-HPLC/ XAD-4	39.6–88.6	0.13–3.80	–	(Jung, *et al.*, 2006)
Tap-Lake-Leachate	**SPE-HPLC/ Si-Ti@CN/IL**	**73.39–105.54**	**0.82-4.19**	**0.83–0.95**	**Current Study**

3.5 Conclusion

In summary, the characterization results clarified the formation of new silica-titania oxide sol–gel based ionic liquid (**Si-Ti@CN/IL**) in acidic catalysed condition. The **Si-Ti@CN/IL** was successfully used as a new adsorbent in solid phase extraction (SPE) for a simple, fast and efficient extraction/preconcentration of CPs from environmental water samples using HPLC-UV. The optimum SPE conditions for the extraction of CPs were, 5 mL of methanol, followed by 5 mL of ultra-purified water as the conditioning solvent, 10 mL sample (pH = 2), and 4 mL of methanol containing 1 % acetic acid as the eluting solvent. Extraction/preconcentration of CPs onto **Si-Ti@CN/IL** from aqueous solution was systematically investigated under various conditions and it is concluded that the presence of cyano group and IL in new solid-phase extractor (**Si-Ti@CN/IL**), played a key role and enhanced the adsorption capability for the selected CPs. The extraction of CPs is strongly pH dependent, and field studies showed that **Si-Ti@CN/IL** could be successfully used for the extraction of CPs from aqueous environment. Therefore, **Si-Ti@CN/IL** was a promising adsorbent for determination of CPs in environmental samples. Thus, it is believed that this adsorbent can be a promising material for SPE.

CHAPTER 4: CYANO-IONIC LIQUID FUNCTIONALIZED MAGNETIC NANOPARTICLES FOR MAGNETIC SOLID PHASE EXTRACTION OF SELECTED CHLOROPHENOLS & POLYCYCLIC AROMATIC HYDROCARBONS

4.1 Introduction

Magnetic solid phase extraction (MSPE) methods have been employed as new form of SPE based on the use of magnetic adsorbent for pretreatment of environmental samples especially aqueous samples. Magnetic adsorbents make the pretreatment process easier than the traditional SPE. The magnetic adsorbent does not require to be packed in SPE cartridge and separation/ preconcentration is proceeded under an external magnetic field (Akbarzadeh, *et al.*, 2012; Alvand and Shemirani, 2014; Asgharinezhad, *et al.*, 2014; Faraji, *et al.*, 2010; Heidari, *et al.*, 2012; Madrakian, *et al.*, 2013; Mashhadizadeh and Karami, 2011; Sadeghi and Aboobakri, 2012). The goal of this research is to synthesis and characterize a new MSPE adsorbent (**MNP@CN/IL**) through sol-gel polymerization process. The magnetic nanoparticle (**MNP**) surface as an inorganic core of hybrid material was modified with cyanopropyltriethoxysilane and 1-benzyl-3-(trimethoxysilylpropyl)imidazolium chloride ionic liquid (**BTMP-IM**) as organic cores of material. The main consideration of this new material is the presence of benzyl groups in the cationic part of the imidazolium-based ionic liquid, to improve π-π stacking interaction with aromatic moieties and presence of cyano group which forms intermolecular with hydrogen bond accepter sites in analytes. This provides adsorbent with the selectivity towards wider range of organic pollutants. The newly synthesised **MNP@CN/IL** was characterized by fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), field emission scanning electron microscopy

(FESEM), vibrating sample magnetometer (VSM), energy-dispersive X-ray spectroscopy (EDX), elemental analyses with CHNS and X-ray diffraction (XRD). In continue, an effective method of MSPE has been developed utilizing **MNP@CN/IL** adsorbent for the determination of aromatic compounds *i.e.*, CPs (2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP)) and PAHs (flourene (FLO), fluoranthene (FLU), pyrene (PYR), chrysene(CRY), benzo(a)pyrene (BaP)).

4.2 Experimental

4.2.1 Chemical and reagent

All chemicals and reagents were of analytical and chromatographic grades. Cyanopropyltriethoxysilane, n-benzylimidazole, 3-(chloropropyl)-trimethoxysilane and ammonium hydroxide solution 25 % were purchased from Sigma-Aldrich (Steinheim, Germany). $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ was obtained from (Guangdong, China) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) from (R&M Chemical, toluene and ethyl acetate from R&M Chemical (UK) and 2-propanol from J.TBaker. Diethyl ether was purchased from Fisher-Scientific (Leicestershire, UK). Dichloromethane (DCM) was obtained from Sigma-Aldrich (USA). Hydrochloric acid (HCl), and HPLC grade acetonitrile, methanol and n-hexane were purchased from Merk (Darmstadt, Germany). The selected analytes (Table 4.1): flourene (FLO), fluoranthene (FLU), pyrene (PYR), chrysene (CRY), benzo(a)pyrene (BaP) were purchased from SupelcoAnalitical (USA). 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and 2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP) were purchased from Sigma-Aldrich (Steinheim, Germany).

4.2.2 Instruments

The characterization study was obtained by using Perkin Elmer X1FTIR Fourier Transform Infrared Spectroscopy (FTIR) in KBR mode in the range of 400 – 4000 cm^{-1}. X-ray diffraction (XRD) was measured with a PANalytical Empyrean X-ray diffractometer (40 mA, 40 kV) using Cu Kα radiation in the scanning range of 5 (2θ) to 80 ° (2θ) at rate of 0.07 ° min^{-1}.The elemental composition were analysed with energy-dispersive X-ray spectroscopy (EDX). The magnetic properties was analysed by using vibrating sample magnetometer (VSM LakeShore 7400 series). The size and morphology of magnetic particles were observed by transmission electron microscopy (TEM) (Tecnai G2 20 S-Twin). The HPLC system CHNS and TGA instruments and their methods are similar as it is explained in Section 3.2.2.

4.2.3 Chromatographic conditions

The isocratic separation was carried out using purified water/methanol (both acidified to 1 % with acetic acid) (20:80) for CPs and purified water/acetonitrile (20:80) for PAHs at flow rate 1 mL min^{-1}. The HPLC column temperature was constant on 40 ^{o}C. The sample injection volume for CPs was constant on 20 μL and 10 μL for PAHs throughout the study. The DAD detection for all the selected CPs was carried out at 280 nm, while selected were analyzed at multiple wave lengths *i.e.*, 254, 284, 270 and 266 nm for FLO, FLU, PYR, CRY and BaP respectively.

4.2.4 Synthesis

Synthesis of **MNP@CN/IL** was proceed in three steps, including preparation of **MNP** through chemical co-precipitation, preparation of **MNP@CN** and at the end preparation of **MNP@CN/IL** through sol-gel method.

4.2.4.1 Preparation magnetic nanoparticles (MNP)

Fe_3O_4 magnetic nanoparticles (**MNP**) (Figure 4.1A) were prepared via the modification of previously reported procedure. 0.5 g of $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ and 1 g $FeCl_3{\cdot}6H_2O$ were dissolved in 30 mL of deionized water and stirred vigorously for 5 min at 50°C. Following the drop wise addition of 5 mL of ammonia solution (32%), reaction mixture was further stirred at room temperature for 5 h. The resulting black Fe_3O_4 nanoparticles were collected using external magnet and washed with excess of deionized water and dried under vacuum at 80°C for 24 h

4.2.4.2 Preparation of cyano group functionalized magnetic nanoparticle (MNP@CN)

The cyano-group functionalized magnetic nanoparticles (**MNP@CN**) were prepared as follow, 0.6 g of the freshly prepared Fe_3O_4 were dispersed in 2-propanol/water solution (5:1) and sonication for 15 min under room temperature. Following the addition of 10 mL ammonia solution (25%), 3 mL of cyanopropyltriethoxysilane added rapidly the reaction mixture was stirred for 24 at room temperature (Figure 4.1B). Finally, the resultant slightly darker brown **MNP@CN** nanoparticles were collected and washed with deionized water and ethanol. The **MNP@CN** was then dried under vacuum at 80°C for 20 h.

4.2.4.3 Preparation of cyano-ionic liquid functionalized magnetic nanoparticle (MNP@CN/IL)

Cyano-ionic liquid functionalized magnetic nanoparticles (**MNP@CN/IL**) were prepared as follow; the prepared **MNP@CN** was suspended in 50 mL toluene, following the 15 min sonication 2.21 g of **BTMP-IM** (Section 3.3.1) and 4 mL aqueous triethylamine (as catalyst) were added and reaction mixture was stirred at 80 ^{o}C for 24 h. Finally, the resultant **MNP@CN/IL** nanoparticles were collected and washed with deionized water and ethanol. The **MNP@CN/IL** was then dried under vacuum at 80°C for 24 h (Figure 4.1C).

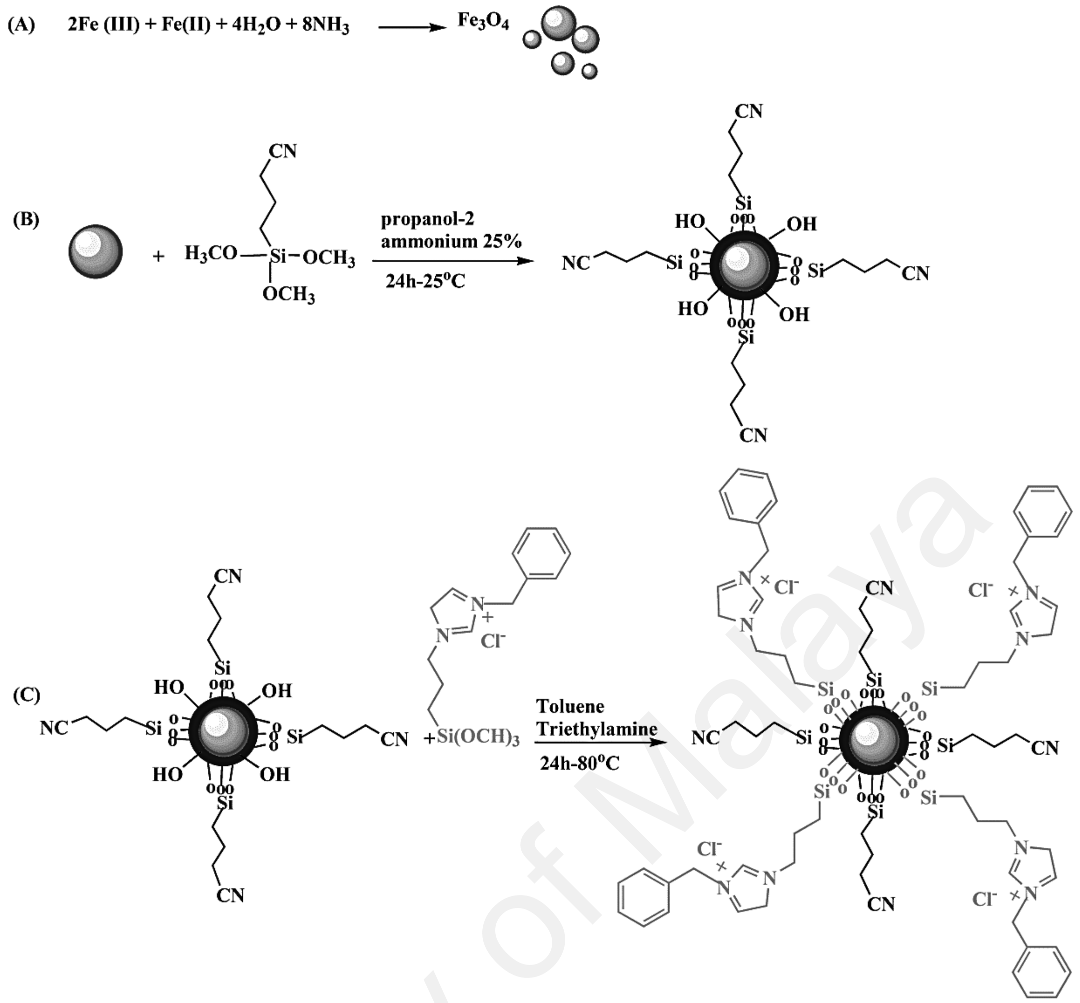


Figure 4.1: Schematic for the synthesis of (A) **MNP**, (B) **MNP@CN**, (C) **MNP@CN/IL**.

4.2.5 MSPE procedure

The MSPE method was proceed in two separate run for CPs and for PAHs as it is described in follow. The run MSPE method for CPs, 30 mg **MNP@CN/IL** was placed in a vial containing 50 mL of sample solution (0.5 ppm mixed solution) at pH 6, the mixture was mechanically stirred at room temperature for 10 min and then allowed to stand for 5 min under magnetic field separation. After discarding the sample solution, analytes were eluted from **MNP@CN/IL** with 1000 μL of methanol/acetic acid (1 %) and mechanically stirred for 10 min more, this step repeated twice. Then the eluent was collected and dried under a stream of nitrogen and then re-dissolved in 500 μL methanol. Finally, the re-dissolved solution was analysed by HPLC. While, the MSPE procedure for PAHs extraction was same as CPs extraction except; 10 mg adsorbent with 100 mL sample solution (0.1 ppm mixed solution) and 2500 µL dichloromethane (DCM) as desorption solvent. In this research, six important factors were studied to find the best performance of MSPE:

Various solvents were utilised as elution solvent for both CPs (methanol, methanol with 1 % acetic acid, acetonitrile) and PAHs (ethyl acetate, acetonitrile, dichloromethane and n-hexane). The elution solvent volume was studied in the range of 250 to 1500 μL for CPs and 750 – 3000 μL for PAHs. The effect of extraction time was studied between 1 – 20 min for CPs and 10 – 30 min for PAHs. The sample pH was studied between 2 – 10 for both CPs and PAHs. The proper pH was adjusted with 0.01 M HCl and 0.01 M NaOH using pH meter model Ella Instrument. The sample loading volume was studied between 15 to 100 mL for CPs and 15 – 150 mL for PAHs. Effect of sorbent mass was studied with addition of 10 – 40 mg of adsorbent for CPs and 5 – 20 mg of adsorbent for PAHs.

4.2.6 Method validation

4.2.6.1 Comparative study

For the purpose of MSPE performance comparison between newly synthesised **MNP@CN/IL** and available median adsorbents including the **MNP** and **MNP@CN** and **MNP@IL**, the same amount of optimum sorbent mass was used for sorbent comparison, this means 10 mg of adsorbent for PAHs and 30 mg for CPs analysis. The peak area value was used to show the comparison between adsorbents.

4.2.6.2 Real sample analysis

To identify the matrix effect of the optimised method, 4 μg L^{-1} and 100 μg L^{-1} of CPs and PAHs were spiked separately in the leachate and sludge from landfill site, Jeram, Kuala Selangor. The collected leachate was filtered by 110 mm filter paper, immediately after bringing to the laboratory. Then, the filtered samples were stored in the dark at 4 ^{o}C. Also, the sludge samples were dried in the room temperature. Then the samples were grinded and kept in the dark at 4 ^{o}C in glass bottle. Finally for the sample preparation, 1 g of sludge was weighted and placed in a 50 mL plastic centrifuge tube with 3 mL of methanol as extraction solvent and sonicated for 10 min. Then, the suspended sludge was kept in centrifuge at 3500 rpm for 5 min. Then the supernatant filtered through PTFE syringe filter (13 mm, 0.22 μm) and transferred to the volumetric flask and added standard analytes and diluted with ultra-pure water then proceed for magnetic solid phase extraction. The percent recovery (% R) was determined from the equation (3.2) in Section 3.3.5.1.

4.2.6.3 Linearity and precision

The linearity was studied with seven different concentration levels. The repeatability as relative standard deviation and precision of the developed method was evaluated by 5 variances with spiking level of 50 μgL^{-1} for CPs and 10 μgL^{-1} for PAHs mixture in ultra-purified water. Standard deviation (SD) and RSD were determined by same equations (3.3) and (3.4) introduced in Section 3.3.5.3.

4.2.6.4 Limit of detection (LOD) and Limit of quantification (LOQ)

The limit of detection (LOD) and the limit of quantification (LOQ) are two important factors in method validation that determined the lowest concentration of an analyte that can be reliably detected by an analytical procedure. The limit of detection and quantification were determined from the standard deviation of the blank ($\boldsymbol{\sigma}$) and slope of calibration curve (S) by using the same equation (3.5) and (3.6) introduced in Section 3.3.5.4.

4.3 Result and discussion

4.3.1 Characterization

4.3.1.1 FT-IR analysis

Comparative FT-IR spectral analysis for the confirmation of different functional groups in pure **MNP**, **MNP@CN** and newly **MNP@CN/IL** is represented in Figure 4.2. Sharp and strong Fe–O stretching vibration can be seen in **MNP** at around 640 cm^{-1} (Figure 4.2A), while following the cyano-functionalization and then modification with **IL** the Fe–O stretching peak intensity is comparatively decreased in case of **MNP@CN** and **MNP@CN/IL** (Figure 4.2B&C). The bands at 3440 cm^{-1} and 1648 cm^{-1} in **MNPs** are attributed to the O-H stretching and bending vibration of water molecule (physically adsorbed) respectively. The successful functionalization of **MNPs** with cyanopropyltriethoxysilane can be shown by the additional bands in **MNP@CN** (Figure 4.2B) at 2955, 2250 and 1160 cm^{-1} for C-H, cyano group (C≡N) and Si–O stretching respectively. As compared to the **MNP@CN**, the 1-benzyl-3-(trimethoxysilylpropyl) imidazolium modified magnetic nanocomposites **MNP@CN/IL** possessed some additional peaks at 3178, 1568, 1527, 1462, 1450 cm^{-1}. It can be seen that following the modification process the resultant **MNP@CN/IL** showed C-H (aromatic) stretching vibration at 3178 cm^{-1} , band at 1568 cm^{-1} represents the C=C of benzyl ring, while C=N stretching vibration of imidazolium ring can be predicted by band at 1450 cm^{-1}. In addition the presence of a strong cyano group (C≡N) stretching band at 2250 cm^{-1} also confirmed that incoming cyanopropyltriethoxysilane reacts with hydroxyl groups of **MNP@CN/IL**.

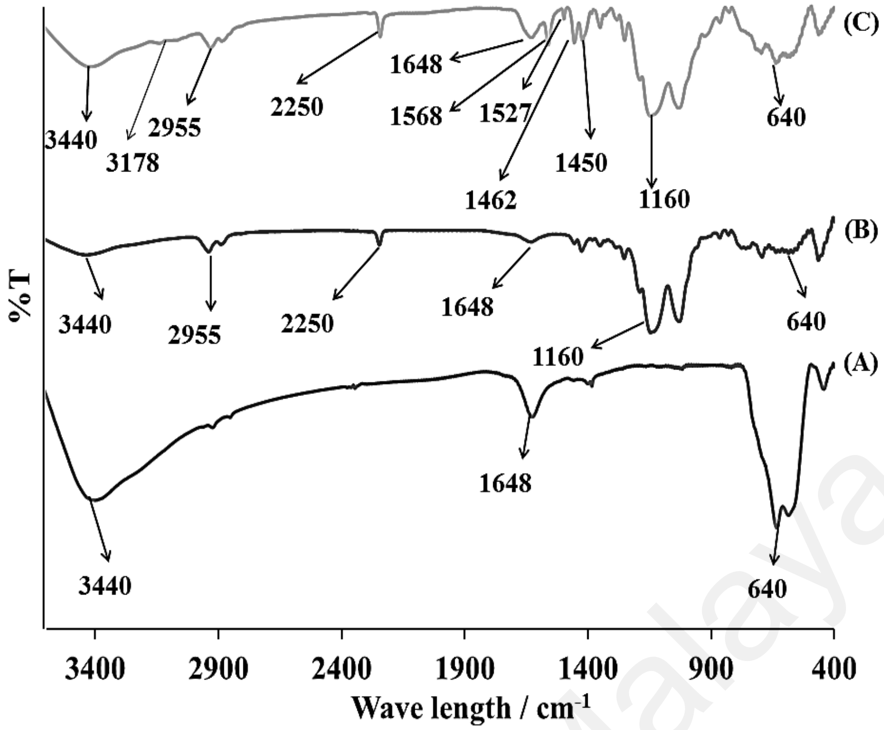


Figure 4.2: IR spectra of bare **MNP** (A), **MNP@CN** (B) and **MNP@CN/IL** (C).

4.3.1.2 XRD analysis

The crystalline profile of the **MNP**, **MNP@CN** and **MNP@CN/IL** were analysed using XRD and the X-ray diffraction profiles are shown in Figure 4.3, respectively. The characteristic peaks of **MNP** compliance with the standard Fe_3O_4 crystal XRD profile (JCPDS card number 19-0629) (Lu, *et al.*, 2014) The characteristic peaks at $2\theta = 30.25\,^{o}$, $35.74\,^{o}$, $43.44\,^{o}$, $53.65\,^{o}$, $57.37\,^{o}$ and $63.01\,^{o}$ where attributed to the (220), (311), (400), (422), (511) and (440) reflections, respectively. The same peaks were detected in **MNP@CN** and **MNP@CN/IL** which indicates that the magnetic crystalline profile was not changed during the modification process with CN and IL.

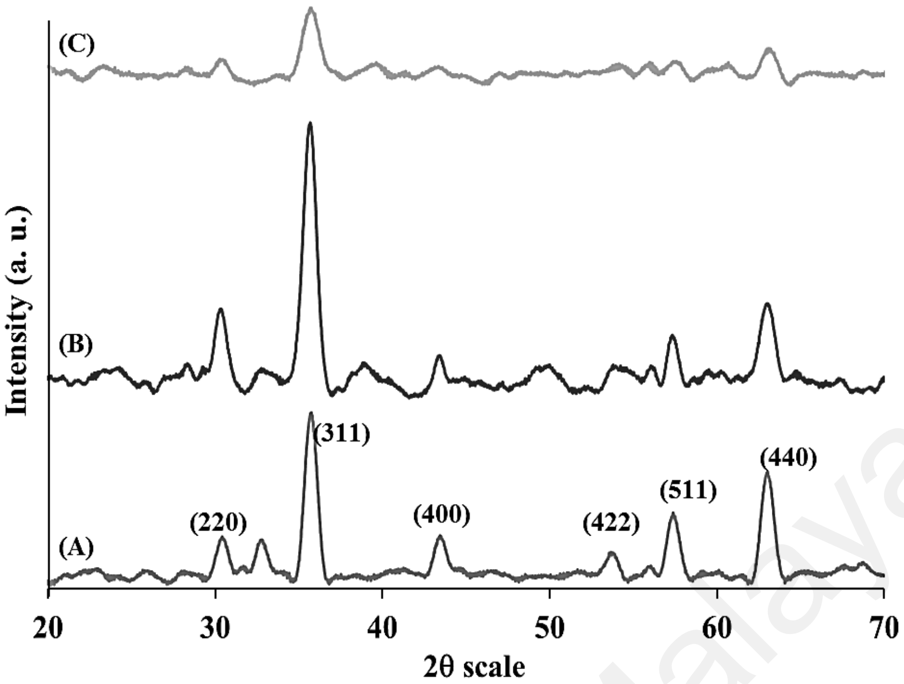
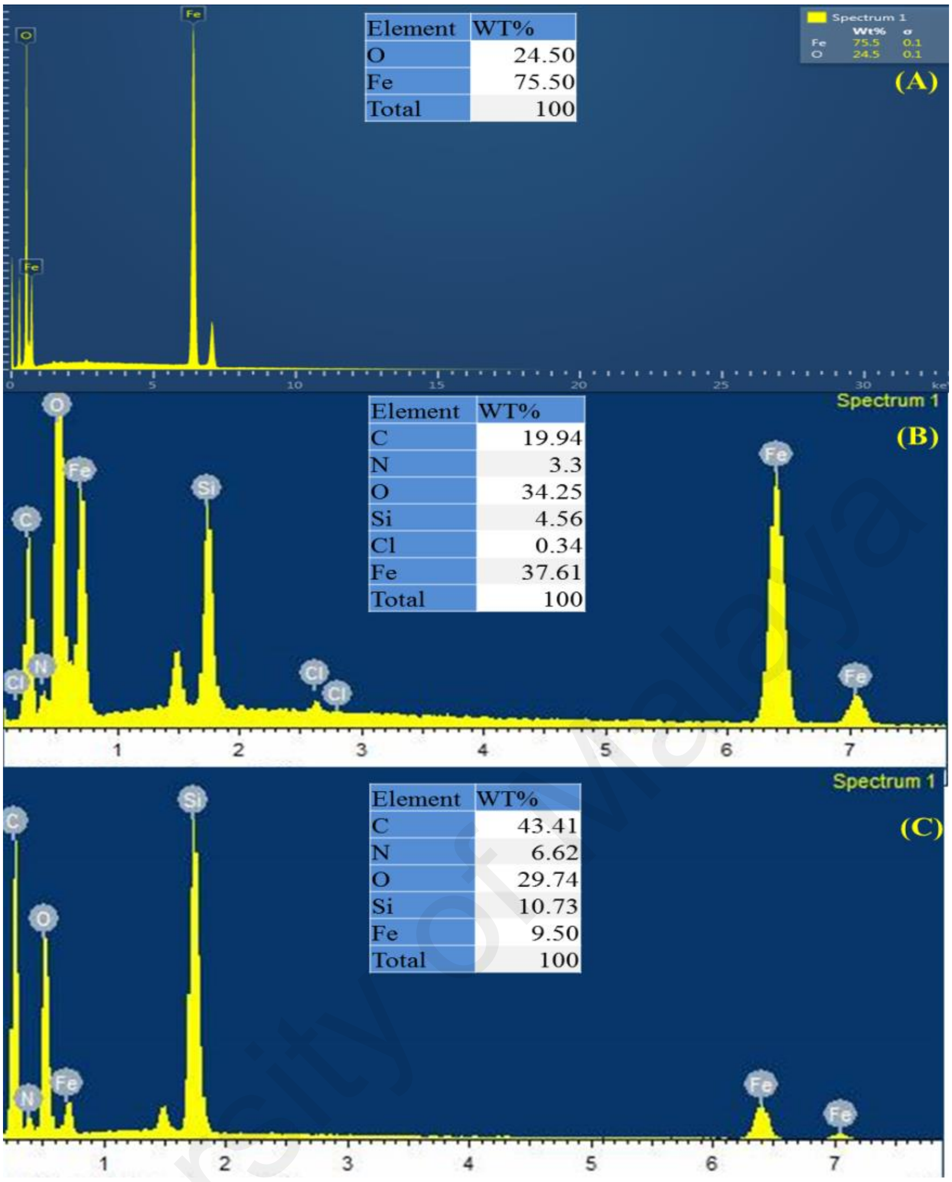


Figure 4.3: XRD profile of bare **MNP** (A), **MNP@CN** (B) and **MNP@CN/IL** (C).

4.3.1.3 Elemental analysis (EDX) and (CHNS)

The elemental composition of the magnetic nanocomposites was studied using EDX analysis as shown in Figure 4.4. The EDX results for MNP (Figure 4.4A) showed 24.50 % & 75.50 % of Fe and O respectively. Meanwhile following the modification process the results unambiguously showed the presence of (Si, N and C) in **MNP@CN** and **MNP@CN/IL**.

In addition, elemental analysis *i.e.*, CHNS results as represented in Table 4.1 also confirmed the successful coating of **BTMP-IM** and cyanopropyltriethoxysilane on surface of **MNP**. It is clear from the results that **MNP@CN/IL** contains 5.46 % of N and 47.56 % of C. The increase in N and C percentage is due to the attachment of **BTMP-IM.** The small amount of N % in **MNP** might be due to presence of ammonium in sample from preparation step.



Element	WT%
O	24.50
Fe	75.50
Total	100

Element	WT%
C	19.94
N	3.3
O	34.25
Si	4.56
Cl	0.34
Fe	37.61
Total	100

Element	WT%
C	43.41
N	6.62
O	29.74
Si	10.73
Fe	9.50
Total	100

Figure 4.4: EDX elemental composition of bare **MNP** (A), **MNP@CN** (B) and **MNP@CN/IL** (C).

Table 4.1: Elemental analysis of synthesis adsorbents by CHNS analyser

Sample	C (%)	H (%)	N (%)
MNP@CN/IL	47.56	4.03	5.46
MNP@CN	15.06	3.33	4.29
MNP	0	0.16	0.98

Elemental analysis was performed by Elemental analyser (Perkin Elmer CHNS).

4.3.1.4 Magnetic properties

Strong magnetization is of great importance for separation of target analytes through MSPE process. The magnetic behaviour of the **MNP**, **MNP@CN** and **MNP@CN/IL** were investigated by using vibration sample magnetometry (VSM) at room temperature. The hysteresis loops of nanoparticles are illustrated in Figure 4.5. The mass saturation magnetization (M_s) for bare **MNP**, **MNP@CN** and **MNP@CN/IL** were found 63.2 emug^{-1}, 19.8 emug^{-1} and 34.6 emug^{-1}, respectively. Figure 4.5B&C shows the value of M_s for modified adsorbents (**MNP@CN** and **MNP@CN/IL**) was reduced as compared **MNP** (Figure 4.5A). This importance indicates the coating of **MNP** with cyanopropyltriethoxysilane and IL which apparently causes a reduction in the magnetic strength. There was an increase in M_s value of **MNP@CN/IL** compared to **MNP@CN**. An additional stabilization of MNP core of **MNP@CN/IL** with IL through the electrostatic interaction provides a protection shell around the MNP core. Therefore, it prevents the aggregation of **MNP@CN/IL** and increases its magnetic properties (Janiak, 2014).

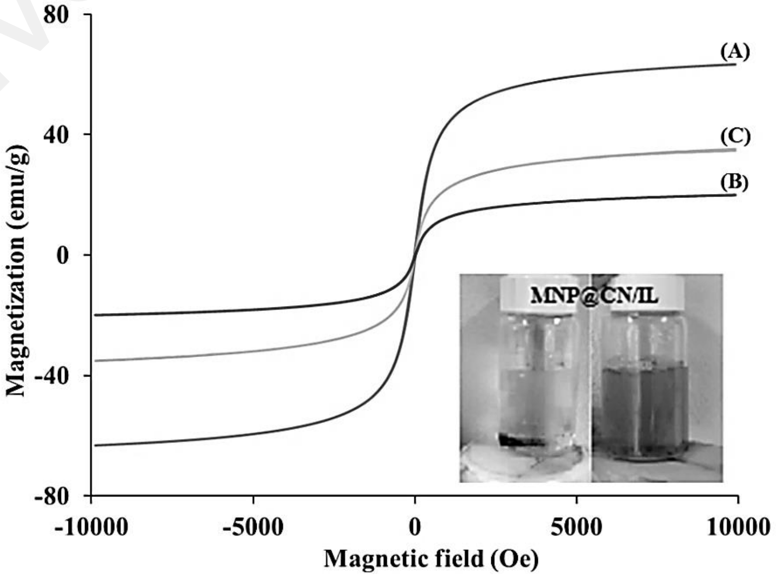


Figure 4.5: Hysteresis loop of bare **MNP** (A), **MNP@CN** (B) and **MNP@CN/IL** (C).

4.3.1.5 Thermal stability

The thermal stability of the synthesised **MNP**, **MNP@CN** and **MNP@CN/IL** can be accessed from Figure 4.6. MNP showed high thermal stability up to 900 °C with the mass loss of about 3 % (Figure 4.6A). In the case of **MNP@CN** (Figure 4.6B) and **MNP@CN/IL** (Figure 4.6C), approximately 1.7 % weight loss bellow 250 °C is due to loss of physically adsorbed organic volatiles and water molecules. The 32.4 % weight loss for **MNP@CN** (Figure 4.6C) between 250 °C and 900 °C is most probably due the combustion cyanopropyltriethoxysilane. The **MNP@CN/IL** (Figure 4.6C), the 24% weight loss between 240-630 °C corresponds to the thermal carbonization and the decomposition of organic groups such as IL combustion. Only 24.0 %, weight loss for **MNP@CN/IL** between 250 °C and 900 °C indicates that synthesized magnetic nanoparticles are highly thermally stable (Figure 4.6C).

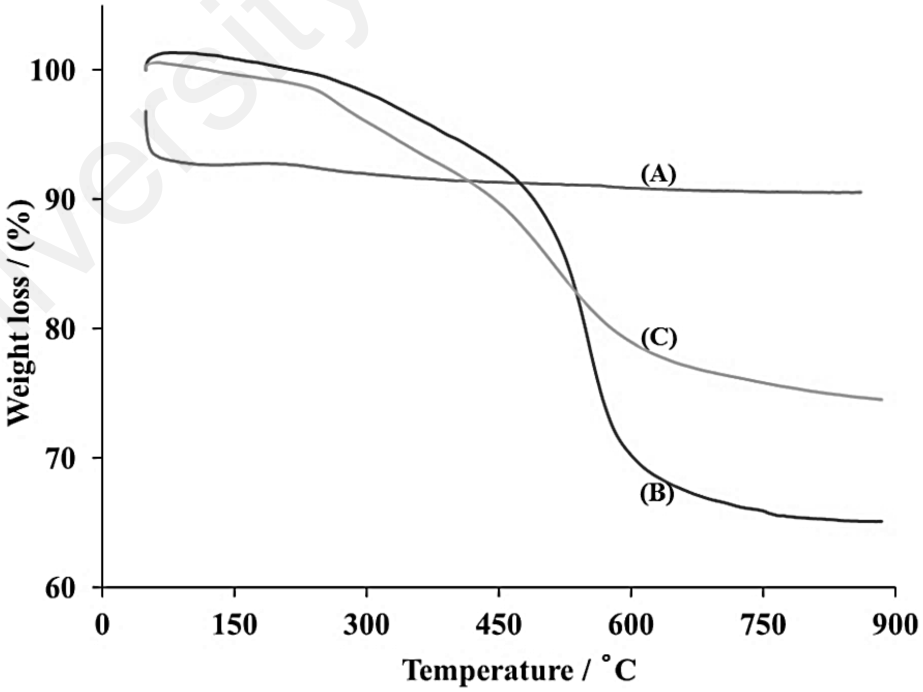


Figure 4.6: TGA curves of bare **MNP** (A), **MNP@CN** (B) and **MNP@CN/IL** (C).

4.3.1.6 TEM

The TEM images of the **MNP**, **MNP@CN** and **MNP@CN/IL** are demonstrated in Figure 4.7. The TEM image of **MNP** confirmed a spherical agglomerate morphology with average diameter of the bare particles around 11.90 nm. As it can be seen in Figure 4.7B, the average diameter of nanoparticles slightly increased to 14.90 nm with spherical agglomerate morphology after the modification of **MNP** using cyanopropyltriethoxysilane. Further coating on the surface of **MNP@CN** with IL produced nanoparticles with spherical morphology and well dispersed with average diameter of 16.60 nm as shown in Figure 4.7C.

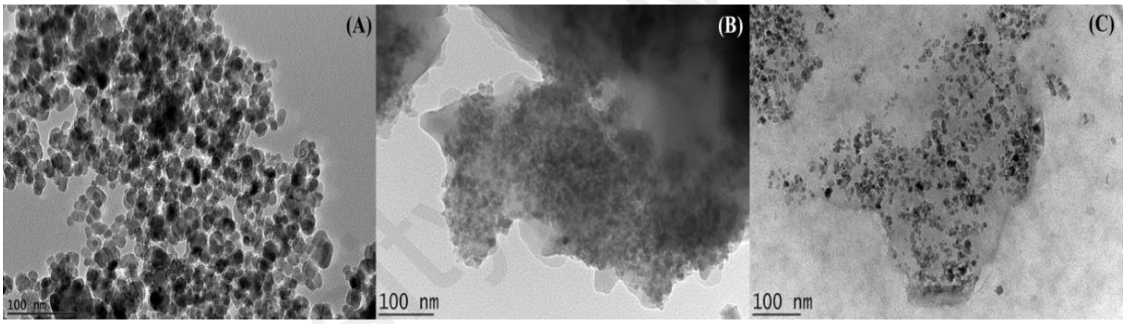


Figure 4.7: TEM image of bare **MNP** (A), **MNP@CN** (B) and **MNP@CN/IL** (C).

4.3.2 MSPE optimization

The MSPE method development including optimization study, method validation and real sample application was proceed in two separate run, firstly for CPs and then for PAHs. Several experimental parameters, such as sample volume, elution solvent and its volume, sample pH, extraction time and sorbent mass, were optimized to achieve the highest extraction efficiency of CPs and PAHs using **MNP@CN/IL**. The optimizations were performed by using the spiked level of 0.5 ppm of mixture solution of CPs and 0.1 ppm of mixture solution of PAHs. To evaluate the influence of each parameter on extraction efficiency of sorbent to the target analytes, the peak area was used.

4.3.2.1 Elution solvent

Elution solvent is an important parameter in extraction methods, since it directly affect the sensitivity and efficiency (Ibrahim, *et al.*, 2012). The effect of desorption solvent on MSPE performance has been investigated using methanol, methanol containing 1 % acetic acid and acetonitrile. As it is obvious from the desorption results (Figure 4.8A) of CPs from the **MNP@CN/IL** that addition of 1 % (as ratio with methanol) acetic acid to methanol increased the desorption ability toward CPs. This might be due to high competition of acetic acid with CPs to form hydrogen bonds with cyano group on the surface of **MNP@CN/IL**. In order to obtain a high enrichment factor the elution solvent volume (250 to 1500 µL of methanol/acetic acid 1 %) was investigated (Figure 4.8B). By increasing the volume (250 to 1500 µL), the enrichment factor/ peak area ratio increased slightly and it attained a maximum at 1000 µL of elution solvent volume. Beyond the 1000 µL of elution solvent volume there is no significant change in the peak area was observed, consequently 1000 µL was chosen as the optimized elution solvent volume for further analysis. The effect of elution solvent in case of PAHs has been examined by using DCM, acetonitrile, n-hexane and ethyl acetate as eluting solvents. Obtained results (Figure 4.8C), indicated that DCM is the best eluting solvent and satisfactory results for all the selected FLO, FLU, PYR, CRY and BaP were achieved by using DCM. The high peak area/desorption of PAHs in DCM might be due to hydrophobic nature of both *i.e.*, selected analytes (PAHs) and solvent (DCM) which increase the hydrophobic interaction. Consequently, DCM was selected to be the most suitable eluting solvent for subsequent experiments. The influence of eluting solvent volume was tested in the range of 750 to 3000 μL of DCM, Figure 8D. The extraction improves slightly with the increase of the eluent volume from 750 to 2500 μL; but when eluent volume increased more, extraction efficiency decreased. Satisfactory, extraction efficiency of PAHs were obtained by using the 2500 μL of DCM.

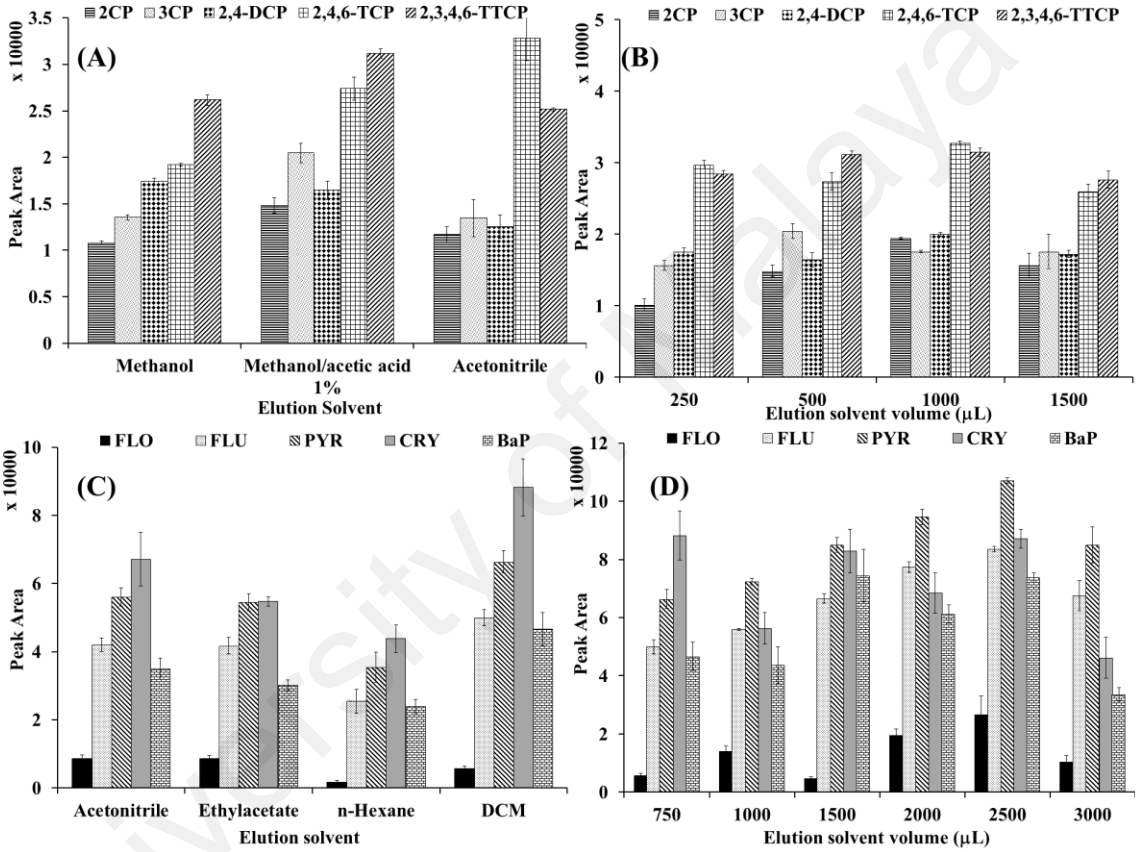


Figure 4.8: MSPE method development study: A) Elution solvent CPs, B) Elution solvent volume (μL) CPs, C) Elution solvent PAHs, D) Elution solvent volume (μL) PAHs.

4.3.2.2 Extraction time

The extraction time is also the key parameter for an effective MSPE. To optimize the influence of extraction time for the adsorption of CPs and PAHs onto **MNP@CN/IL** trials ranging from 1 to 30 min were conducted.(Figure 4.9A&B). The recovery of selected CPs and PAHs rapidly increased during the first 10 min and there is no significant effect beyond the 10 min extraction time. Since, highest peak area ratio was observed at 10 min of extraction time. Consequently, it was selected that 10 min of contact time is enough for the isolation of targeted analytes (CPs and PAHs) by newly **MNP@CN/IL**. Thus 10 min of extraction time is chosen for the subsequent experiments.

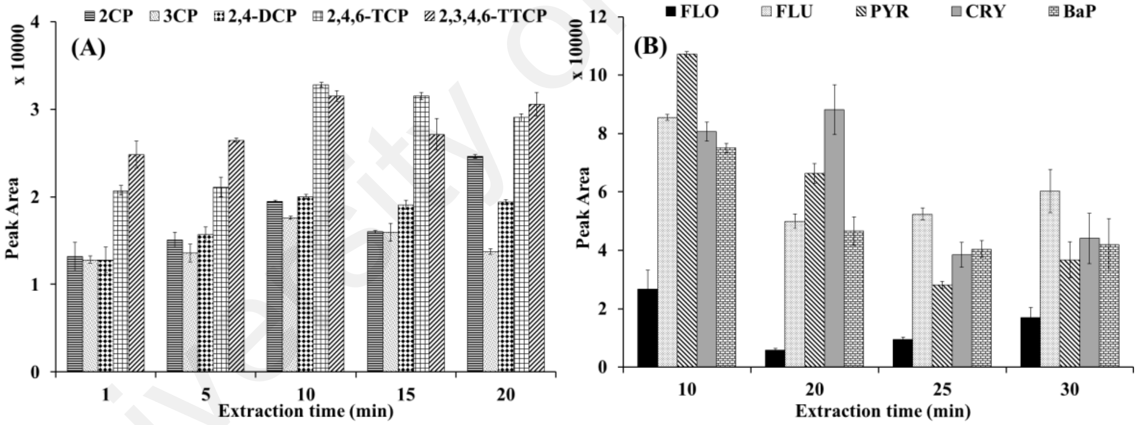


Figure 4.9: Effect of extraction time (min): A) CPs and B) PAHs.

4.3.2.3 Sample pH

pH is also one of the crucial parameters and play an essential role during the adsorption process. Because it affects both the chemistry of analytes as well as the dissociation of functional groups on the active sites of the adsorbent. Consequently, effect of pH on the adsorption of selected CPs and PAHs onto newly **MNP@CN/IL** was scrutinized at different pHs (*i.e.*, 2, 4, 6. 8 and 10). It can be seen that (Figure 4.10A) the peak area of the selected CPs in acidic condition (pH=2-6) was higher as compared to basic media (pH=8-10). The high peak area for CPs at pH 2-6 can be explained on the basis of pK_a values that are in the range 9.12 to 5.62. The chlorophenols are deprotonated when the pH is higher than their pK_a, therefore to avoid ionization of CPs, it is necessary to keep pH lower than pK_a (Raoov, *et al.*, 2014). While in case of PAHs (Figure 4.10B), the extraction efficiency of PAHs increased by increasing the pH from 2 to 6 and maximum extraction (peak area) was achieved at slightly acidic pH (pH=6). At basic pH, decrease in extraction efficiency of CPs might be due to the repulsion between negative charged surface of adsorbent and selected CPs. Because, at higher pH (pH 8 &10), both **MNP@CN/IL** and CPs becomes deprotonated (anionic form) and there may be strong repulsive forces between the anionic sites of both *i.e.*, adsorbent as well as targeted analytes.

In contrast, the low recoveries for all PAHs were observed when pH is in slightly acidic medium. This phenomenon may be explained from the change of charge species and density on the surface of adsorbent **(MNP@CN/IL)**. At acidic condition, there is huge amount of protons available due to protonation of remaining hydroxyl groups from **MNPs** surface and may saturate the adsorbent sites making the surface of the adsorbent more cationic. While at basic condition the deprotonation of remaining hydroxyl groups from **MNPs** making the surface of the adsorbent more anionic. These changes reduce the hydrophobicity of **MNP@CN/IL** which effects the hydrophobic interaction between PAHs and **MNP@CN/IL**.

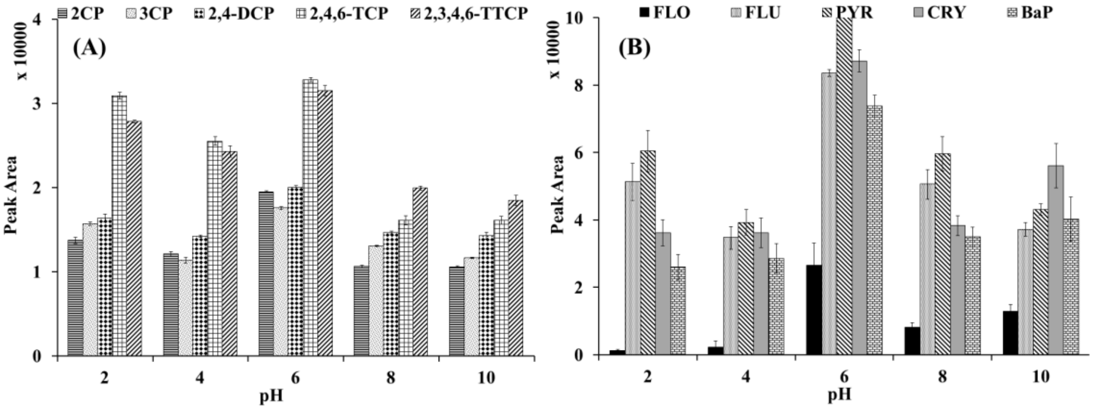


Figure 4.10: Effect of pH: A) CPs and B) PAHs.

4.3.2.4 Sample loading volume

In order to obtain a quantitative extraction recovery of CPs and PAHs the sample volume was investigated in the range of 15 to 150 mL (Figure 4.11A&B). By increasing the volume (15–50 mL), the extraction recoveries for selected CPs increased and peak area ratio attained a maximum at 50 mL of sample loading volume. The peak area improved by increasing the sample loading volume up to 50 mL for the selected CPs and beyond the 50 mL additional of the solution volume did not further affect the extraction efficiency. While in case of PAHs the 100 mL of sample loading volume showed highest peak area for all the selected PAHs. Consequently, for the significant extraction of PAHs 100 mL of sample loading volume were optimized and used for subsequent experiments.

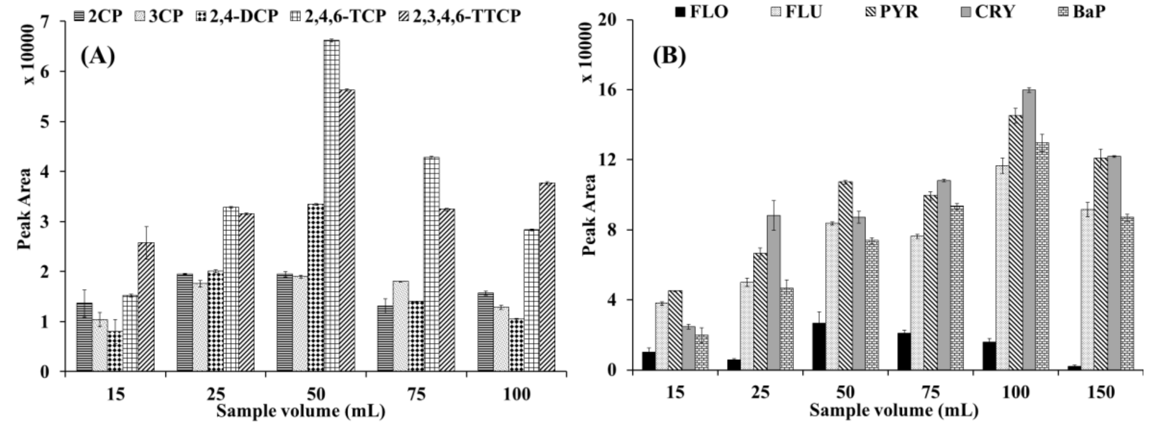


Figure 4.11: Effect of sample loading volume (mL): A) CPs and B) PAHs.

4.3.2.5 Sorbent mass

The weight of the adsorbent is another important factor for determining the quantitative recovery of a target analyte. For this reason, the weight of **MNP@CN/IL** was optimized within the range of 5 – 40 mg for both selected CPs and PAHs. Based on the results shown in Figure 4.12A, quantitative peak area of selected CPs were obtained using 30 mg of new (**MNP@CN/IL**) magnetic adsorbent; above 30 mg of adsorbent, the weight peak area remained nearly constant. In case of PAHs the acquired results (Figure 4.12B) showed that the peak area for all the selected PAHs increased dramatically by increasing the adsorbent dosage from 5 to 10 mg and there is no further improvement in peak area beyond 10 mg of dosage. Therefore, 30 & 10 mg of adsorbent dosage was selected for the effective adsorption of CPs and PAHs, respectively in subsequent experiments. Looking through the results of sample volume and mass dosage optimization shows that the optimum ratio of sample volume to mass dosage is 100 mL per 10 mg for MSPE in this study.

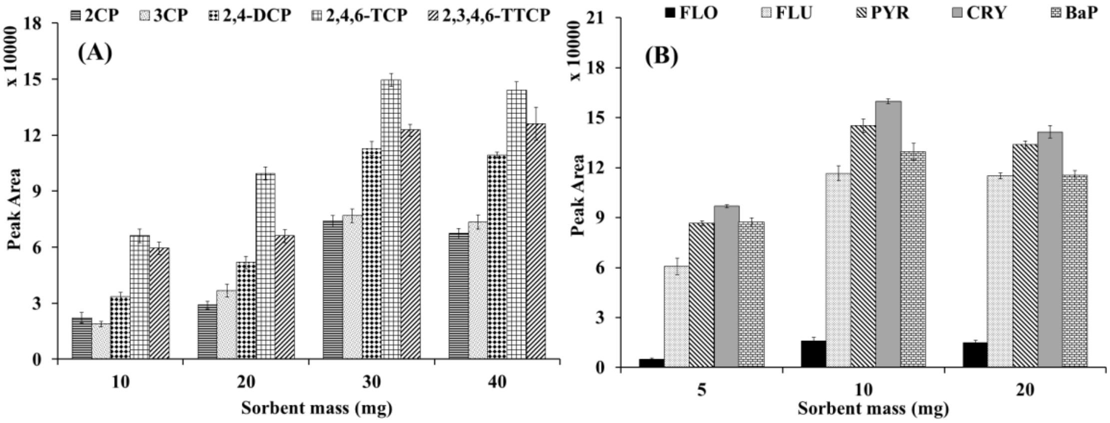


Figure 4.12: Effect of sorbent mass (mg): A) CPs and B) PAHs.

4.3.3 Method validation

The analytical performance of the proposed magnetic solid phase extraction MSPE method based on **MNP@CN/IL** was validated using different analytical parameters such as linearity, limit of detection (LOD), limit of quantification (LOQ) and precision (RSD%) and results are summarized in Table 4.2. MSPE was carried out using the optimum extraction conditions. Each concentration were triplicate and the mean value of peak area was taken for plotting calibration curve at optimum condition (30 mg adsorbent, 50 mL sample, 10 min extraction time, 1000 μL methanol/acetic acid (1%) as desorption solvent and pH 6 for CPs) and (10 mg adsorbent, 100 mL sample, 10 min extraction time, twice 2500 DCM as desorption solvent and pH 6 for PAHs).The linearity was studied at seven concentration levels in the range of (3 – 100 μg L^{-1} for CPs) and (0.1 – 100 μg L^{-1} for PAHs) with coefficient of determination (r^2)>0.99. The LOD and the LOQ for MSPE extraction using **MNP@CN/IL** adsorbent for CPs (0.35 – 0.67; 1.16 – 2.25 μg L^{-1}) and for PAHs (0.4 – 0.59; 1.35 – 1.98 μg L^{-1}) were lower in comparison with **MNP**, **MNP@CN** and **MNP@IL**. The precision of optimum method was obtained using 5 replicate for intra-day and 3 replicate during 3 days for inter-day at the concentration of 50 μg L^{-1} of CPs mixture solution and 10 μg L^{-1} of PAHs. The extraction performance of **MNP@CN/IL** with the mean value of peak area indicated highest extraction efficiency in contrast with the median adsorbents *i.e.*, **MNP**, **MNP@CN** and **MNP@IL** (Figure 4.13). Obtained results (Table 4.2) demonstrate the proposed method to be precise with %RSD>4.5 for both CPs and PAHs batch which indicates good repeatability of **MNP@CN/IL**. The lowest value of LOD and LOQ and highest extraction efficiency of **MNP@CN/IL** compare to median adsorbents justifies the increased sensitivity, affinity and capacity of adsorbent towards the CPs and PAHs by formation of a strong π–π interaction between the imidazolium/benzyl rings of IL with aromatic core of CPs and PAHs as well as hydrogen bonding between chlorine/hydroxyl groups of CPs with cyano group. Also, the proposed method provided high enrichment factors of 100 for CPs and 200 for PAHs.

Table 4.2: Analytical figures of merits of MNP@CN/IL, MNP@CN, MNP@IL and MNP in MSPE: repeatability (%RSDs), LOD (μg L^{-1}) and LOQ (μg L^{-1}) of CPs and PAHs.

	MNP			MNP@CN			MNP@IL			MNP@CN/IL				
											RSDs			
Analyte	RSDs	LOD	LOQ	RSDs	LOD	LOQ	RSDs	LOD	LOQ	r^2	Intra (n = 5)	Inter (n = 3)	LOD	LOQ
2-CP	2.07	8.86	29.53	4.00	8.14	27.15	4.72	9.17	30.56	0.9942	4.46	1.70	0.44	1.47
3-CP	3.51	9.22	30.73	4.74	3.24	10.81	2.23	6.6	21.97	0.9941	2.24	2.17	0.67	2.25
2,4-DCP	3.87	6.71	22.38	3.96	2.75	9.18	2.61	2.67	8.91	0.9904	2.63	0.60	0.35	1.16
2,4,6-TCP	3.73	7.04	23.48	4.64	2.9	9.68	3.64	2.71	9.05	0.9938	3.05	0.31	0.45	1.5
2,3,4,6-TTCP	3.98	8.75	29.18	4.88	2.67	8.9	2.38	2.47	8.24	0.9951	2.22	1.01	0.46	1.54
FLO	3.56	8.2	27.33	4.91	1.09	3.64	3.22	0.87	2.9	0.9912	1.71	0.73	0.59	1.98
FLU	3.01	4.14	13.8	5.07	1.31	4.36	3.09	0.86	2.88	0.9956	2.49	1.33	0.43	1.42
PYR	4.59	3.12	10.39	5.00	1.31	4.36	2.21	1.66	5.54	0.9967	1.81	1.17	0.48	1.61
CRY	4.01	5.13	17.09	4.14	1.03	3.43	4.68	1.95	6.52	0.9923	0.84	0.46	0.40	1.35
BaP	2.63	7.77	25.89	3.75	0.68	2.27	4.39	1.17	3.91	0.9907	0.58	0.65	0.40	1.35

Linearity ranges: for all adsorbents in CPs study was between 3 – 100 μg L^{-1}, in PAHs study: (0.1 – 100 μg L^{-1}).

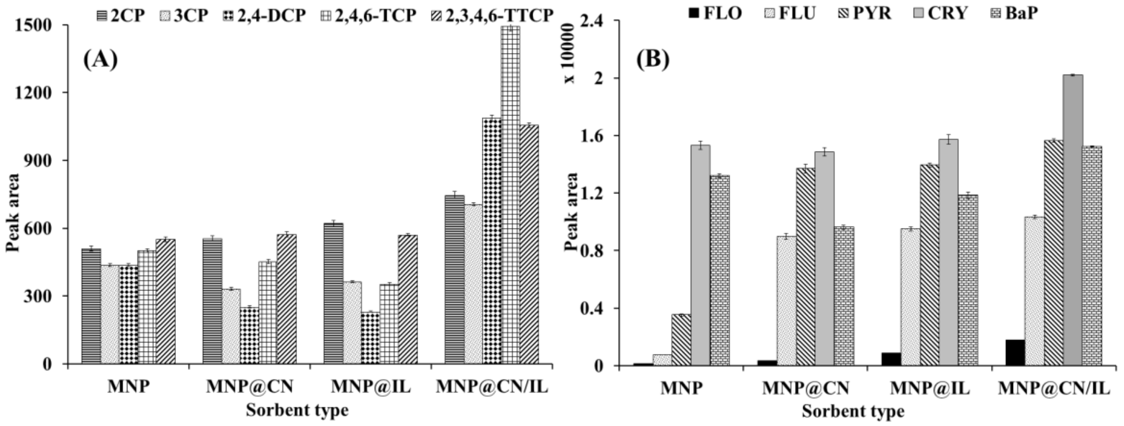


Figure 4.13: Comparison of the performance of **MNP@CN/IL** with **MNP**, **MNP@CN** and **MNP@IL** for the MSPE of A) CPs and B) PAHs.

4.3.4 Real sample analysis

In order to assess the field application of the proposed MSPE method, selected CPs and PAHs were isolated from environmental samples *i.e.*, leachate and sludge from landfill site at concentration of 100 μg L^{-1} and 4 μg L^{-1}. Table 4.3 shows that the percent recovery for CPs for leachate and sludge were satisfactory between 80.67 – 111.8 % and 103.5 – 112.7 % and their repeatability were in the range of 1.26 – 4.89 % and 0.92 – 4.51 %, respectively. While, the percent recovery of PAHs in leachate was in the range of 89.50 – 110.2 % with RSDs 1.35 – 4.49 % and in sludge were in the range of 93.80 – 107.5 % with RSDs 1.16 – 4.12 %. The typical chromatogram of blank analysis and spiked leachate and sludge are illustrated in Figure 4.14.

Table 4.3: The recovery and %RSDs (n=5) of CPs and PAHs in the environmental samples (leachate and sludge) with a spiked concentration of 100 and 4 μg L^{-1}.

	Leachate		**Sludge**	
Analyte	Recovery (RSDs)% 100 μg L^{-1}	Recovery (RSDs)% 4 μg L^{-1}	Recovery (RSDs)% 100 μg L^{-1}	Recovery (RSDs)% 4 μg L^{-1}
2-CP	80.67 (4.69)	80.62 (3.90)	104.4 (2.58)	105.5 (2.59)
3-CP	111.8 (3.43)	111.5 (4.65)	112.6 (3.24)	108.1 (3.67)
2,4-DCP	90.75 (3.16)	106.0 (4.89)	109.0 (0.92)	110.6 (2.16)
2,4,6-TCP	94.75 (1.80)	100.8 (1.43)	112.7 (2.09)	112.5 (2.50)
2,3,4,6-TTCP	106.4 (2.26)	99.37 (1.26)	106.8 (4.51)	103.5 (3.24)
FLO	107.8 (2.30)	107.0 (4.49)	99.33 (1.16)	100.8 (2.86)
FLU	99.20 (3.37)	89.50 (3.64)	105.5 (3.98)	105 (4.12)
PYR	110.2 (1.35)	108.0 (4.43)	93.80 (2.77)	107.5 (2.32)
CRY	107.0 (2.28)	92.50 (2.70)	102.6 (1.49)	102.5 (2.43)
BaP	102.3 (1.49)	94.00 (2.85)	104.3 (1.99)	104.2 (3.66)

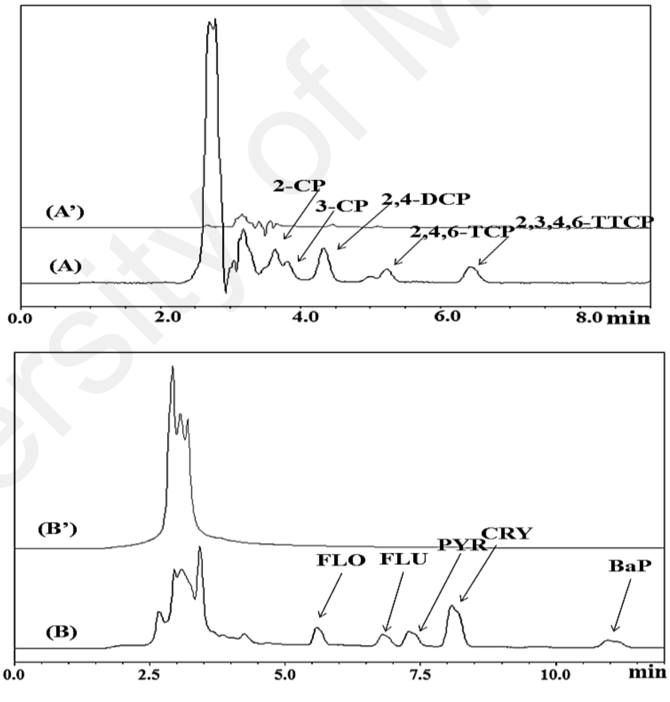


Figure 4.14: Chromatograms of leachate using **MNP@CN/IL** as the MSPE adsorbent A) spiked with CPs of 4 μg L^{-1},A') unspiked sludge, B) spiked with PAHs of 4 μ gL^{-1} and B') unspiked leachate.

4.3.5 Comparison of MNP@CN/IL with previously reported adsorbents

The newly proposed magnetic solid phase extraction MSPE method based on **MNP@CN/IL** was compared with the previously reported adsorbents for the extraction/determination of CPs and PAHs from aqueous environment (Table 4.4). The results of previous studies has shown the applied MSPE methods were used comparably higher mass sorbent than current study. The current study had higher percent recovery with better RSDs value and in some cases provided lower LOD value. Also, the applied methods in previous studies were capable of extracting either CPs or PAHs, while the current method has proved that the **MNP@CN/IL** is capable of extracting both CPs and PAHs. In overall, the results revealed that the newly proposed MSPE method based on **MNP@CN/IL** as a rapid, reliable and highly efficient method for the preconcentration/extraction of CPs and PAHs from environmental samples with low LOD and RSD values with good percent recoveries as compared to the many other reported materials (Table 4.4).

Table 4.4: The comparison performance data of proposed MSPE method using **MNP@CN/IL** with other methods for extraction of CPs and PAHs in water samples.

Sample	Technique/ Adsorbent	Adsorbent mass (mg)	Recovery %	RSDs%	LOD(μgL^{-1})	Ref.
CPs	MSPE-HPLC-UV/ CTAB-MNP	60	83-98	<5.9	0.11-0.15	(Li, Zhao, *et al.*, 2008)
CPs	MSPE-HPLC-UV/ CZNC	-	93-102	<10.2	0.1-2	(Alizadeh, 2016)
CPs	MSPE-HPLC-UV/ MNP-IL	100	70.3-88.8	<6.0	0.2-0.35	(Yang, *et al.*, 2011)
CPs	**MSPE-HPLC-DAD/ MNP@CN/IL**	**30**	**80.67-112.7**	**<4.89**	**0.35-0.67**	**This study**
PAHs	MSPE-HPLC-UV/ Fe_3O_4@AuNPs	100	63.8-110.7	<5.4	0.26-0.52	(Li, *et al.*, 2014)
PAHs	HPLC-FLD/ MNP-C18	50	35-99	<10	0.8-36	(Liu, *et al.*, 2009)
PAHs	GC-MS/ Fe_3O_4-IL	-	75-102	<8.9	0.04-1.11	(Galan-Cano, *et al.*, 2013)
PAHs	**MSPE-HPLC-DAD/ MNP@CN/IL**	**10**	**89.50-110.2**	**<4.49**	**0.40-0.59**	**This study**

4.4 Conclusion

In summary, the new cyano-ionic liquid functionalized magnetic nanoparticle (**MNP@CN/IL)** was successfully synthesised with good magnetic properties and used as a new adsorbent in magnetic solid phase extraction (MSPE) for the simple, fast and efficient preconcentration of trace CPs and PAHs from environmental samples. The MSPE parameters affecting the extraction/preconcentration of CPs and PAHs were optimized and the results showed that the proposed MSPE method has acceptable percent recovery and repeatability for CPs and PAHs in environmental samples. Therefore, it was conducted that the presences of cyano group of cyanopropylsiloxanes and benzyl group of IL in new magnetic solid-phase extractor (**MNP@CN/IL**), significantly contributed and increased the adsorption capability for CPs and PAHs.

CHAPTER 5: CONCLUSIONS AND FUTURE DIRECTIONS

5.1 Conclusion

Two new cyano group- ionic liquid functionalized hybrid materials as new adsorbents synthesised in order to enhance extraction capability toward aromatic moieties. The cyanopropyltriethoxysilane and 1-benzyl-3-(trimethoxysilylpropyl)imidazolium chloride ionic liquid (**BTMP-IM**) were applied in two different inorganic solid state support. Firstly, the characterization results clarified the formation of **Si-Ti@CN/IL** via sol-gel acidic condition through immobilization of 1-benzyl-3-(trimethoxysilylpropyl)imidazolium on the surface of cyano functionalized silica-titania mixed oxide and **MNP@CN/IL** via sol-gel polymerization of cyanopropyltriethoxysilane and 1-benzyl-3-(trimethoxysilylpropyl)imidazolium on the surface of magnetic nano-particles with good magnetic properties.

Secondly, the LOD and LOQ performance of **Si-Ti@CN/IL** and **MNP@CN/IL** was compared with median adsorbents and exhibited low detection which indicated their high sensitivity towards aromatic moieties. The successful application study of **Si-Ti@CN/IL** as a new SPE adsorbent and **MNP@CN/IL** as a new MSPE adsorbent, on real samples indicated an effective option for the analysis of aromatic moieties in aqueous environmental samples. Higher recoveries were achieved with both adsorbents compared to other median adsorbents due to combination of cyano group and ionic liquid on the surface of solid state which provide imparting π–π interactions between the adsorbent and benzyl rings in the aromatic moieties, in addition, formation of hydrogen bonds through unshared electron pair of cyano groups with target analytes.

Finally, the results shows both methods of SPE and MSPE had good applicability of adsorbent which is the combination of cyano group and ionic liquid on the back bone of silica-titania mixed oxide and magnetic nanoparticle. From the observed result, it is concluded that the MSPE is a fast and simple method while SPE is more laborious method, regarding to cartridge packing and controlling the flow rate during the process. Next, there was less sorbent mass needed for MSPE (10 & 30 mg) in contrast with SPE (100 mg). The enrichment factor in MSPE is higher (100 for CPs and 200 for PAHs) in compare with SPE (20 for CPs). The LOD/LOQ study shows MSPE provides lower values (0.35 - 0.67; 1.16 – 2.25 μg L^{-1} for CPs) and (0.40 - 0.59; 1.35 – 1.98 μg L^{-1} for PAHs) in comparison with SPE (0.83 - 0.95; 2.77 - 3.17 μg L^{-1} for CPs), Therefore, MSPE is a more sensitive method.

5.2 Future directions

In this study, due to our availability, we have investigated the extraction capability of aromatic moieties, while it is expected the adsorbents might be capable of extracting various compounds. Therefore, a further study on application of both prepared adsorbents is needed with other organic moieties. Furthermore, the cationic part of imidazolium-based ionic liquid plays a very important role in maintain and control the properties of the polymers. Thus, it would be interesting to study the effects of other groups at cationic part of the ionic liquids in structure of prepared adsorbents. Meanwhile, the effect of various anions is not included in this study, maintaining the anions could improve the selectivity of the adsorbents. Therefore, another future direction could be on study of effects of anions on adsorbents.

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LIST OF PUBLICATIONS AND PRESENTATIONS

Shabnam Bakhshaei, Muhammad Afzal Kamboh, Hamid Rashidi Nodeh, Sharifuddin Md Zain, Siti Khalijah Mahmad Rozi, Sharifah Mohamad, "Magnetic solid phase extraction of polycyclic aromatic hydrocarbons and chlorophenols based on cyano-ionic liquid functionalized magnetic nanoparticles and their determination by HPLC-DAD ", RSC Advances (2016): 6, 77047-77058.

Shabnam Bakhshaei, Muhammad Afzal Kamboh, Sharifah Mohamad, Sharifuddin Md Zain, Azman Ma'amor, "A novel cyano functionalized silica-titania oxide sol–gel based ionic liquid for the extraction of hazardous chlorophenols from aqueous environment", RSC Advances (2016): 6, 49358-49369.

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