AN INVESTIGATION ON THE USE OF IONIC LIQUID LOADED MAGNETIC NANOPARTICLE GRAFTED β-CYCLODEXTRIN POLYMER FOR THE EXTRACTION OF PARABENS

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by

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LIST OF ABBREVIATIONS

ArP	Benzyl paraben
As V	Arsenic V
BET	Brunauer-Emmett-Teller
BP	Butyl paraben
CAM	Citric acid monohydrate
CDs	Cyclodextrins
CHN	Carbon, hydrogen and nitrogen analyzer
EP	Ethyl paraben
EPC	Epichlorohydrine
FT-IR	Fourier transform infrared spectroscopy
GC-PID	Gas chromatography with photoionization detection
GC-FID	Gas chromatography with flame ionization detection
HDI	Hexamethylene diisocyanate
HPLC-DAD	High-performance liquid chromatography with diode array detection
HPLC-UV	High-performance liquid chromatography with ultraviolet detection
HPLC-ED	High-performance liquid chromatography with electrochemical detection
HPLC-C-CAD	High-performance liquid chromatography with charged aerosol detection
HPLC-MS/MS	High-performance liquid chromatography with mass spectroscopy detection
ILs	Ionic liquids
IL-MNP-βCD-TDI	Ionic liquid loaded Magnetic nanoparticles grafted beta cyclodextrins polymer (toluene-2,4-diisocyanate)
LOD	Limit of detection
LOQ	Limit of quantification
MFCNT	Metal-filled carbon nanotubes
MNPs	Magnetic nanoparticles
MNP-βCD-TDI	Magnetic nanoparticles grafted beta cyclodextrin polymer (toluene-2,4-diisocyanate)

MP	Methyl paraben
MSPE	Magnetic solid phase extraction
ND	Not detected
OPA	Octadecylphosphonic acid
PANI	Polyaniline
PP	Propyl paraben
P3TArH	Poly(phenyl-(4-(6-thiophen-3-yl-hexyloxy)-benzylidene)-amine)
RSD	Relative standard deviation
RTILs	Room Temperature Ionic Liquids
SEM	Scanning electronic microscope
SiO_2/G	Silica grapheme
SiO_2/C_{18}	C_{18}-functionalized mesoporous silica
TDI	Toluene diisocyanate
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis
UPLC-DAD	Ultra-performance liquid chromatography with diode array detection
VSM	Vibrating sample magnetometer
XRD	X-ray diffractometer
A	Absorbance of targeted analyte at each βCD concentration
Å	Amstrong
α	The initial sorption rate
α-CD	Alpha cyclodextrins
b_T	Temkin constant related to the heat adsorption
β	The rate of adsorption
β-CD	Beta cyclodextrins
βCD-TDI	Beta cyclodextrins polymer
C	Intercept
C_o	The initial adsorbate capacity at equilibrium
C_e	The equilibrium concentration of the adsorbate
$[CD]$	The concentration of βCD
$[C_4MIM][PF_6]$	1-butyl-3-methylimidazolium hexafluorophosphate

$[C_4MIM][BF_6]$	1-butyl-3-methylimidazolium tetrafluoroborate
$[G]_o$	The initial concentration of targeted analyte
h	Initial adsorption rate
K	The intraparticle diffusion rate constant
K_d	Equilibrium constant
K_F	Freundlich constant that related to multilayer adsorption capacity
K_T	The equilibrium binding constant corresponding to the maximum binding energy
k_1	The rate constant of pseudo first order adsorption
k_2	The rate constant of pseudo second order adsorption
N	The number of data points
n_F	Obtained from the deviation of the linear adsorption
q_{cal}	Calculated adsorption capacities
q_e	The amount of analytes adsorbed on the synthesized adsorbent at equilibrium
q_{exp}	Experimental adsorption capacities
q_m	Langmuir constant related to the adsorption capacity
R	Universal gas constant
R_L	Dimensionless separation factor
R^2	Correlation of determination
$\frac{1}{n_F}$	The heterogeneity factor
ΔG^o	Gibb's energy change
ΔH^o	Enthalpy change
ΔS^o	Entropy change
ε	Molar absorptivity
^1H NMR	Proton Nuclear Magnetic Resonance
2D NOESY	Two dimensional Nuclear Overhauser Effect Spectroscopy
Δq	The normalized standard deviations
γ-CD	Gamma cyclodextrins

SUATU PENYIASATAN CECAIR IONIK YANG DIMUATKAN DALAM NANOZARAH MAGNET DAN DICANTUMKAN BERSAMA β-SIKLODEKSTRIN POLIMER UNTUK PENGEKSTRAKAN PARABEN

ABSTRAK

Kerja ini menunjukkan penggunaan nanozarah magnetik (MNP) yang dicantumkan kepada polimer sebagai penjerap untuk penyingkiran dan pengekstrakan bahan kimia endokrin (EDCs) yang merupakan sebatian paraben, iaitu metil paraben (MP), etil paraben (EP), propyl paraben (PP), butil paraben (BP) dan benzyl paraben (ArP). Dalam kajian ini, penjerap polimer bersalutkan superparamagnetik yang mudah dan cekap telah berjaya disintesis melalui kaedah ko-pemendakan. Pertama, β-siklodekstrin (βCD) telah dipolimerisasi menggunakan penghubung toluena-2,4- diisosianat (TDI) sebelum ia dicantumkan kepada MNP untuk membentuk MNP-βCD-TDI. Prestasi bahan-bahan berasaskan cecair ionik (ILs) dinilai dengan memuatkan IL-hidrofilik, 1-butyl-3-methylimidazolium klorida (BMIM-Cl) ke permukaan MNP-βCD-TDI untuk membentuk cecair ionik baru berasaskan polimer magnetik penjerap (IL-MNP-βCD-TDI) sebagai pendekatan baru dalam kajian ini. Pembentukan MNP, MNP-βCD-TDI, IL-MNP-βCD-TDI dicirikan dan dibandingkan dengan beberapa pilihan teknik analisis antaranya FT-IR, CHN, VSM, SEM, TEM, BET, TGA dan XRD. Selepas itu, kajian penjerapan juga dilakukan dan penyingkiran PP, BP dan ArP didapati bergantung kepada pH dan pH 6 yang optimum telah dipilih untuk kajian penjerapan kumpulan bagi parabens yang dikaji. Seterusnya, hasil termodinamik menunjukkan bahawa proses penjerapan parabens adalah bersifat eksotermik kerana nilai negatif [(PP) -22.80, (BP) -16.74, dan (ArP) -28.22] $\Delta H°$ diperolehi untuk semua parabens yang dikaji. Interaksi kompleks dan interaksi π-π host-guest antara β-cyclodextrin (βCD) dan ArP diselidik dengan melakukan analisis NMR dan spektroskopik. Kecekapan penjerapan bahan yang dibangunkan diuji pada air paip, air longkang dan air sisa industri. Tambahan pula, penerapan IL-MNP-βCD-TDI telah diselidik secara menyeluruh dengan melakukan pengekstrakan magnet fasa pepejal (MSPE) MP, EP, PP, dan BP yang diikuti oleh kromatografi cecair berprestasi tinggi dengan pengesan array dioda (HPLC-DAD) dalam sampel alam sekitar dan kosmetik. Beberapa pemboleh ubah telah dioptimumkan termasuk jenis penjerap yang digunakan, kepekatan cecair ionik yang dimuatkan, jumlah penjerap, masa pengekstrakan dan nyah jerap, jenis dan jumlah pelarut nyah jerap, pH sampel, penambahan garam dan jumlah sampel. Linear yang sangat baik telah dicapai dalam julat 0.3-500.0 $\mu g\ L^{-1}$ untuk MP dan EP, dan dalam julat 0.1-500.0 $\mu g\ L^{-1}$ untuk PP dan BP, dengan korelasi penentuan R^2> 0.999. Kepekaan tinggi dengan had pengesanan (LODs: 0.02-0.09 $\mu g\ L^{-1}$) dan kuantiti (LOQs: 0.05-0.28 $\mu g\ L^{-1}$), dan perolehan semula (80.3% -117.3%) diperoleh dengan sisihan piawai relatif yang memuaskan (RSD: 1.1% -14.9%). Berdasarkan hasil yang diperoleh, penjerap IL-MNP-βCD-TDI terbukti sebagai penjerap yang mudah, dan boleh berfungsi sebagai penjerap alternatif lagi berkesan untuk penyingkiran dan pengekstrakan sebatian paraben.

AN INVESTIGATION ON THE USE OF IONIC LIQUID LOADED MAGNETIC NANOPARTICLE GRAFTED β-CYCLODEXTRIN POLYMER FOR THE EXTRACTION OF PARABENS

ABSTRACT

This work demonstrated on the use of magnetic nanoparticle (MNP) grafted onto the polymer as an adsorbent for the removal and extraction of endocrine disruptor chemicals (EDCs), namely paraben compounds, i.e. methyl paraben (MP), ethyl paraben (EP), propyl paraben (PP), butyl paraben (BP) and benzyl paraben (ArP). In this study, a simple and efficient superparamagnetic coated polymeric adsorbent was successfully synthesized via a co-precipitation method. Firstly, β-cyclodextrin (βCD) was polymerized using toluene-2,4- diisocyanate (TDI) linker before it was grafted onto MNP to form MNP-βCD-TDI. The performance of ionic liquids (ILs) based material was evaluated by loading a hydrophilic ILs, 1-butyl-3-methylimidazolium chloride (BMIM-Cl) onto the surface of MNP-βCD-TDI to form a new ionic liquid loaded based magnetic polymeric adsorbent (IL-MNP-βCD-TDI) as a new approach in this study. The formation of MNPs, MNP-βCD-TDI, IL-MNP-βCD-TDI were characterized and compared using few selections of analytical techniques namely FT-IR, CHN, VSM, SEM, TEM, BET, TGA and XRD techniques. Subsequently, the adsorption studies were also performed, where the removal of PP, BP and ArP were found to be pH dependent and the optimum pH 6 was selected for the following batch adsorption study from the investigated parabens. Furthermore, the thermodynamic results showed that the adsorption process of parabens were exothermic in nature since negative values [(PP) -22.80, (BP) -16.74, and (ArP) -28.22] of $\Delta H°$ were obtained for all investigated parabens. The interaction of host-guest inclusion complex and π-π interaction between β-cyclodextrin (βCD) and ArP was investigated by performing NMR and the spectroscopic analyses. The adsorption efficiency of the developed material was tested on tap water, drain water and industrial wastewater. Moreover, the applicability of IL-MNP-βCD-TDI was thoroughly investigated by performing magnetic solid phase extraction (MSPE) of MP, EP, PP, and BP followed by high-performance liquid chromatography with diode-array detection (HPLC-DAD) in environmental and cosmetic samples. Several variables were optimized including the types of adsorbents used, concentration of ionic liquid loaded, amount of adsorbent, extraction and desorption time, types and volumes of desorption solvent, sample pH, salt addition, and sample volumes. Excellent linearity was achieved in the range of 0.3–500.0 μg L^{-1} for MP and EP, and 0.1–500.0 μg L^{-1} for PP and BP, with correlation of determination R^2>0.999. High sensitivity with limit of detections (LODs: 0.02-0.09 μg L^{-1}) and quantifications (LOQs: 0.05-0.28 μg L^{-1}), and good recoveries (80.3%-117.3%) were obtained with satisfactory relative standard deviation (RSD: 1.1%-14.9%). Based on the results obtained, the IL-MNP-βCD-TDI adsorbent was proven to be a simple, rapid, robust, and effective alternative adsorbent for the removal and the extraction of paraben compounds.

CHAPTER 1

INTRODUCTION

1.1 Background of this study

Parabens are a class of compound that commonly used as preservatives in cosmetic, pharmaceutical, food and health care products. The compound was derived from a series of parahydroxybenzoates or ester of parahydroxybenzoic acid. Moreover, parabens exist in a very low concentration, especially in environmental water samples (Noorashikin et al., 2014).

1.2 Problem statement

The pollution of fresh water might occur via a large amount of contaminants that originated from the wastewater of industrial, domestic municipal, and household areas, which may lead to cross reaction (Błędzka et al., 2014; Haman et al., 2015; Sasi et al., 2015). Paraben is a scientifically proven compound to disrupt hormone function, causes infertility, early puberty in children, early menopause for women, and may also cause cancer. Recently, paraben compounds have gained concern on its potential impact towards health of organisms due to being an emerging pollutant (Ocaña-González et al., 2015). The underlying reason is because paraben compounds are considered as an endocrine disrupting chemical (EDC), where the compounds alter the endocrine system, and consequently inducing adverse impact on the health of an organism (Darbre & Harvey, 2008; Boberg et al., 2010; Dodson et al., 2012). For an example, in Denmark, paraben compounds were banned in children cosmetics because of its life-threatening characteristics, and similar situations can be also observed in European Union and Japan (SCCS, 2011).

In addressing this matter, recent studies had focused on the developments of the new nano-size materials, such as the magnetic nanoparticles (MNPs) based material to extract or remove the pollutants from samples. Generally, MNPs are known as a class of nano-materials that existed in nano-sizes and shapes. The material also has magnetic properties comprised of two components related to iron, nickel and cobalt, and chemical component that have its own functionalities. Furthermore, MNPs were synthesized to be used for magnetic solid phase extraction (MSPE) due to its ability to shorten the sample preparation period and increase the enrichment process. The developments of MNPs were always subjected to the easiest approach to isolate compounds via external magnetic field (Giakisikli & Anthemidis, 2013a; Khan et al., 2014; Somayeh et al., 2014). One of the examples was that MNPs demonstrated that with its utilization, the proficiency of MSPE improve due to the extensive surface region of MNP (Karimi et al., 2016). However, MNPs are not sufficient to enrich the selectivity of targeted analytes, but with some modification onto the surface of the MNPs, its ability can be significantly improved.

An alternative approach is to graft the MNPs by applying natural supramolecular molecule. Supramolecular chemistry is an interesting topic in chemistry, especially for host-guest types of interactions, such as hydrophobic interactions. Recently, the study on host-guest compound always subjected to the use of cyclodextrins (CDs) due to its ability to form host-guest interactions (Badruddoza et al., 2010). The CDs are basically a natural product that is formed from the degradation of starch through bacterial enzyme conversion. The compound comprised of six to eight glucose units and well-established series of macro cyclic oligosaccharides consisted of 6,7, or 8 D-glucose units connected by α-1,4-glucosidic linkages, which are classified as α-CD, β-CD, or γ-CD, respectively. In comparison to other CDs, β-CD was chosen as the effective guest molecule to be studied in the present study because it is the most stable and economical molecule. β-CD is broadly known to have an ability to form solid inclusion complexes with an extensive variety of solid, fluid, and vaporous compound by means of atomic complexation (Mohamad et al., 2011; Sambasevam et al., 2013; Subramaniam et al., 2010).

In conjunction to the properties of β-CD, numerous methods have been developed in combining the β-CD with the ionic liquids (ILs) due to the presence of ILs that proved to have more chemical interactions between targeted analytes (Ping et al., 2013; Ping et al., 2014; Qin & Zhu, 2016; Raoov et al., 2013a; Raoov et al., 2013b; Raoov et al., 2014). The ILs are a type of salt within liquid at either the room temperature (RTILs) or below 100 ºC. ILs are the salts of ion that is poorly coordinated and a good solvent for a wide range of inorganic and organic materials (Xue & Shreeve, 2005). Thus, ILs are quite famous among researchers due to its novel properties, namely, non-unpredictability, non-combustibility, low thickness, and electrochemical solidness (McEwen et al., 1999).

In this research, the main focus is to modify the native MNPs by using β-CD and ILs to form a new generation material. Furthermore, β-CD itself is soluble in water, thus the polymerization process took place by the addition of toluene-2,4-diisocyanate (TDI) to produce water insoluble material. Therefore, the CD polymer became an interest of many researchers to apply the compound as a coating layer with MNPs due to its high enhancement in parabens' removal and extraction efficiencies (Badruddoza et al., 2010; Badruddoza et al., 2013a; Badruddoza et al., 2013b; Fan et al., 2012; Gong et al., 2014; Kiasat & Nazari, 2012). Thus, five different types of parabens, namely methyl paraben (MP), ethyl paraben (EP), propyl paraben (PP), butyl paraben (BP), and benzyl paraben (ArP) were investigated in the present study. Meanwhile, the loading of ILs were sparked as an interest of the present investigation to develop a new ionic liquid loaded polymeric material. In combination of these three properties (MNP, βCD-TDI, and ILs), the ionic liquid loaded magnetic nanoparticles grafted β-CD polymer (IL-MNP-βCD-TDI) was successfully synthesized for the removal and the extraction of paraben compounds.

1.3 Scope of this study

This study describes the development of the new generation material IL-MNP-βCD-TDI, which will be characterized by utilizing Fourier Transform Infrared (FT-IR) Spectroscopy, Carbon, Hydrogen and Nitrogen (CHN) Analyzer, vibrating sample magnetometer (VSM), scanning electronic microscope (SEM), transmission electron microscope (TEM), Brunauer-Emmett-Teller (BET), thermogravimetric analysis (TGA) and X-ray diffractometer (XRD) techniques. The performance of IL-MNP-βCD-TDI will be elucidated by performing the preliminary batch adsorption study for the removal of PP, BP, and ArP. The interaction mechanism behind the adsorption process will be studied using βCD and one selected paraben which is ArP. Lastly, the IL-MNP-βCD-TDI will be used as an adsorbent for MSPE of MP, EP, BP and ArP from environmental water samples and cosmetic products using HPLC-DAD.

1.4 Objectives of this study

The main objectives of this study are to develop a new water insoluble ionic liquid loaded magnetic nanoparticles grafted β-CD polymer (IL-MNP-βCD-TDI) for the removal and extraction of parabens.

In order to overcome the aforementioned problems and to restrict the scope of research, several objectives have been listed. The present research focuses on the following objectives:

a) To synthesize the ionic liquid loaded magnetic nanoparticles grafted β-CD polymer (IL-MNP-βCD-TDI)
b) To characterize and compare the new IL-MNP-βCD-TDI with magnetic nanoparticles grafted β-CD polymer (MNP-βCD-TDI) and native magnetic nanoparticles (MNPs).
c) To optimize and compare the parameters from batch adsorption studies such as effects of pH, contact time, concentration, temperatures, and sorbent dosage using newly synthesized IL-MNP-βCD-TDI for the removal of PP, BP, and ArP.
d) To use the newly synthesized IL-MNP-βCD-TDI as an adsorbent for magnetic solid phase extraction (MSPE) and to optimize the MSPE parameters for the extraction of MP, EP, BP and ArP from environmental water samples and cosmetic products using high performance liquid chromatography with diode array detection (HPLC-DAD).

1.5 Outline of this study

This thesis is sorted into five chapters. Chapter 1 provided an introduction of this research, research objectives and the scope of the study. In Chapter 2, the literature study of the research is thoroughly reviewed in detail. The methodologies of this investigation are outlined in Chapter 3. Chapter 4 presents the data represented by characterizing the results of IL-MNP-βCD-TDI, MNP-βCD-TDI and native MNPs. Thereafter, a thorough preliminary batch adsorption and MSPE study of the paraben compounds is conducted. The optimization and comparison parameters of batch adsorption studies, such as effect of pH solution, contact time, concentration, temperature, and sorbent dosage by using newly synthesized IL-MNP-βCD-TDI for the removal of PP, BP, and ArP are also described in Chapter 4. In addition, the development of the newly synthesized IL-MNP-βCD-TDI as an adsorbent for magnetic solid phase extraction (MSPE), and the optimization of MSPE parameters for the extraction of MP, EP, BP and ArP from environmental water samples and cosmetic products are also described. Finally, in Chapter 5, the overall conclusion of the study alongside the recommendations are presented.

CHAPTER 2

LITERATURE REVIEW

2.2 Magnetic nanoparticles (MNPs)

Magnetic nanoparticles or also known as MNPs became a great potential sorbent among researchers. It has the ability to capture or extract any pollutant in such a huge amount effectively (Lu et al., 2007). MNPs are a class of nanoparticles agglomerates like a small particle size that can be manipulated using external magnetic field (Giakisikli & Anthemidis, 2013b). MNPs are quite famous among researchers because of its nano-material sizes ranging typically around 10-20 nm and corresponds to mesoporous type of materials. Nano-materials or nanoparticles are materials of two or more dimensions, and it exhibited a unique size-dependency in terms of physical and chemical properties (Sanvicens & Marco, 2008). Generally, super paramagnetic or ferromagnetic materials consisted of magnetic element such as iron, nickel, cobalt, or their oxides.

The most commonly used MNPs are magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), while other types of MNPs are pure metals (Fe and Co) and spinal types ferromagnetic ($MeO.Fe_2O_3$, where M=Ni, Co, Mg, Zn, Mn). In order to develop new promising materials, MNPs alone are not sufficient to enrich the selectivity of targeted analytes. However, modifying MNPs with other materials demonstrated good extraction efficiency when dealt with small sample volumes due to the large surface area (Schladt et al., 2011). **Table 2.1** has summarized the MNPs that have been modified with some other materials.

Table 2.1. Previous studies of MNPs with other materials.

MNPs materials coating	Application	References
Fatty acids	Extraction of PAHs from waste cooking oil.	Rozi et al., 2016
Silica graphene (SiO_2/G)	Extraction of PAHs from environmental waste water	Baharin et al., 2016
Poly(phenyl-(4-(6-thiophen-3-yl-hexyloxy)-benzylidene)-amine) (P3TArH)	Extraction of phthalates ester from mineral water and commercial fresh milk.	Baharin et al., 2016
Polyaniline (PANI)	Extraction of parabens in wastewater and toothpaste.	Tahmasebi et al., 2012
Octadecylphosphonic acid (OPA)	Extraction of PAHs from lake waters and hospital sewage samples.	Ding et al., 2010
Carbon (C)	Extraction of organophoshorus from aqueous samples.	Heidari & Razmi, 2012
Metal-filled carbon nanotubes (MFCNT)	Extraction of organochlorine from honey and tea.	Du et al., 2013
C_{18}-functionalized mesoporous silica (SiO_2/C_{18})	Extraction of parabens in sea and swimming pool water samples	Alcudia-León et al., 2013
Polyaniline (PANI)	Extraction of methylmercury in sea water samples	Mehdinia et al., 2011

In this study, CDs are chosen to be coated with MNPs to ensure the selectivity of the targeted analytes increases.

2.2 Cyclodextrins

Supramolecular chemistry is an interesting topic, especially involving host-guest intermolecular interaction study. Throughout the year, the encapsulation of host-guest molecules sparked academic interests especially in the use of CDs due to its semi natural product that created from the degradation of starch, which are renewable and natural materials by a generally simple chemicals' transformation (Szejtli, 1998; Brocos et al., 2010). As a result, these molecules often applied in a wide range of fields, especially in supramolecular studies.

The CDs or otherwise called cycloamyloses, are a group of aggravates that are comprised of sugars and are limited together in a ring (cyclic oligosaccharides). The widely used applications of CDs are in pharmaceuticals, food, drug delivery, chemicals, and other relevant applications, which had become a phenomenon due to its unique structural characteristics. The CDs result from the cyclomaltodextrin glucanotransferase, where there are three basic CDs with 6, 7 or 8 D-glucopyranonsyl residues, i.e. α-CDs (have six glucose units) namely cyclohexaamylose or cyclomaltohexaose, β-CDs (seven glucose units) or also known as cycloheptaamylose or cyclomaltoheptaose, and γ-CDs (eight glucose units) named cyclooctaamylose or cyclomaltooctaose respectively linked in a ring by α-1,4 glycosidic linkages (He & Shen, 2008). From all of these CDs, the bond length and orientation must have similar structures. The compound existed in unlimited bowl-formed (truncated cone) and particle hardened by hydrogen holding between the 3-OH and 2-OH bunches surrounding the external edge as shown in **Figure 2.1**.

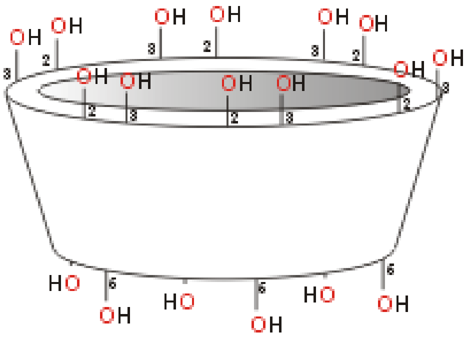


Figure 2.1. Shape of CD (Pessine et al. 2012).

The full illustrations of chemical structures for different types of CDs are shown in **Figure 2.2.** In CDs, the glucose units are associated through glycosidic α-1,4 bonds as outlined in **Figure 2.3**. This bond is corresponding to the development of doughnut-molded molecule having one edge line with n primary hydroxyl groups, where else the other edge 1 with 2n secondary hydroxyl groups and inside of the cavity lined with (from secondary hydroxyl rim inwards) a line of CH groups (C-3 carbons), at the point column of glycosidic oxygen, and afterward a line of C-5 CH group (Szejtli, 1998). The cross section of the CD molecules that represent the hydrophilic side and hydrophobic cavity is shown in **Figure 2.4**.

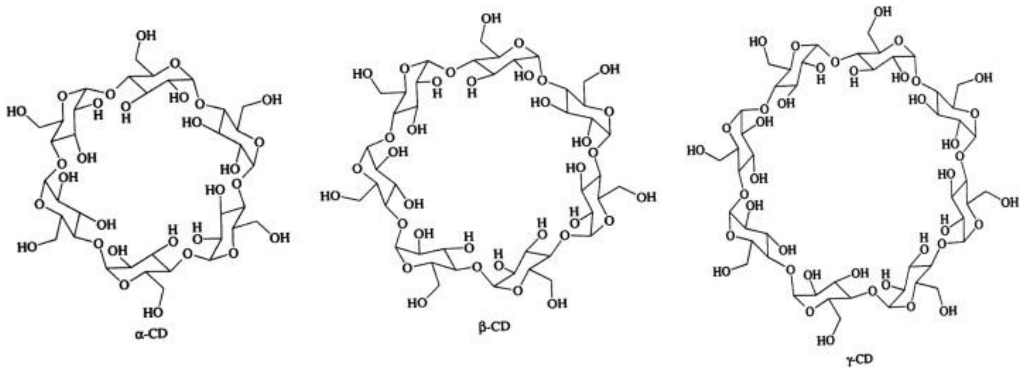


Figure 2.2. Chemical structure of α-CDs, β-CDs and γ-CDs (Astray et al., 2009).

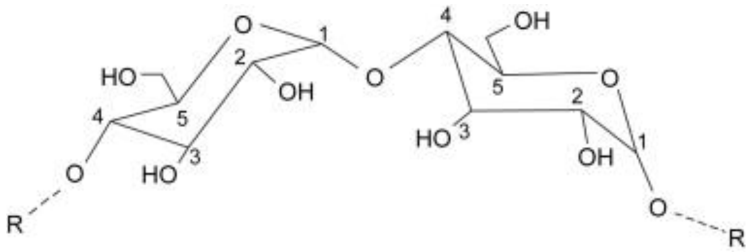


Figure 2.3. Glycosidic linkage of α-1,4 molecule (Astray et al., 2009).

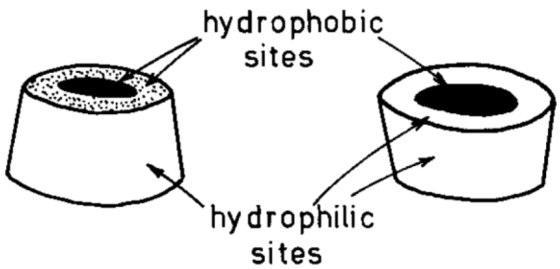


Figure 2.4. Schematic representations of the hydrophilic side and hydrophobic cavity of a CD cylinder (Szejtli, 1998).

The cavities of CDs have different diameters relies on the quantity or number of glucose units (6, 7 or 8 glucose units). The side rim depth of all CDs found to be the same at about 0.8 nm. **Figure 2.5** shows the rim depth and rim diameter of the following CDs. Furthermore, the properties of the main CDs were described in **Table 2.2**.

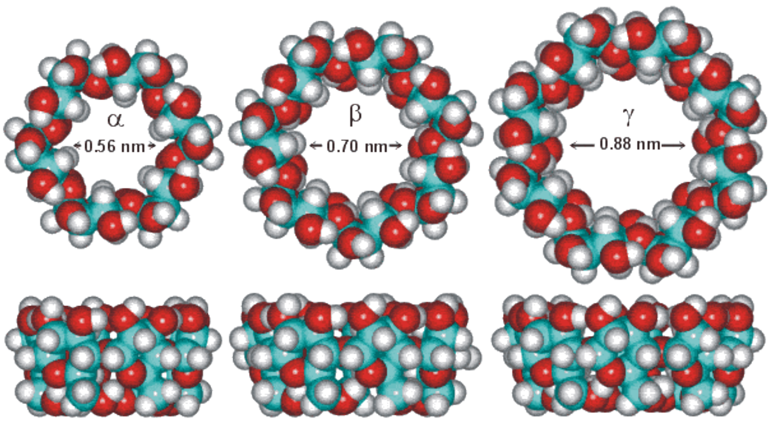


Figure 2.5. Types of CD molecules (Khalafi & Rafiee, 2013).

Table 2.2. The physicochemical properties of main CDs.

CDs	Molecular weight (g mol^{-1})	Outer diameter (nm)	Cavity diameter (nm)		Cavity volume (mL g^{-1})	Solubility, g kg^{-1} H_2O	Hydrate H_2O	
			Inner	Outer			Cavity	External
α-	972	1.52	0.45	0.53	0.10	129.5	2.0	4.4
β-	1135	1.66	0.60	0.65	0.14	18.4	6.0	3.6
γ-	1297	1.77	0.75	0.85	0.20	249.2	8.8	5.4

In recent study, CDs have been changed from water soluble molecule to water insoluble by means of polymerization upon cross-linking.

2.3 Cross-linker

Polymerization is a process of combining a small molecule to become a large molecule. It is the process to react all these small monomer molecules together in a chemical reaction to form a new three-dimensional network. Polymer is a large molecule, or macromolecule composed of many repeated subunits. In chemical compounds, polymerization occurs via a variety of reaction mechanism or cross-linking reaction that vary in complexity because of functional group that present in reacting compound. The cross-linking agents are normally used to polymerize or the process of chemically joining two or more molecules by a covalent bond and alter the molecule to become water insoluble molecule (Lu et al., 2017). **Table 2.3** summaries some studies that used cross-linker especially in the used of bi- and multi-functional molecules for removal, adsorption and extraction studies such as epichlorohydrine (EPC), hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI) and citric acid monohydrate (CAM). Every researcher has their own thought about the selections of the best cross linker in their studies. Owing to the properties of CD which have many hydroxyl groups, the best cross-linking agent is diisocyanate linker or toluene 2,4 diisocyanate (TDI), this is because the TDI linker is very reactive towards hydroxyl group.

Table 2.3. Summary of cross-linking agents.

Cross linker	Application	Reference
Epichlorohydrine (EPC)	Adsorption of Bisphenol A	Kitaoka & Hayashi, 2002
Hexamethylene diisocyanate (HDI)	Adsorption of aromatic amino acids	Tang et al., 2006
Hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI)	Removal of organic pollutants from water	Mhlanga et al., 2007
Epichlorohydrine (EPC)	Removal of cationic dyes from aqueous solution	Crini, 2008
Citric acid monohydrate (CAM)	Adsorption toward aniline	Zhao et al., 2009
Hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI)	Removal of organic pollutants and heavy metals from water	Mahlambi et al., 2010
Toluene diisocyanate (TDI)	Removal of 2,4-dichlorophenol	Raoov et al., 2013a
Toluene diisocyanate (TDI)	Removal of phenols and As (V)	Raoov et al., 2013b
Toluene diisocyanate (TDI)	Extraction of phenol	Raoov et al., 2014
Hexamethylene diisocyanate (HDI)	Determination of allura red	Qin & Zhu, 2016

In brief, cross linker is the best agent to polymerize any molecule to become water insoluble molecule. In this study, TDI has been chosen to be used in transforming βCD molecule into three-dimensional network polymer.

2.4 β-cyclodextrin polymer

β-cyclodextrin (βCD) is a normal starch inferred particles which is torus-formed cyclic oligosaccharide with inner hydrophobic cavity (Szejtli, 1998). βCD was chosen to be used in this study because it is inexpensive and has an ability to form solid inclusion complexes with a very extensive variety of strong, fluid and vaporous mixes by means of atomic complexation (Mohamad et al., 2011; Sambasevam et al., 2013) and through different sort of interactions, i.e. van der waals forces, hydrophobic interactions, electrostatic affinities, dipole-dipole interactions, and hydrogen bonding (Zhang et al., 2011). In this study, the experiment is being led to assess the likelihood of the utilized polysaccharides, in particular starch and starch derivatives as an adsorbent to extract and remove pollutants from environment. Since the CD can form inclusion complexes by surrounding the guest molecule in the hydrophobic cavity, the molecule or targeted analytes will be micro-encapsulated into the cavity via hydrophobic interaction as shown in **Figure 2.6**.

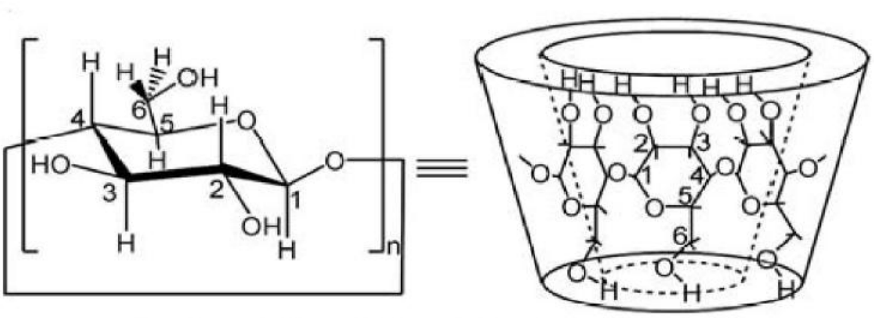


Figure 2.6. Inclusion complex formation (Mohamad et al., 2011).

This phenomenon may lead to numerous kind of points of interest that adjustment in the compound and physical properties of the guest molecule, for example, adjustment of light or oxygen sensitive substances, alteration of the chemical reactivity of guest molecule, fixation of very volatile substances, change of dissolvability of substances, modification of liquid substances to powder, protection against degradation of substances by micro-organisms, masking of ill smell and taste, masking pigments or the color of substances, and catalytic activity of CD with guest molecules (Del Valle, 2004).

Cross linking occurs when a reagent introduces the intermolecular bridge or crosslink between βCD macromolecule. βCD can be cross connected by a response between the hydroxyl groups gatherings of the bind with coupling agent to frame water insoluble system (Chin et al., 2010; Ozmen et al., 2007) such as TDI linker. The cross linking agent can react to the macromolecules linear chain or polymerized in alkaline medium. The cross linked polymers are obtained in homogeneous and heterogeneous condition by using reticulation with bi- or multi-functional cross linking agents. There are numerous studies confirmed that the uses of βCD polymer with the cross linking agent (TDI) as the best sorbent for various applications. Those studies were summarized in **Table 2.4**.

Table 2.4. Summary of application of βCD with TDI as cross linking agents.

Application	Reference
Removal of organic pollutants.	Salipira et al., 2008
Extraction of phenols	Romo et al., 2008
As a potential optical receptor for the detection of organic compound.	Ng & Narayanaswamy, 2009
Adsorption of aromatic molecules	García-Zubiri et al., 2009
Extraction of patulin from apple juice.	Appell & Jackson, 2010
Removal of paraben from water samples.	Chin et al., 2010

As proved, βCD polymer has good potential in adsorption and extraction studies. Therefore, the studies of grafting βCD polymer onto the surface of MNPs become interest in this research due to its ability to be easier to separate from the solution.

2.5 MNP grafted β-CD polymer

After some reviews about β-CD polymer, to improve the selectivity towards studied analytes the finding of the best adsorbent is not stop until here. To make this research become more interesting, the polymeric adsorbent was found to be more applicable and easier to be used when it was in magnetite form. Furthermore, CD polymer also become the academic interests in combining with magnetic nanoparticles (MNPs) or chemically named Fe_3O_4 (Fan et al., 2012). Surface modification of MNPs is frequently used method to keep the internal superior magnetic properties when combining with the polymeric adsorbents. In this manner, the conglomeration of MNPs and the change of magnetite (Fe_3O_4) to maghemite (γ-Fe_2O_3) attributed to the response of Fe (II) cations with reached oxygen can be anticipated (Li et al., 2011). The unique characteristics for the combination of these types of adsorbents are the innermost MNPs itself which can feel and respond to an external magnetic field while the outermost CD polymer can be functioning as inclusion sites and specific container for targeted analytes. Therefore, the modification of MNPs with CD polymer shows an increase in extraction and removal efficiencies. **Table 2.5** summarized some literatures that related to the modification of MNPs grafted to β-CD polymer.

Table 2.5. Some studies on modification of MNPs with β-CD polymer.

Types of βCD modified MNPs	Application	Reference
Fabrication of cyclodextrin-functionalized superparamagnetic Fe_3O_4/amino-silane core–shell nanoparticles via layer-by-layer method.	Applications in magnetic drug delivery technology and bioseparation	Cao et al., 2009
Synthesis of carboxymethyl-β-cyclodextrin conjugated magnetic nano-adsorbent	Removal of methylene blue	Badruddoza et al., 2010
Superparamagnetic β-cyclodextrin-functionalized composite nanoparticles with core–shell structures.	Synthesizing new materials	Li et al., 2011
Carboxymethyl-β-cyclodextrin conjugated magnetic nanoparticles	Removal of copper ions.	Badruddoza et al., 2011
β-Cyclodextrin/Fe_3O_4 hybrid magnetic nano-composite modified glassy carbon electrode	Tryptophan sensing	Wang et al., 2012
Magnetic nanoparticles grafted with β-cyclodextrin–polyurethane polymer	As efficient phase-transfer catalyst for nucleophilic substitution reactions of benzyl halides	Kiasat & Nazari, 2012
Carboxymethyl-β-cyclodextrin polymer grafted onto magnetic nanoadsorbents.	Removal of endocrine disrupters and toxic metal ions	Badruddoza et al., 2013a
Fe_3O_4/cyclodextrin polymer nanocomposites	Removal targeted metal ions in wastewater	Badruddoza et al., 2013b
Cyclodextrin polymer/Fe_3O_4 nanocomposites	Analysis of rutin	Gong et al., 2014
Synthesis of water-dispersed magnetic nanoparticles (H_2O-DMNPs) of β-cyclodextrin modified Fe_3O_4	Accelerating the catalysis of phosphonate synthesis.	Rostamnia & Doustkhah, 2015
Magnetite nanoparticles coated with β-cyclodextrin functionalized-ionic liquid.	Recognize Bisphenol A.	Sinniah et al., 2015

In the nut shell, the grafting of MNPs and βCD polymer has great potential in separation science. In order to increase the selectivity of targeted analytes, the introduction of ionic liquids (ILs) onto the surface of polymer sparked interest in recent study.

2.6 Introduction to ionic liquids (ILs)

Ionic liquids (ILs) are types of salts in the form of fluids below 100 ^{o}C or even room temperature or ambient, known as Room Temperature Ionic Liquids (RTILs) (Subramaniam et al., 2010). RTILs are are increasing wide acknowledgment as novel solvent in chemistry because of non-volatility, non-flammability, low viscosity and electrochemical stability are common and unique characteristics of ILs, giving them an advantage in various types of applications especially in extraction, separation and supramolecular materials (Anderson et al., 2002; McEwen et al., 1999). Literally, ILs are made up of bulky 1,3-dialkylimidazolium, alkylammonium, alkylphosphonium or alkylpyridinium organic cations and inorganic anions such as most frequently $AlCl_4^-$, BF_4^- or PF_6^-, NO_3^-, ClO_4^-, CF_3COO^-, $CF_3SO_3^-$ or CH_3COO^- and other anions (as shown in **Figure 2.7**) (Wasserscheid & Welton, 2008). 1-butyl-3-methyl-imidazolium hexafluorophosphate [C_4MIM][PF_6] or 1-butyl-3-methyl-imidazolium tetrafluoroborate [C_4MIM][BF_6] is a standout amongst the most frequently used neutral ILs.

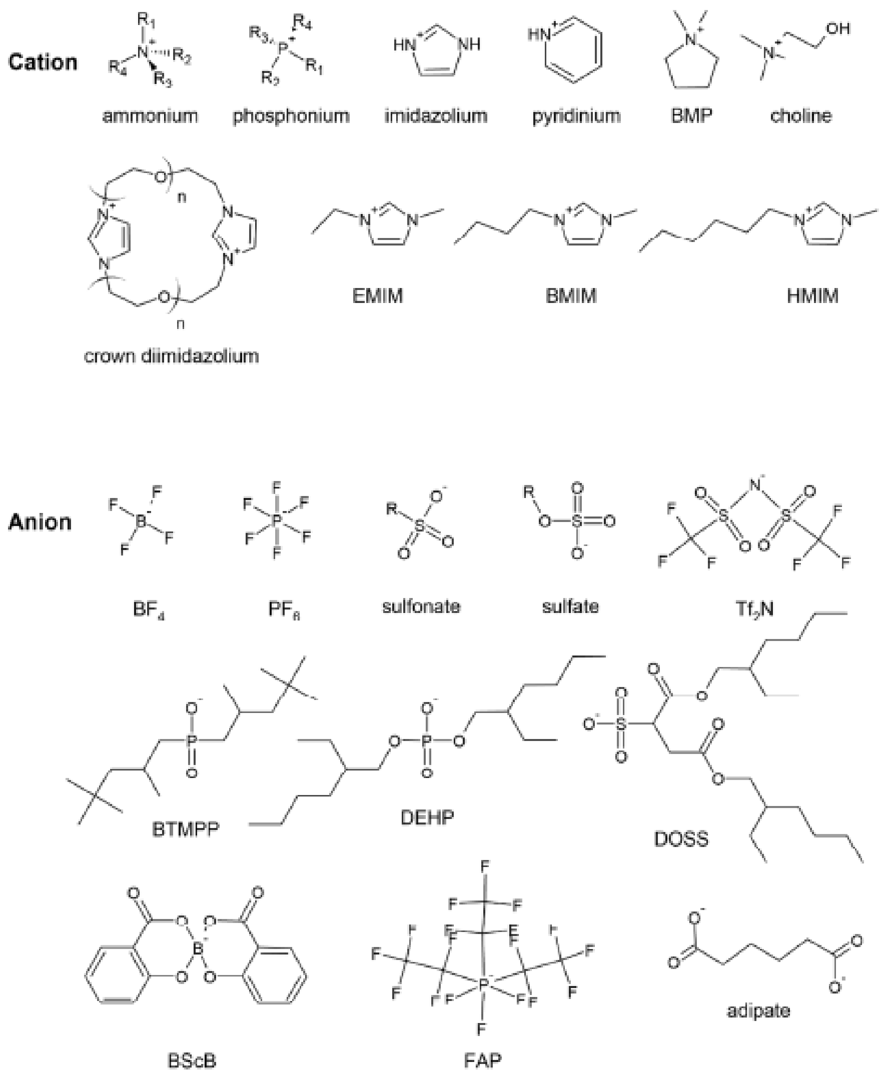


Figure 2.7. Typical cationic and anionic of ILs components (Zhou & Qu, 2017).

ILs gives a lot of advantages to consumers due to its applicability especially in analytical chemistry. The application in separation science of interest is eligible because of their remarkable properties, for example, irrelevant vapor pressure, great thermal stability, tunable viscocity and miscibility with water and organic solvents, and in addition great extractability for different natural mixes and metal particles. The physicochemical properties of ILs are depending on the nature and size of both their cations and anions constituents. The unique properties of ILs have been summarized in **Figure 2.8**.

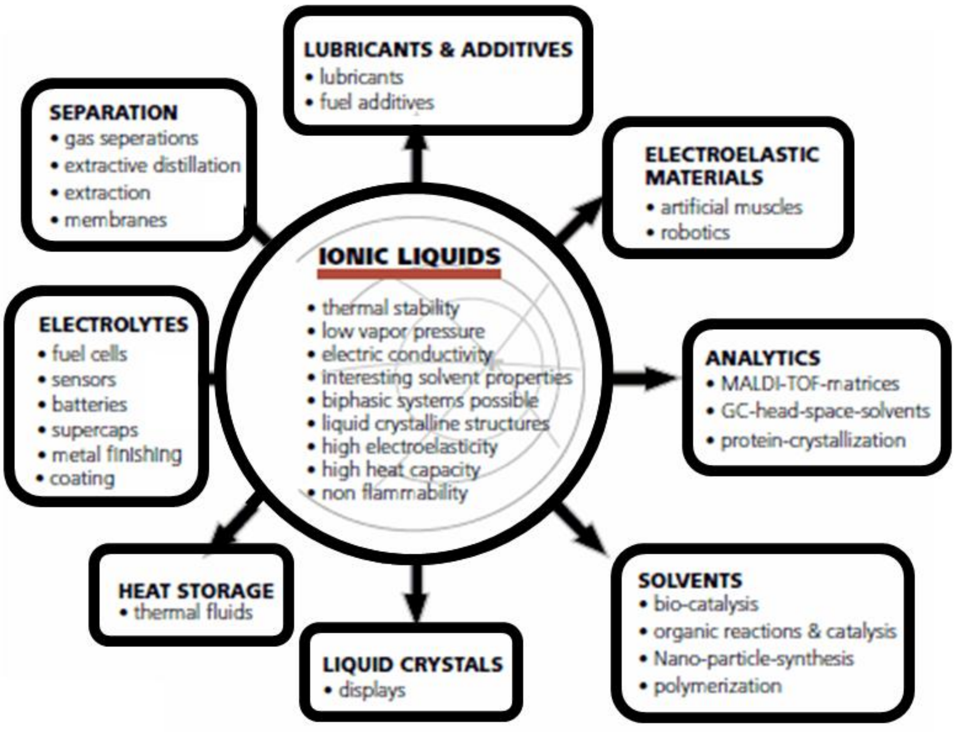


Figure 2.8. The properties of ILs and their potentials and current applications.

2.7 The loading of ILs

Owing to the properties of ILs, the study about the combination of ILs with other developing adsorbents had been sparked our interest. There are numerous methods that had been developed in functionalizing ILs with other adsorbents. In the meantime, there are some other researchers who are not focusing on the combination of ILs with other adsorbents via functionalizing, but they are trying to find some other ways to develop the new, simple and effective adsorbents that are not consume much time to synthesize the material. In this research, the loading of ILs to the new synthesized adsorbent (MNPs grafted βCD polymer) was studied. At the first stage of this study, the idea was the loading ILs onto the surface of βCD polymer. After some consideration, the loading of ILs onto the surface of MNPs is more convincing and compromising. The summary of the previous study are discussed in the following **Table 2.6**.

Table 2.6. Previous studies about the loading of ILs with βCD polymer or MNPs.

Materials	Application	Reference
ILs loaded βCD polymer	Separation/analysis of chysophanol	Ping et al., 2013
	Determination of rhodamine B in food	Ping et al., 2014
	Separation/analysis of linuron in fruit and vegetable samples	Feng et al., 2015
MNPs coated ILs	Lipase immobalization of enzyme activity in catalyzing esterification.	Jiang et al., 2009
	Removal of dye from aqueous samples	Absalan et al., 2011
	Removal of reactive black 5 (dye) from waste water	Poursaberi & Hassanisadi, 2013
	Adsorption of DNA	Ghaemi & Absalan, 2014
	Extraction of chromium (VI)	Karimi et al., 2016

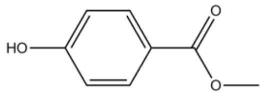
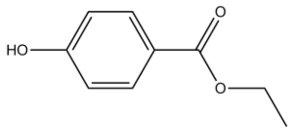
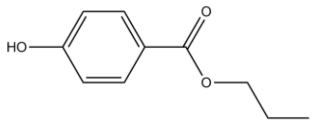
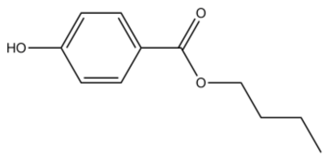
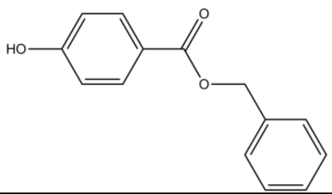
Above materials can be used to remove any pollutants from the environment. The adsorption considers towards those synthesized material could be evaluated through adsorption process. The adsorption procedure was assessed to guarantee the selectivity of the studied analytes are great by utilizing the new incorporated material and to examine the interaction mechanism amongst adsorbent and adsorbates.

2.8 Paraben compounds

Paraben is a compound derived from a family of synthetic ester of *p*-hydroxybenzoic acid that generally utilized as additives in preservatives and can be easily found in cosmetics and health-care products. There are 5 types of parabens in this study which are methyl paraben (MP), ethyl paraben (EP), propyl paraben (PP), butyl paraben (BP) and benzyl paraben (ArP). The physicochemical properties of parabens had been described in **Table 2.7**.

Previously in other literatures, states that MP and PP are the most frequent paraben used in cosmetic products as antimicrobial preservatives (Berke et al., 1982; Decker Jr & Wenninger, 1987; Gruvberger et al., 1998; Soni et al., 2001). The unpredictable influence to human health may happen if the parabens exceed the tolerable limits that have been set. According to European Scientific Committee on Consumer Safety (SCCS, 2010), the tolerable amount of parabens can be used in such cosmetic product is 8 g/kg with no single paraben that have concentration more than 4 g/kg. In addition, SCCS also confirmed that the tolerable limits for smaller chain of parabens (MP and EP) are considered safe but for longer chain of parabens (PP, BP and ArP) must be lower than 1.9 g/kg. Whereas, other literatures also state that, the paraben concentrations are usually less than 0.3% in single preservative system but may range up to 1% (Soni et al., 2002).

Table 2.7. Physicochemical properties of studied parabens.

No.	Name	Abbreviation	Structure	Molecular formula	Molecular weight (g/mol)	pKa	Log K_{ow}
1.	Methyl paraben	MP		$C_8H_8O_3$	152.15	8.4	1.96
2.	Ethyl Paraben	EP		$C_9H_{10}O_3$	166.17	8.34	2.47
3.	Propyl paraben	PP		$C_{10}H_{12}O_3$	180.20	7.91	3.04
4.	Butyl paraben	BP		$C_{11}H_{14}O_3$	194.23	8.47	3.57
5.	Benzyl paraben	ArP		$C_{14}H_{12}O_3$	228.25	8.41	3.60

In recent years, concern has increased as to the role of parabens in producing potentially serious health side effects such as cancer. According to Harvey and Everett (2004) supported details by Darbre et al. (2004), the additives which were utilized as a part of the antiperspirants were likewise found in ester *p*-hydroxybenzoic acid has been detected in human breast tumor from the used of underarm cosmetic and other consumer products. This is because parabens can mimic estrogen which can then stimulate the division of breast cells and because your body finds it hard to break down synthetic estrogen could lead to accumulation of fat cells that can then lead to the development of tumors. Thus, magnetic nanoparticles (MNPs) were suggested to extract the residual parabens from the environment and cosmetic products to ensure the safety on the human and environment.

2.9 Adsorption study

An adsorption process is the adhesion of species to a surface that involves physisorption, chemisorption, or electrostatic attraction (Wu et al., 2017). This method is usually used to improve water quality by removing of toxic organic pollutants or any kinds of chemical species include organic compounds and trace metals (Crini, 2005; Raoov et al., 2013a). Adsorption process involves in interaction between two phases which is the adsorbate which is the species that accumulates on adsorption site and the adsorbent which is the surface layer where the adsorption site is located (Oladoja et al., 2017). Recently, adsorption process seems to be vital in biological, chemical, analytical, and environmental field especially when dealing with such amount of contaminants. Thus, the best adsorbent must be obtained to ensure the adequate surface area for adsorption process to deal with those specified