

**ADSORPTION OF PARABENS IN AQUEOUS SOLUTION  
ONTO  $\beta$ -CYCLODEXTRIN CROSS-LINKED POLYMER**

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## ABSTRACT

$\beta$ -cyclodextrin cross-linked polymers were prepared from hexamethylene diisocyanate (HMDI) and toluene-2,6-diisocyanate (TDI) as a cross-linker. Two types of polymers were synthesized, namely  $\beta$ -CD-HMDI and  $\beta$ -CD-TDI. The polymers were characterized and  $\beta$ -CD-TDI with the molar ratio of 1:7 for  $\beta$ -CD:TDI was chosen for further studies as it gave the highest adsorption of parabens.

The adsorption mechanisms were studied with adsorption kinetic models and adsorption isotherm models. Kinetic study was done for single paraben solutions and a mixture of four parabens solution. For the kinetic study, the experimental data were analysed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models. Adsorptions follow pseudo-second-order model in both solutions and follow intraparticle diffusion model in a solution mixture of a mixture of four parabens solution. This shows that mechanism of adsorption is affected by the competition among parabens molecules. Langmuir and Freundlich isotherm model were used to further describe the process of adsorption. The two isotherm models are applicable onto the adsorption process for different types of paraben in different condition.

The same polymer was reused for nine regenerations in the same conditions to study how effective the recycled polymer was for paraben removal. Adsorption capacities are between 75.6 to 112.8% after regeneration.  $\beta$ -CD-TDI were applied on 10 real aqueous samples and all show positive results.

## ABSTRAK

Polimer bersilang  $\beta$ -cyclodextrin telah disintesis dengan menggunakan diisosianat hexamethylene (HMDI) dan toluena-2,6-diisosianat (TDI) digunakan sebagai pengikat silang. Dua jenis polimer telah disintesis, iaitu  $\beta$ -CD-HMDI dan  $\beta$ -CD-TDI. Polimer telah dicirikan dan  $\beta$ -CD-TDI dengan nisbah molar 1:7 bagi  $\beta$ -CD:TDI telah dipilih untuk penyelidikan selanjutnya kerana ia memberikan penjerapan paraben tertinggi.

Mekanisme penjerapan telah dikaji dengan model kinetik penjerapan dan model isoterma penjerapan. Kajian kinetik telah dilakukan dalam larutan paraben tunggal dan larutan campuran empat paraben. Bagi kajian kinetik, data-data ujikaji telah dianalisis dengan menggunakan model kinetik tertib-pertama, model kinetik tertib-kedua, dan model kinetik penjerapan intrapartikal. Penjerapan mengikuti model kinetik tertib-kedua model dalam kedua-dua jenis larutan dan model kinetik peresapan intrapartikal dalam larutan campuran empat paraben. Ini menunjukkan bahawa mekanisme penjerapan boleh dipengaruhi dengan persaingan antara molekul paraben. Model isoterma Langmuir dan Freundlich telah digunakan untuk menerangkan proses penjerapan. Kedua-dua model isoterma sesuai untuk menerangkan proses penjerapan untuk jenis paraben yang berbeza dalam keadaan yang berbeza.

Polimer yang sama diguna semula untuk sembilan kali dalam keadaan yang sama untuk mengkaji kebolegunaan semula polimer bagi penyingkiran paraben. Kapasiti penjerapan adalah antara 75.6-112.8% selepas diguna semula.  $\beta$ -CD-TDI telah digunakan ke atas 10 sampel akueus sebenar dan semua menunjukkan hasil positif.

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## LIST OF ABBREVIATIONS AND SYMBOLS

$\beta$ -CD	$\beta$ -cyclodextrin
HMDI	1,6-hexamethylene diisocyanate
TDI	toluene-2,6-diisocyanate
$\beta$ -CD-HMDI	$\beta$ -cyclodextrin-1,6-hexamethylene diisocyanate cross-linked polymer
$\beta$ -CD-TDI	$\beta$ -cyclodextrin- toluene-2,6-diisocyanate cross-linked polymer
MP	methyl paraben
EP	ethyl paraben
PP	propyl paraben
BuP	butyl paraben
BP	benzyl paraben
M	molar
mmol	milli mol
rpm	revolutions per minute
ppb	parts per billion
MAC	maximum authorized concentration
DBP	disinfection by product
DMF	N,N-dimethylformamide
FT-IR	fourier transform infrared
HPLC	high performance liquid chromatography
t	time
k	rate constant
$k_1$	pseudo-first-order rate constant
$k_2$	pseudo-second-order rate constant
$k_i$	intraparticle diffusion rate constant
$R^2$	linear fitting value
$q_e$	amount of sorbate adsorbed at equilibrium
$q_{max}$	maximum adsorption capacity of the adsorbent
$q_t$	amount of sorbate adsorbed at time t
$C_e$	concentration of solute in solution at equilibrium
$C_0$	initial concentration of sorbate in solution
$K_L$	Langmuir isotherm constant
$K_F$	Freundlich isotherm constant
$R_L$	Langmuir isotherm constant separation factor
$n_F$	Freundlich isotherm exponent

## CHAPTER 1 INTRODUCTION

### 1.1 Background of Study

Since 1920's, parabens had been widely used as preservative in food, pharmaceutical, and cosmetic products (Darbre, 2006) due to their suitability as antimicrobial compounds (Soni et al., 2005). Therefore, trace parabens are commonly found in wastewater (Andersen et al., 2007; González-Mariño et al., 2009; Peng et al., 2008). Parabens can still be found in various kinds of water, although removal of parabens in wastewater treatment plant is efficient (Andersen et al., 2007).

They can be absorbed through gastrointestinal tract and skin as shown in animal studies (Darbre, 2006; Kitagawa et al., 1997). Studies have also shown that parabens exhibit estrogen agonistic activity (Harvery & Darbre, 2004). The position of the phenolic hydroxyl groups in parabens is similar to meso-hexaestrol and 17 $\beta$ -estradiol (Byford et al., 2002), therefore it can bind into the ligand binding pocket of the crystal structure of the ligand binding domain of the oestrogen receptor  $\alpha$  (Darbre, 2006). Since estrogen is known to influence the incidence of breast cancer (Lipworth, 1995), hence parabens could potentially cause breast cancer (Darbre et al., 2004). Parabens may cause testis mitochondrial dysfunction causing male infertility (Tavares et al., 2009).

Ecological risk assessment of parabens shows that they can induce vitellogenin, an egg yolk protein precursor in male aquatic organisms (Pedersen et al., 2000; Yamamoto et al., 2011).

Parabens were still found in waste water treatment plants effluent even after the treatment in waste water plant (Andersen et al., 2007; Yamamoto et al., 2011). Various studies show that concentration of parabens ranged from the order of 0.01 to 1  $\mu\text{g L}^{-1}$  in waste water treatment plants effluent. Removal methods such as photosensitized degradation (Gryglik et al., 2009), ozonation (Tay et al., 2010), and chlorine dioxide treatment (Andersen et al., 2007), are efficient too but gave unwanted by-products (Tchobanoglous, 2003), which are not preferred due to the environmental safety requirements.

Hence, the adsorption method may offer a much safer way for removing parabens from water and wastewaters since it is a method free of harmful substances, and is environmentally friendlier, has a low initial cost, flexible and simple in design and operation (Crini, 2005, 2008). Recently, much attention has been focused on biopolymers and natural molecules as they are environment friendly and easily accessible. Natural polymers such as chitin (Ravi Kumar, 2000; Synowiecki & Al-Khateeb, 2003), chitosan (Juang et al., 1997; Rinaudo, 2006), starch (Guo et al., 2009; Guo et al., 2008; Mostafa et al., 2008), and cyclodextrin (Crini & Morcellet, 2002; Murai et al., 1998; Yilmaz et al., 2009) are used as adsorbent in different kinds of adsorption applications. Cyclodextrin (CD) is chosen in this study due to its special chemical structure. It has a hydrophobic cavity which can entrap different kinds of compounds including, organic, inorganic, organometallic and metalloorganic which may be neutral, cationic, anionic or even radical (Stoddart, 1989). CD are environmental friendly because they are produced from enzymatic degradation of starch, biodegradable (Lu et al., 2008) and harmless to humans and environment (Murai et al., 1996). There are three main types of CD,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrin, which has six, seven, and eight

glucopyranose units.  $\beta$ -CD has been considered as the adsorbent for parabens because it is the most accessible CD and is economically preferable (Del Valle, 2004).

However,  $\beta$ -CD is soluble in water which makes it inconvenient to use as adsorbent in water (Mamba et al., 2007). Therefore,  $\beta$ -CD polymers which are insoluble in water are prepared.  $\beta$ -CD polymers have gained prominence in recent years. They had been used in various application such as removal of phenol from waste water (Yamasaki et al., 2006), extraction of steroidal compounds (Moon et al., 2008), solid-phase extraction (Bhaskar et al., 2004), as fluorescence sensor (Wang et al., 2006), etc.  $\beta$ -CD units are linked together by covalent bonds thus by using different kind of cross-linkers  $\beta$ -CD cross-linked polymers are formed. Physical and chemical properties will be different if prepared by different cross-linkers and different conditions.

In this study, 1,6-hexamethylene diisocyanate (HMDI) and toluene-2,6-diisocyanate (TDI) are used as cross-linkers and  $\beta$ -CD-HMDI and  $\beta$ -CD-TDI are generated as adsorbents. The polymers prepared had been characterised using fourier transform infrared (FT-IR) spectrometer and CHN analyser. In view of the fact that parabens are able to form inclusion complex with  $\beta$ -CD (Chan et al., 2000; de Vries & Cairra, 2008; de Vries et al., 2009), we are investigating the efficiency of  $\beta$ -CD polymer as an adsorbent for the removal of parabens from various matrices. The effects of varoius experimental parameters such as types and ratio of cross-linkers, water adsorption, and reusability of polymer are presented and discussed. In addition, adsorption kinetics and adsorption isotherms are studied to develop better understanding of the mechanisms which is important for faster and more accurate simulations and design of the adsorption processes. Application of the polymers on water samples is being studied.

## 1.2 Objectives of Study

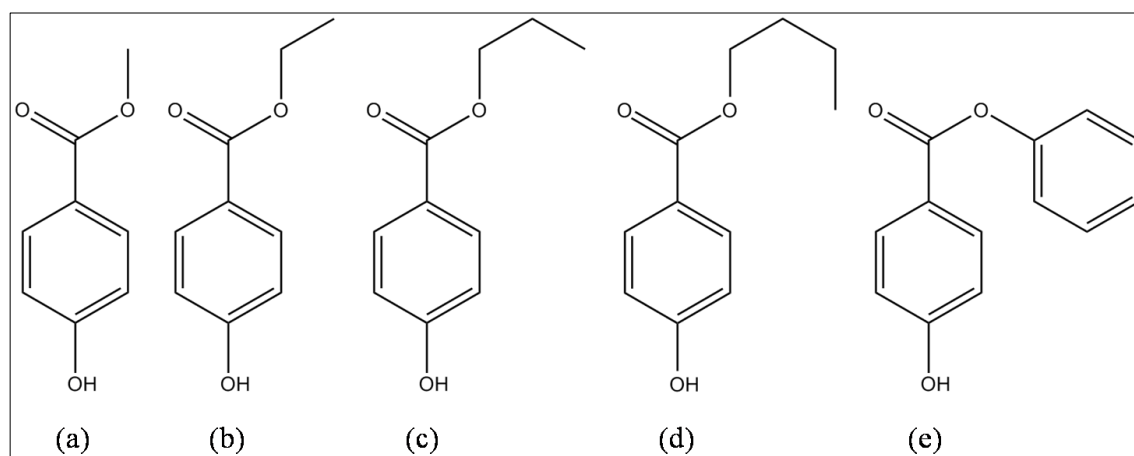
The objectives of this study are:

- a) To synthesize  $\beta$ -CD cross-linked polymer, i.e.,  $\beta$ -CD-HMDI and  $\beta$ -CD-TDI.
- b) To characterise  $\beta$ -CD-HMDI and  $\beta$ -CD-TDI.
- c) To study the adsorption kinetics and adsorption isotherms of  $\beta$ -CD-TDI.
- d) To apply  $\beta$ -CD-TDI as adsorbents for removal of parabens in real samples.



## 2.1 Paraben

Paraben is the name given to a group of homologous series of esters of para-hydroxybenzoic acid that have various substitutions at the para position of benzene ring. The term 'paraben' is the abbreviation that is commonly used to name para-hydroxybenzoic acid (Cashman & Warshaw, 2005). The commonly used parabens are methyl paraben (MP), ethyl paraben (EP), propyl paraben (PP) (Bhaskar et al., 2004), butyl paraben (BuP), and benzyl paraben (BP). Their chemical structures are shown in Figure 2.1. Less common paraben include isopropyl paraben, isobutyl paraben, and paraben sodium salts.



**Figure 2.1: Chemical structures of (a) methyl paraben, (b) ethyl paraben, (c) propyl paraben, (d) butyl paraben, and (e) benzyl paraben**

### 2.1.1 Antimicrobial Effect and Their Uses

Parabens were used as preservatives in personal care and pharmaceutical products since 1920's (Darbre, 2006). They are the most widely used preservatives in food, pharmaceutical, and cosmetic products due to their low cost, low toxicity, inertness, stability over pH range (pH 4.5 – 7.5), broad spectrum of antimicrobial activity and worldwide legislative acceptance (Routledge et al., 1998; Soni et al., 2005). Antimicrobial activity increases as the chain length of the paraben ester group increases, but water solubility decreases (Elder, 1984). Therefore, parabens are used in combination typically to enhance their efficiency.

Generally, parabens give their inhibitory effects on membrane transport and mitochondrial function processes (Soni et al., 2005). Their antimicrobial effects are more effective against fungi compare to bacteria (Cashman & Warshaw, 2005). Additionally, antibacterial activity of parabens is greater against gram-positive organisms (Cashman & Warshaw, 2005). Some gram-negative organisms, such as, *Enterobacter cloacae*, *Acinetobacter*, *Rhodopseudomona palustris*, and *Burkholderia cepacia* contain specific enzymes that can degrade parabens (Bertani et al., 2001; Hutchinson et al., 2004; Kok et al., 1998; Valkova et al., 2003; Valkova et al., 2001).

### 2.1.2 Metabolism of Parabens in Human Body

The average amount of parabens that an adult human intake from food is estimated 5 mg/kg daily (Byford et al., 2002). Hydrophilicity of parabens decreases and lipophilicity increases as the alkyl chain length increases (Cashman & Warshaw, 2005) and BP has the lowest water solubility and highest lipid solubility. Therefore, BP is the paraben that is the most easily absorbed by skin and followed by longer chain alkyl parabens. Parabens applied on skin can be partially hydrolysed by carboxylesterases, i.e. the enzyme that hydrolyse carboxylic ester, it is found in skin and subcutaneous fat (Andersen, 2008; Cashman & Warshaw, 2005). Products of the hydrolysis are *p*-hydroxybenzoic acid and their respective side chains (Cashman & Warshaw, 2005). Parabens absorbed from gastrointestinal tract will be metabolised into *p*-hydroxybenzoic acid and the glycine, glucuronic acid, and sulphuric acid conjugates of *p*-hydroxybenzoic acid (Soni et al., 2005). This hydroxybenzoic acid was detected in human blood and milk samples with concentration of 44 ppb in adults' blood, 73 ppb in pregnant women's blood, 96 ppb in umbilical cord's blood and 108 ppb in human milk (Oishi, 2004). Other than that, *p*-hydroxybenzoic acid and its conjugates are excreted in the urine and as urinary biomarkers of exposure in humans (Kiwada et al., 1979; Ye et al., 2006). Although parabens can be hydrolysed in human body, but they still can be adsorbed and retained. Darbre et al., (2004) reported that parabens can be found in breast tumour cells in high concentration, 20.6 ng g<sup>-1</sup> of tissue with MP present at highest level (62.0%).

### 2.1.3 Estrogenic Activities of Parabens

Parabens are xeno-estrogens (Darbre, 2006), i.e. compounds that can mimic the effects of the main natural estrogen, 17 $\beta$ -estradiol thus binding to the estrogen receptor and influencing the estrogen dependent functions in human endocrine system. Estrogenic activity of parabens was first described by Routledge et al. (1998). Butyl paraben is the most potent among alkyl parabens and has estrogenic effects of 10,000 fold less potent than 17 $\beta$ -estradiol in vitro. Byford et al. (2002) also show that parabens can competitively inhibit [<sup>3</sup>H] estradiol binding to MCF7 human breast cancer cells estrogen receptors. Expression of transfected (*ERE-CAT reporter gene*) and endogenous (*pS2*) oestrogen-regulated genes in MCF 7 cells can increase if concentration of parabens is 10<sup>-6</sup> M and above.

Since parabens are lipophilic, they can easily accumulate in fatty tissues of the body over a long time especially human breast (Darbre, 2006). Studies always linked breast cancer to the exposure of estrogens; the increase of exposure to estrogens can increase correspondingly to the risk of breast cancer (Darbre, 2006; Feigelson & Henderson, 1996; Key et al., 2001). Increased exposure to estrogens can result from early onset of menarche, late onset of menopause, obesity in postmenopausal women, high concentration of endogenous estradiol, intake of oral contraceptives, hormonal therapy for menopause, and consume of alcoholic drink which can increase plasma estrogen level (Darbre, 2006; Feigelson & Henderson, 1996; Key et al., 2001). The estrogenic property of parabens stimulates cell division and increase the likelihood that a cell will become abnormal and the abnormalities will be passed on as cells divide. This is how cancer cells develop.

Molecular modelling has shown that parabens molecules (singly or in pairs) can bind with ligand binding pocket of the crystal structure of the ligand binding domain of estrogen receptor  $\alpha$  in place of the  $17\beta$ -estradiol, and their phenolic hydroxyl groups positioned similarly to those of meso-hexaestrol and  $17\beta$ -estradiol (Byford et al., 2002). Table 2.1 shows the relative estrogen agonist activities of parabens and p-hydroxybenzoic acid in assay systems in MCF7 human breast cancer cells (Darbre, 2006). This shows that parabens are ‘half-estrogens’, binding to the ligand binding domain in pairs rather than singly (Darbre, 2006).

**Table 2.1: Relative estrogen agonist activities of parabens and p-hydroxybenzoic acid in assay systems in MCF7 human breast cancer cells (Darbre, 2006)**

Compound	Binding to estrogen receptor	Reporter gene	Reporter gene	Cell proliferation
	Inhibition of 3H-E binding	24 h ERE-CAT induction	7 day ERE-CAT induction	Growth after 12-14 days
	Molar excess to achieve 50% inhibition	Molar concentrations to achieve 50% of response with $10^{-8}$ M estradiol	Molar concentrations to achieve 50% of response with $10^{-8}$ M estradiol	Molar concentrations to achieve 50% of response with $10^{-8}$ M estradiol
<b>Estradiol</b>	3 X		$1 \times 10^{-11}$ M	$2 \times 10^{-11}$ M
<b>p-hydroxybenzoic acid</b>	5 000 000 X	$> 5 \times 10^{-4}$ M	$> 10^{-3}$ M	
<b>MP</b>	3 000 000 X	$6 \times 10^{-4}$ M	$> 5 \times 10^{-4}$ M	$1 \times 10^{-4}$ M
<b>EP</b>	500 000 X	$> 10^{-4}$ M	$> 10^{-4}$ M	$2 \times 10^{-5}$ M
<b>PP</b>	300 000 X	$> 10^{-4}$ M	$> 10^{-4}$ M	$2 \times 10^{-6}$ M
<b>BuP</b>	100 000 X	$> 10^{-4}$ M	$> 10^{-4}$ M	$9 \times 10^{-7}$ M
<b>Isobutyl paraben</b>	40 000 X	$2 \times 10^{-6}$ M	$2 \times 10^{-7}$ M	$7 \times 10^{-7}$ M
<b>BP</b>	50 000 X	$3 \times 10^{-6}$ M	$3 \times 10^{-6}$ M	$1 \times 10^{-6}$ M

#### **2.1.4 Parabens and Males Infertility**

Parabens are known to have inhibitory effects on respiratory capacities and depress mitochondrial membrane potential on isolated testis mitochondrial since 1998 (Nakagawa & Moldéus, 1998; Tavares et al., 2009). Sone et al. have suggested that parabens can induce the rise of cytosolic free  $\text{Ca}^{2+}$  in guinea pig ileum smooth muscle with the results of activation of calcium channel (Nakagawa & Moldéus, 1998). The increase of  $\text{Ca}^{2+}$  will increase the permeability of the mitochondria inner membrane to small ions and molecules (Gunter & Pfeiffer, 1990; Imberti et al., 1993; Nakagawa & Moldéus, 1998; Nieminen et al., 1990; Park et al., 1994). This will leads to collapse of mitochondrial membrane potential and swelling of the organelles (Gunter & Pfeiffer, 1990; Imberti et al., 1993; Nakagawa & Moldéus, 1998; Nieminen et al., 1990; Park et al. 1994). Amount of ATP (adenosine-5'-triphosphate) in cell reduced when mitochondrial membrane potential collapsed as the function of mitochondria is to produce ATP which is use for energy-requiring reactions in cellular level. Testis metabolism and sperm activities which are highly depend on the function of mitochondria may be disturbed (Tavares et al., 2009).

#### **2.1.5 Legislations for Parabens**

Due to their potential impacts on human health, many countries have introduced legislation to control the use of parabens. The guideline for usage of parabens in cosmetic products is called maximum authorized concentration (MAC). MAC of individual parabens in cosmetic products is 0.4% (w/w) in China, 1.0% (w/w) in Japan. The Council Directive 76/768/EC of European Community restricts the use of MP, EP, PP, BuP and BP to a MAC of 0.4% (w/w) for single paraben and total of 0.8% (w/w)

for paraben mixtures. Studies of parabens on human health have generated review (Soni et al., 2005) and call for reassessment (Byford et al., 2002; Routledge et al., 1998; Soni et al., 2005) of the safety of their widespread uses.

In USA (United State of America), FDA (Food and Drug Administration) had listed MP and PP as GRAS (Generally Recognised as Safe- allowed in foods) up to 0.1% each (Steinberg, 2006). MP, EP, and PP are allowed for ingestion in European Union and BP is the only paraben that not allowed for ingestion in Japan (Steinberg, 2006).

### **2.1.6 Environmental Aspect of Parabens**

Parabens are continuously being released into environment through domestic wastewater effluent. Although parabens removal in conventional wastewater treatment plant are efficient (Andersen et al., 2007), but residual of parabens are still found in wastewater effluent (Benijts et al., 2004; Blanco et al., 2009; Lee et al. 2005; Regueiro et al., 2009; Trenholm et al., 2008). Wastewater treatment methods such as chlorination (Canosa et al., 2006), chloride dioxide treatment (Andersen et al., 2007), and ozonation (Tay et al., 2010) produce high percentage of disinfection by products (DBPs) (Tchobanoglous et al., 2003). Chlorinated parabens were formed after chlorination of wastewater (Canosa et al., 2006). Bromo- and bromochloro-parabens were detected due to the trace bromine in tap water (Canosa, 2006). Chlorite ( $\text{ClO}_2^-$ ) and dichlorine dioxide ( $\text{Cl}_2\text{O}_2$ ) which are potentially toxic are the by-products of chloride dioxide treatment of wastewater (Tchobanoglous, 2003). A variety of hydroxylated parabens were formed after ozonation process (Tay et al., 2010). These DBPs are potentially toxic to human and others biology organisms since they are possible endocrine disrupter (Canosa et al., 2006). Therefore, a wastewater treatment method that is free of DBPs has

been developed in this study to remove parabens from aqueous solution. Adsorption technique has been used in this study since it is more environmental friendlier, has a low initial cost, flexible and simple in design and operation (Crini, 2005, 2008). Various materials had been use as adsorbent to adsorb parabens, such as commercial filter membranes (Bin et al., 2000) and multi-walled carbon nanotubes (Márquez-Sillero et al. 2010). However, these adsorbent are relatively expensive.

## **2.2 Adsorption Theory**

Adsorption is the adhesion of species to a surface that involves physisorption, chemisorption, or electrostatic attraction. This is a command method that used to improve water quality by removing various kinds of chemical species include organic compounds and trace metals (Crini, 2005). Adsorption process involves interaction between two phases. The species that accumulates on an adsorption site is called adsorbate and the surface or layer where the adsorption site located is called adsorbent. Adsorbate is usually transported by liquid or gas as medium. Activated carbon (Adhoum & Monser, 2004; Méndez-Díaz et al., 2012; L. Wang et al., 2010) and clays (Pinto & Pires, 2012) are the well-known adsorbents to remove different kinds of chemical species in water. Other adsorbents include calcium carbonate (Zhao & Gao, 2010), magnesium hydroxide (Lin & Wang, 2009), activated alumina (Ghorai & Pant, 2005) and etc. In this study, parabens are adsorbate,  $\beta$ -CD polymers are adsorbent, and water is the transportation medium. Experimental data will be collected and analysed using adsorption kinetics and adsorption isotherms theory. Adsorption kinetics and adsorption isotherms studies were done to determine the adsorption mechanism of  $\beta$ -CD polymers. The understanding of adsorption are useful for the designing the adsorption



and desorption system (Crini, 2005) and to apply the polymers into adsorption application, like waste water effluent treatment.

### **2.2.1 Adsorption Kinetic**

Generally, adsorption kinetic involves adsorption rate and mass transfer pathways. In this liquid-solid adsorption study, mass transfer may include: mass transfer in solution, mass transfer in solution inside the adsorbent, adsorption at solid adsorption sites, and diffusion within the solid (Hall et al., 1966).

At the time when adsorption of parabens reached a constant value and no further increase of adsorption happened, it is called equilibrium achieved. The time required to achieve equilibrium is called equilibrium time,  $t_e$  (in minutes) and the amount of parabens being adsorbed at  $t_e$  is the maximum adsorption which we called adsorption capacity,  $q_e$  (in mmol of paraben per g of polymer, mmol/g).

Many studies have been done to investigate the adsorption kinetic of  $\beta$ -CD polymers. As reported, adsorption of cationic dyes onto  $\beta$ -CD polymer can reach equilibrium in 120 minutes (Crini, 2008), adsorption of phenol is within 5 minutes, and adsorption of aromatic compounds in water within 2 hours.

### 2.2.1.1 Pseudo-first-order Kinetic Model

Lagergren's pseudo-first-order kinetic model is widely used in adsorption of various solutes from aqueous solution onto different kinds of solid adsorbents (Ho, 2004). Lagergren has developed a kinetic equation to describe the adsorption of liquid-solid systems based on the solid capacity (determined from concentration of solution). This equation is written as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

Where  $q_t$  (mg/g) and  $q_e$  (mg/g) are the amount of parabens adsorbed onto the polymer at time  $t$  (min) and equilibrium and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of pseudo-first-order adsorption. When Equation (1) is integrated in condition  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , it will become

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303} t \quad (2)$$

Then, rearrangement of Equation (2) is done to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

If the experimental data can fit into this kinetic model, graph plotted with  $\log(q_e - q_t)$  versus  $t$  is a straight line. Generally, when adsorption is initiated by diffusion through a boundary, the kinetics will follow pseudo-first-order model in most cases (Crini et al., 2007). On the other hand, diffusion is not the rate determining step if the data do not fit into this equation.

### 2.2.1.2 Pseudo-second-order Kinetic Model

An example of pseudo-second-order kinetic model was described by Coleman et al. (1955) in the binding of Cu(II) by peat. In Coleman et al. study, peat-Cu(II) reaction can be written as:



where P is the concentration of peat functional group. As described by Ho & McKay (1999), if this reaction follow pseudo-second-order kinetic model, the rate law will be:

$$\frac{d(P)_t}{dx} = k[(P)_0 - (P)_t]^2 \quad (5)$$

where  $(P)_t$  and  $(P)_0$  are the number of active sites occupied on the sorbent at time t and active sites available on the adsorbent. Assumption was made that adsorption capacity is proportional to the number of active sites occupied, thus, rate law can be written as

$$\frac{dq_t}{dt} = k[q_e - q_t]^2 \quad (6)$$

$q_e$  and  $q_t$  have the same meaning as described in Section 4.4.1,  $k_2$  (g/mg min) is the equilibrium rate constant of pseudo-second-order kinetic model. Equation (6) can be rearranged as follows:

$$\frac{dq_t}{(q_e - q_t)} = k_2 dt \quad (7)$$

Integrating equation (7) in conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , gives the integrated rate law for pseudo-second-order kinetic model:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (8)$$

Equation (8) is then rearranged to obtain a linear equation:

$$\frac{1}{(q_e - q_t)} = \frac{1 + q_e k_2 t}{q_e}$$

$$q_e - q_t = \frac{q_e}{1 + q_e k_2 t}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$

$$\frac{1}{q_t} = \frac{1 + q_e k_2 t}{q_e^2 k_2 t}$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t \quad (9)$$

The plot of  $\frac{t}{q_t}$  versus  $t$  gives a straight line with  $\frac{1}{q_e}$  and  $\frac{1}{k_2 q_e^2}$  as the slope and intercept if pseudo-second-order is applicable.  $k_2$  and  $q_e$  can be obtained directly from the graph without having to know the parameters beforehand. This kinetic model is more likely to apply onto the whole range of adsorption studies and it shows that chemisorption is the rate determining step (Crini et al., 2007; Ho & McKay, 1999).

### 2.2.1.3 Intraparticle Diffusion Model

Generally, adsorption process include migration of solute from solution to the adsorbent surface, follow by diffusion of the solute through boundary layer to the surface of adsorbent, transport of sorbate from surface to the interior active sites (intraparticle diffusion), and adsorption of the sorbate by active sites via chemical reaction and/or complexation.

Weber and Morris (Weber & Morris, 1963) proposed the intraparticle diffusion model with a linear equation;

$$q_t = k_i t^{\frac{1}{2}} + C \quad (10)$$

$q_t$  and  $t$  have the same meaning as in previous section.  $k_i$  ( $\text{mg/g min}^{1/2}$ ) is the intraparticle diffusion rate constant and its value is the slope of  $q_t$  versus  $t^{1/2}$  plot.  $C$  is the intercept from the plot. The plot will be linear if intraparticle diffusion is involved, and if  $C = 0$ , intraparticle diffusion will be the only rate determining step in the adsorption. If the plot does not pass through origin, it shows that the adsorption mechanism was a multi steps process (Crini, 2005; Crini et al., 2007). The value of  $C$  also shows the abundance of solute adsorbed on the boundary layer.

### 2.2.2 Adsorption Isotherms

Adsorption isotherms were used to describe the equilibrium of the adsorption of a sorbate at the surface of an adsorbent at a given temperature and pH. Isotherms study is generally represented by plotting the equilibrium concentration of a compound in the adsorbent as a function of its equilibrium concentration in solution (Delle Site, 2001). Equilibrium isotherm equations used will describe the isotherm models. Non-linear form equations have to be transformed into linear forms, so that a linear fitting value,  $R^2$  can be obtained.  $R^2$  value which is closest to unity shows that the isotherm model gives the best fit to the experimental data.

In short, adsorption isotherm is use to describe how sorbates interact with the adsorbent and hence, work can be done to optimizing the use of the adsorbent. The isotherm models generally used to understand the adsorption of solute by solid adsorbent are Langmuir and Freundlich models. The symbol and coefficients used in isotherms study are as follow:

$q_e$  = amount of paraben adsorbed at equilibrium, mol/g

$q_{max}$  = maximum adsorption capacity of the adsorbent, mol/g

$C_e$  = concentration of paraben in solution at equilibrium, mol/L

$C_0$  = initial concentration of paraben in solution, mol/L

$K_L$  = Langmuir isotherm constant, L/mol

$K_F$  = Freundlich isotherm constant, mol/g

$R_L$  = Langmuir isotherm constant separation factor

$n_F$  = Freundlich isotherm exponent

### 2.2.2.1 Langmuir Isotherm

Langmuir developed an equilibrium isotherm for the relationship between the amount of gas adsorbed on the surface and the pressure of gas (Langmuir, 1918). The same equation from the model was then extended to liquid systems, where equilibrium involved concentration in solution. The equation was widely applied on various experimental data.

$$q_e = \frac{q_{\max}K_L C_e}{1 + K_L C_e} \quad (11)$$

Several assumptions that applied on this model are (Langmuir, 1916, 1917):

- Adsorption only takes place at specific homogenous sites within the adsorbent, i.e. all the surface adsorption sites have the equal adsorption energy.
- The adsorbent has a finite adsorption capacity and saturation point of adsorption can be reach.
- The adsorption of sorbate is directly proportional to its concentration in solution.

Equation 11 can be rearranged into a linear form,

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max}K_L} \quad (12)$$

From Equation 12, plotting  $\frac{C_e}{q_e}$  against  $C_e$  will obtain a linear plot with  $\frac{1}{q_{\max}}$  as the slope

and  $\frac{1}{q_{\max}K_L}$  as the intercept value. Another important parameter in Langmuir isotherm is

the separation factor,  $R_L$  which defined as (Hall et al., 1966):

$$R_L = \frac{1}{1 + K_L C_0} \quad (13)$$

$R_L = 0$  for irreversible adsorption,  $0 < R_L < 1$  for favourable,  $R_L = 1$  for linear, and  $R_L > 1$  for unfavourable equilibrium (Hall et al., 1966).

### 2.2.2.2 Freundlich Isotherm

Freundlich equation has been used for a hundred years to describe the adsorption equilibrium (Freundlich, 1906). This model applied to the adsorption on heterogenous surfaces which have different adsorption sites with different energy of adsorption. Freundlich equation is as below:

$$q_e = K_F C_e^{\frac{1}{n_F}} \quad (14)$$

As shown in the equation, the adsorption capacity,  $q_e$  increases as the concentration of sorbate increases.  $K_F$  is the Freundlich constant that related to multilayer adsorption capacity and  $\frac{1}{n_F}$  is the heterogeneity factor;  $n_F$  obtain from the deviation from the linear adsorption (adsorption increase linearly as the solution concentration increase) (Crini et al., 2007). The value of  $\frac{1}{n_F}$  gives an idea for the process design of an adsorption system (Tseng & Wu, 2008). If  $n_F < 1$ , it is a chemical adsorption (unfavourable),  $n_F = 1$  for linear adsorption, and  $n_F > 1$  for favourable physical adsorption. Tseng & Wu describe the value of  $n_F$  in further details as in Table 2.2 and it can be used to predict the adsorbent consumption in a designed adsorption system (Tseng & Wu, 2008).

Equation 14 was then expressed in a linear form:

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \quad (15)$$

The experimental data was plotted with  $\log q_e$  versus  $\log C_e$  with  $\log K_F$  as intercept and  $\frac{1}{n_F}$  as gradient for the plot. Linear fitting,  $R^2$  values were used to indicate the suitability of the Freundlich isotherm.  $R^2=1.0$  indicate the highest suitability.



**Table 2.2: Relationship between  $n_F$  value in Freundlich equation, isotherm curve type and its favourable level. (Tseng & Wu, 2008)**

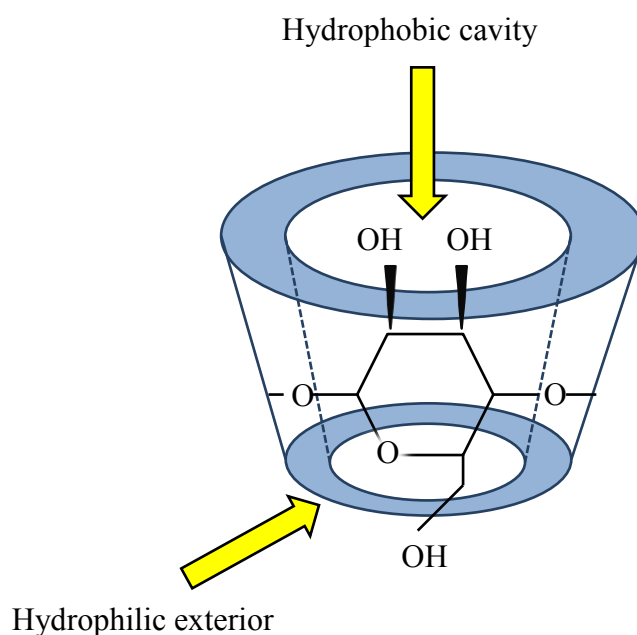
$n_F$	Isotherm curve type	Favourable level
$n_F > 100$	Pseudo-rectangular	Pseudo-irreversible
$100 > n_F > 10$	Hastily rise	Strong favourable
$10 > n_F > 2$	Mildly rise	Favourable
$2 > n_F > 1$	Pseudo-linear	Pseudo-linear
$n_F = 1$	Linear	Linear
$n_F < 1$	Concave up	Unfavourable

### 2.3 Adsorbent

Adsorption is proposed due to the environmental aspect as discussed in section 2.1.6, and hence, adsorbent used in the adsorption process should be environmental friendly too. Activated carbon is the well-known adsorbent for adsorption process (Adhoum & Monser, 2004; Babel & Kurniawan, 2003; Méndez-Díaz et al., 2012; Wang et al., 2010), however, the high cost of production and regeneration led to the search for more economic adsorbents (Crini, 2005). Therefore, biopolymers and natural molecules are the first choice since their production and disposal are more harmless to human and environment. Natural polymers that are commonly used are chitin, chitosan, starch, and cyclodextrins (Crini, 2005). Among these, cyclodextrins have gained prominence in recent years due to their special and very useful chemical properties (Szejtli, 2004).

### 2.3.1 Cyclodextrins

Cyclodextrins (CD) was discovered on 1891, since then, there are explosion-like increasing number of publications and patents related to cyclodextrin (Szejtli, 2004). CDs are macrocyclic oligosaccharides that commonly consist of 6, 7, or 8 glucopyranose units that linked together by  $\alpha$ -1,4-glucosidic bonds (Szejtli, 1998). CDs that contain 6, 7, and 8 glucopyranose units are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrin respectively. CDs with 9 to several hundred units of glucopyranose exist naturally (Andersson et al., 1992; Takaha et al., 1996), but less than 6 glucopyranose units of CD is thought to be too strained to exist based on model calculations (Szejtli, 1988). The typical structure of CD is show in Figure 2.2.



**Figure 2.2: Structure of cyclodextrin**

Cyclodextrin molecules have a hydrophilic exterior and a hydrophobic cavity. The hydrophobic cavity can entrap different kinds of compounds including organic, inorganic, organometallic, and metalloorganic, which may be neutral, cationic, anionic, or even radical (Stoddart, 1989).

The production of cyclodextrins is relatively simple. They are produced from intramolecular transglycosylation reaction of the degradation of starch by cyclodextrin glucanotransferase (CGTase) enzyme (Szejtli, 1998). The synthesized product of CGTases is a mixture of the three main types of cyclodextrins.  $\beta$ -CD can be purified most easily since it has the lowest water solubility (1.85 g/ 100 mL, room temperature) among the three cyclodextrins.  $\beta$ -CD being chosen as the main component from synthesis of adsorbent in this study because it is most accessible and low-priced (Del Valle, 2004). Table 2.3 shows some of the physical properties of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD.

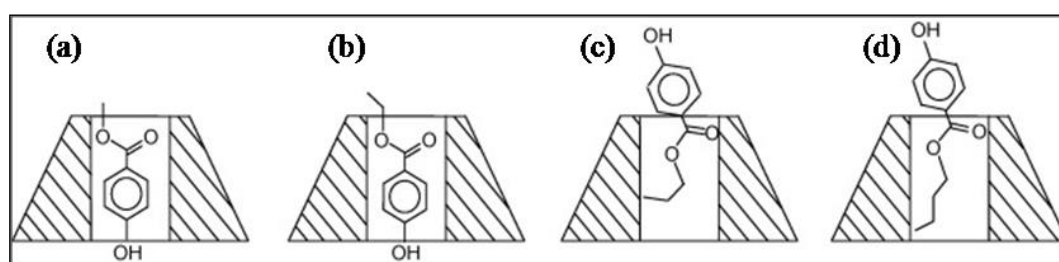
**Table 2.3: Some physical properties of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrin**

<b>Properties</b>	<b><math>\alpha</math>-CD</b>	<b><math>\beta</math>-CD</b>	<b><math>\gamma</math>-CD</b>
<b>Number of glucopyranose units</b>	6	7	8
<b>Molecular weight</b>	972	1134	1296
<b>Approximate inner cavity diameter (pm)</b>	500	620	800
<b>Approximate outer diameter (pm)</b>	1460	1540	1750
<b>Approximate volume of cavity (<math>10^6 \text{ pm}^3</math>)</b>	174	262	427
<b>Solubility in water (g/100 mL, room temperature)</b>	14.5	1.85	23.2
<b>Melting temperature range (<math>^{\circ}\text{C}</math>)</b>	255-260	255-265	240-245
<b>Crystal water content (% of weight)</b>	10.2	13-15	8-18
<b>Water molecules in cavity</b>	6	11	17

### 2.3.2 $\beta$ -cyclodextrin-parabens Inclusion Complex

$\beta$ -CD can easily form inclusion complex with its guest compounds. Previous studies had shown that MP, EP, PP, and BuP can form inclusion complex with  $\beta$ -CD (Chan et al., 2000; de Vries & Caira, 2008; de Vries et al., 2009).

According to Chan et al. (2000), the degree of interaction between  $\beta$ -CD and parabens follows  $EP < PP < MP < BuP$ . For EP, PP, and BuP, the extent of interaction increase regularly due to the decrease of steric strain by appropriate orientation of alkyl chain. MP shows a better extent of interaction because of the small size that can fit well into the cavity of  $\beta$ -CD. Both hydrophobicity and steric energy can influence the degree of interaction between  $\beta$ -CD and parabens. Figure 2.3 shows the formation of inclusion complexes of parabens in  $\beta$ -CD as described by Chan et al. On the other hand, de Vries & Caira (2008) proposed that the orientation of MP and EP in inclusion complexes are influenced by steric interactions and the orientation of PP and BuP are affected by hydrophobicity.



**Figure 2.3: Inclusion complexes of (a) methyl paraben, (b) ethyl paraben, (c) propyl paraben, and (d) butyl paraben (Chan et al., 2000)**

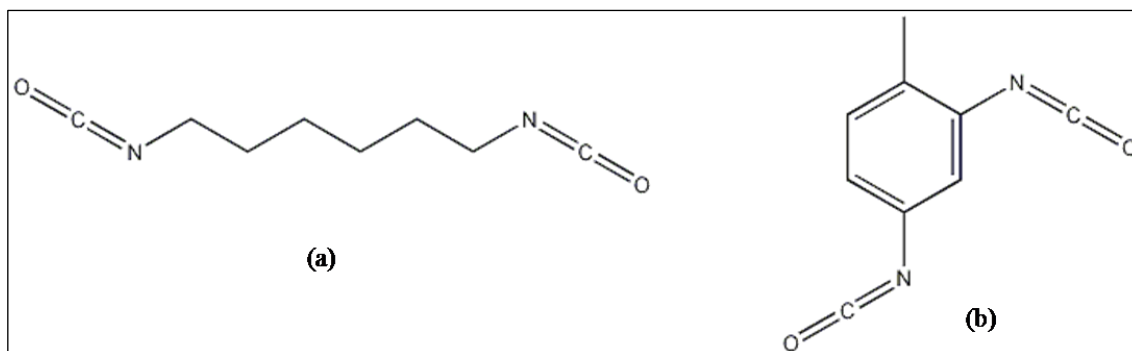
Hence,  $\beta$ -CD shows the suitability to be used as an adsorbent to remove parabens from water. However, its solubility in water makes it inconvenient to be used as an adsorbent for aqueous solution (Mamba et al., 2007). Therefore,  $\beta$ -CD polymers which have lower water solubility were synthesized.

### 2.3.3 $\beta$ -cyclodextrin Cross-linked Polymers

$\beta$ -CD polymers had been used for various purposes including separation of particles from water and pharmaceutical purposes. The hydrophobic cavities of  $\beta$ -CD in the insoluble polymer chain make them very useful to separate soluble or trace particles from water.  $\beta$ -CD polymers had been widely use as solid-phase extraction material (Bhaskar et al., 2004), adsorbent for wastewater treatment (Crini, 2005), adsorbent for pre-concentration of trace elements for further analysis (Zhu et al., 2009) and etc.  $\beta$ -CD polymers are also useful in delivering drugs to target organs. In addition,  $\beta$ -CD polymers used for drug delivery are soluble and drugs involved are usually lipophilic and have low-molecular weight. Drug molecule will form inclusion complex with  $\beta$ -CD which is a physical mixture that permits a greater degree of control of drug release.

In this study,  $\beta$ -CD polymers are synthesized using cross-linking reactions, i.e.  $\beta$ -CD units are linked together by a cross-linker. Various cross-linker are used by researchers, e.g. epichlorohydrin (Crini et al., 2007), 1,6-hexamethylene diisocyanate (García-Zubiri et al., 2009; Zha et al., 2008), and toluene diisocyanate (García-Zubiri et al., 2009). Hydrophilicity of the polymer is the most important properties for the purpose of removing particles from wastewater. Polymers with different physical and chemical properties can be formed by using different cross-linker, ratio of  $\beta$ -CD to cross-linker, and condition during reaction., Two types of  $\beta$ -CD polymers are prepared, one using 1,6-hexamethylene diisocyanate (HMDI) and the other using toluene-2,6-diisocyanate (TDI) as cross-linker. These two cross-linkers are chosen due to their low-priced and ability of forming highly insoluble cross-linked polymers. Chemical structure of HMDI and TDI are shown in Figure 2.4. HDMI consist of an aliphatic

group while TDI consist an aromatic group, hence the effects of adsorbent chemical structure can be studied.



**Figure 2.4: Chemical structure of (a) HMDI and (b) TDI**

### 3.1 Reagents, Solutions, and Instrumentation

All reagents were used without further purification unless indicated otherwise.  $\beta$ -CD hydrate, 99% was purchased from Acros, Hungary. Methyl paraben (MP), ethyl paraben (EP), propyl paraben (Bhaskar et al.), and benzyl paraben (BP) were supplied by Fluka, United Kingdom. Toluene-2,6-diisocyanate (TDI) (90%) was purchased from Fluka, Germany. 1,6-Hexamethylene diisocyanate (HMDI) (90%) was obtained from Aldrich, United States of America and pre-filtered methanol (HPLC grade) was supplied by Merck, Germany. N,N-dimethylformamide (DMF) of analytical grade reagent from Fisher Scientific, United Kingdom, was further purified by distillation.

Single-solute stock solutions with concentration of 100 mg/L paraben were prepared in boiled ultrapure deionised water (Elga, United States of America). Mix-solute solution containing 100 mg/L each of MP, EP, PP, and BP was also prepared in the same manner. Working solutions were prepared daily by appropriate dilution of the stock solution.

Characterization of  $\beta$ -CD polymers were done by fourier transform infrared spectroscopy (FT-IR) and CHN elemental analysis. FT-IR spectra of polymers were taken on a Perkin-Elmer RX1 FT-IR spectrometer from 400–4000  $\text{cm}^{-1}$ . The elemental composition of the  $\beta$ -CD polymers was examined by Perkin-Elmer 2400 Series II CHNS/O Analyzer.

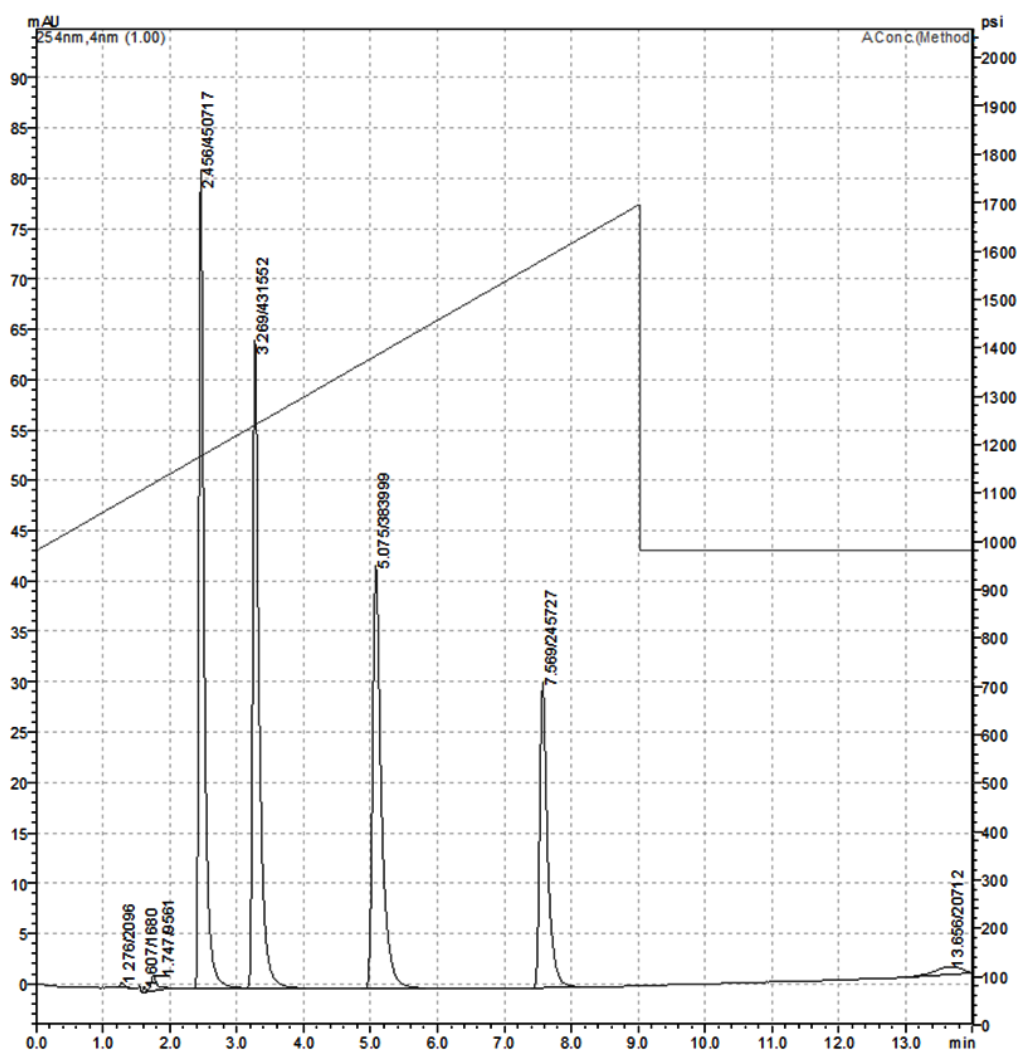
### 3.2 Determination of Parabens Concentration Using High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) was used to determine the concentration of parabens before and after removal. The concentrations of parabens were calculated from:

$$\frac{\text{Area of the peak of paraben in solution}}{\text{Area of peak of paraben in stock solution}} \times 100 \text{ mg/L} \quad (16)$$

HPLC system used consisted of a LC-20AT pump, a SPD-M20A diode array detector, a SIL-20AHT auto sampler, a CTO-20AC column oven and CBM-20A communication bus module (Shimadzu, Japan). The parabens were separated on a reversed-phase Chromolith RP-18 monolithic column (100 mm × 4.6 mm i.d., Merck, Germany). LC Solution Software (release 1.23 SPI) was used to monitor the LC system and data acquisition. The mobile phase consisted of methanol (eluent A) and water (eluent B), gradient elution: 0 (zero) minutes, A 50% and B 50%, 9 minutes, A 79.8% and B 20.2%. Separations were accomplished at a flow rate of 1.00 mL/min at 30°C and an injection volume of 20 µL at detection wavelength of 254 nm. Sample solutions were filtered with 0.2 µm of syringe filter before injection. As shown in Figure 3.1, MP can be separated at 2.456 minute, EP at 3.269 minute, PP at 5.075 minute and BP at 7.569 minute. All the paraben peaks do not overlap on each other.





**Figure 3.1: HPLC chromatogram for determination of MP, EP, PP, and BP concentration in aqueous solution**

### 3.3 Preparation of $\beta$ -CD Cross-linked Polymers

$\beta$ -CD polymers were prepared according to Bhaskar et al. (2004). First, 10 g of  $\beta$ -CD was dissolved in 30 mL of DMF at room temperature. A calculated amount of cross-linker (HMDI or TDI) was then added dropwise and the mixture stirred for 4 hours at 70°C. Polymer formed as white precipitate by the addition of excess methanol. The polymer was then filtered, washed with methanol, and dried in 70°C oven overnight. Dried polymer was ground and sieved using a 53  $\mu$ m sieve before use. Different ratio of  $\beta$ -CD:cross-linker polymer was prepared and the polymer with the highest adsorption capacity towards parabens in each series was chosen for further study. The preparation

of polymer is divided into two series, one using HMDI and another using TDI as cross-linking agent. Each of the series has eight different polymers with ratio of  $\beta$ -CD:cross-linker: 1:4(a), 1:7(b), 1:10(c), 1:13(d), 1:16(e), 1:19(f), and 1:21(g).

### **3.4 Characterization of $\beta$ -CD Cross-linked Polymers**

FT-IR spectra of  $\beta$ -CD polymers were taken to determine the formation of  $\beta$ -CD polymers. The samples were prepared in pellet form using spectroscopic grade KBr powder. Wavelength used is from 400 to 4000  $\text{cm}^{-1}$ . The amount of  $\beta$ -CD units in a given weight and molar ratio of  $\beta$ -CD: cross-linker in the polymers were determined by CHNS/O analyser. Both FT-IR spectrometer and CHNS/O analyser used are described in Section 3.1.

Water adsorption property is one of the factors that will have an effect on adsorption of parabens onto  $\beta$ -CD polymers. Polymers were first packed into an empty solid-phase extraction cartridge and dried in a vacuum desiccator for 24 hours. The cartridge was then attached to a vacuum manifold (Lichrolut, Merck, Germany) and ultrapure deionised water was used to soak the cartridge for 24 hours. After soaking, excess water was drained off at a flow rate of 2 mL/min. Weights of polymers before and after soaking was recorded. Procedures were repeated thrice.

### **3.5 Adsorption of Parabens in Aqueous Solutions onto $\beta$ -CD Cross-linked Polymer**

About 0.05 g of polymer was added into a flask containing parabens solution and shaken at 150 rpm (orbital shaker, YIHDER TS-560, Taiwan). Concentration of parabens in solution was determined before adding polymer and after adsorption. The supernatant was filtered using 0.2  $\mu\text{m}$  pore size polytetrafluoroethylene (PTFE) syringe before HPLC.

#### **3.5.1 Comparison of Adsorption Ability among Polymers**

A study was conducted to compare the adsorption towards parabens among all the polymers prepared. Concentration of solution used was 5 mL of 10 mg/L of each parabens. Supernatants were collected at the interval time of 2 hours and 24 hours after polymer was added into the solution. Polymers with the highest adsorption from each cross-linker will be chosen for further study.

#### **3.5.2 Adsorption Kinetic**

About 0.05 g of  $\beta$ -CD-TDI was added into a flask of 100 mg/L of parabens solution. Two types of solution were prepared: single paraben solutions and a mixture of four parabens solution. Samples were collected at time 5, 15, 30, 45, 60, 80, 100, 120, 150, 180, 240, 300, 360, 420, and 480 minutes. All experiments were done at room temperature.

### **3.5.3 Adsorption Isotherm**

Solutions used were same as the solutions for the adsorption kinetic study. Five different concentrations were used (0.05, 0.10, 0.20, 0.30, and 0.40 mmol/L) for both types of solutions. Experiments were done in 15, 30, 45, and 65°C of temperature and the polymers were filtered after 8 hours of adsorption. No adjustment was done to the pH of the solution. The pH of the solutions was 5.45.

### **3.6 Reusability**

The same polymers were repeatedly used to determine the efficiency of reused polymers. About 0.2 g of polymer was added in the 100 mL of solution containing 100 mg/L of mix parabens and stirred for 5 hours before the supernatant was filtered. Then, the polymer was dried in 70°C oven overnight. 10 mL of methanol was used to elute the adsorbed parabens after drying. Polymer dried in 70°C oven overnight again after parabens were eluted by methanol. The same experiment was repeated for 9 additional cycles to study the efficiency of the polymers.

### **3.7 Application of Polymer into Real Samples**

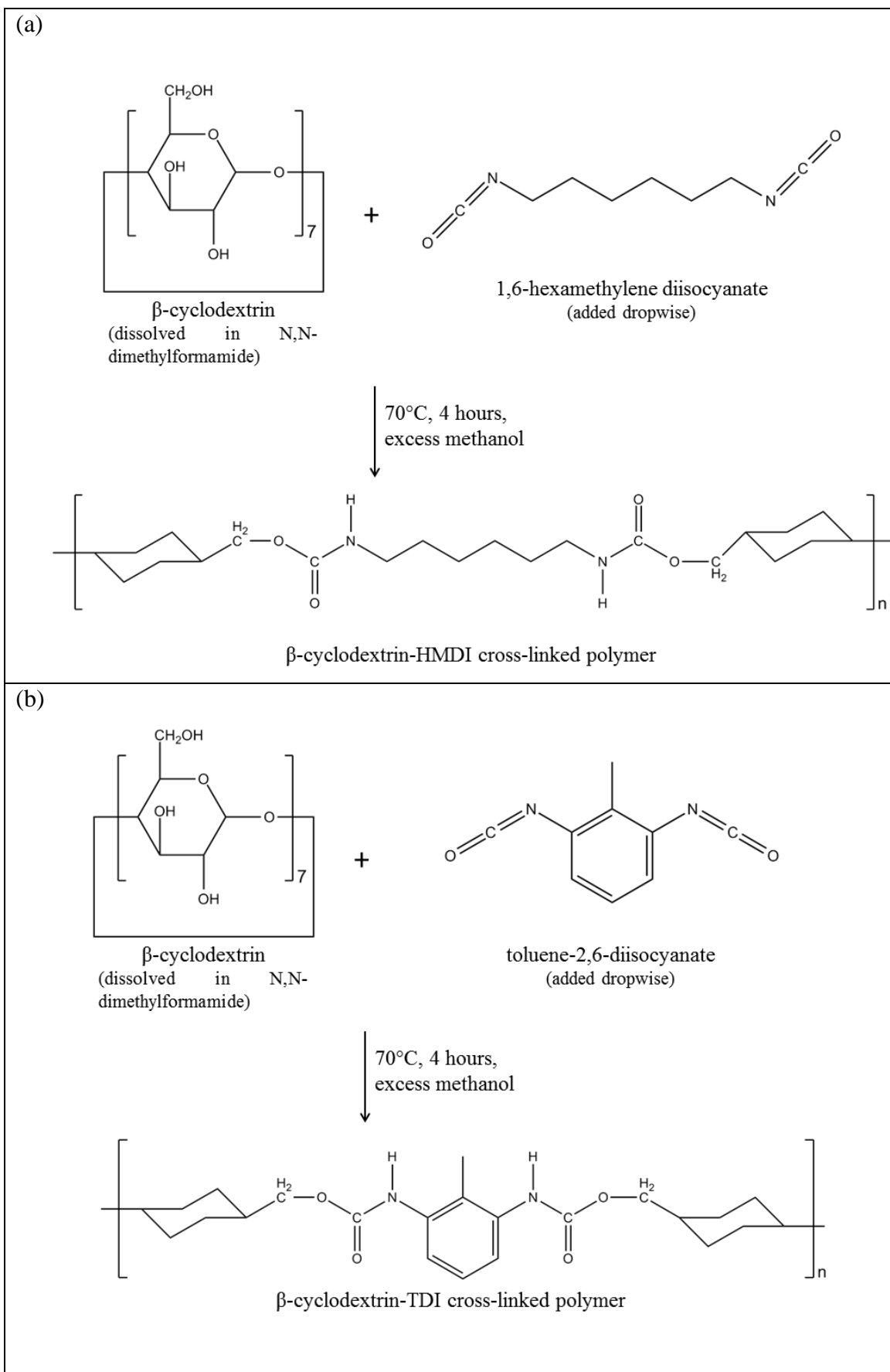
The  $\beta$ -CD polymers prepared were used on the real samples obtained from environmental samples and commercial products in order to determine their efficiency in different matrices. 10 different samples were used in this study. These samples were divided into 3 categories, i.e., water samples, aqueous commercial products and organic based commercial products. Water samples were tap water (from University of Malaya), bottled drinking water (purchased from hypermarket in Kuala Lumpur), swimming pool

water (collected from swimming pool in Sports Centre, University of Malaya), river water (from Sungai Air Batu, Kuala Lumpur), and waste water effluent (from sewage treatment plant in Kuala Lumpur). 50 mL of each sample was used for this study. Soy sauce and mouth rinse were used as aqueous commercial products. Each sample was diluted with 50 mL of deionised water. Two different brands of facial cleanser and a body lotion were used as organic based commercial products. 1 g of each of the samples was sonicated for 30 minutes with 50 mL of deionised water. Parabens can be found in the ingredients list of all commercial samples except soy sauce.

All samples were spiked with 100  $\mu$ L of 100 mg/L of parabens mixture solution. Then, about 0.05 g of  $\beta$ -CD polymer was added to the mixture and shaken for 8 hours. Concentrations of parabens in samples were determined before and after adsorption.

#### 4.1 Characterization of Polymers

Both of the cross-linkers are generally utilized as a strong cross-linker of amino or hydroxyl groups since they possess two isocyanate groups ( $-N=C=O$ ). A proton from the hydroxyl group at  $\beta$ -CD reacts with the nitrogen atom at isocyanate group by electrophilic attack to form urethane product ( $-NH-COO-$ ) (Che et al., 2007; Prabakaran & Mano, 2006). Figure 4.1 shows the preparation of (a)  $\beta$ -CD-HMDI and (b)  $\beta$ -CD-TDI cross-linked polymers.

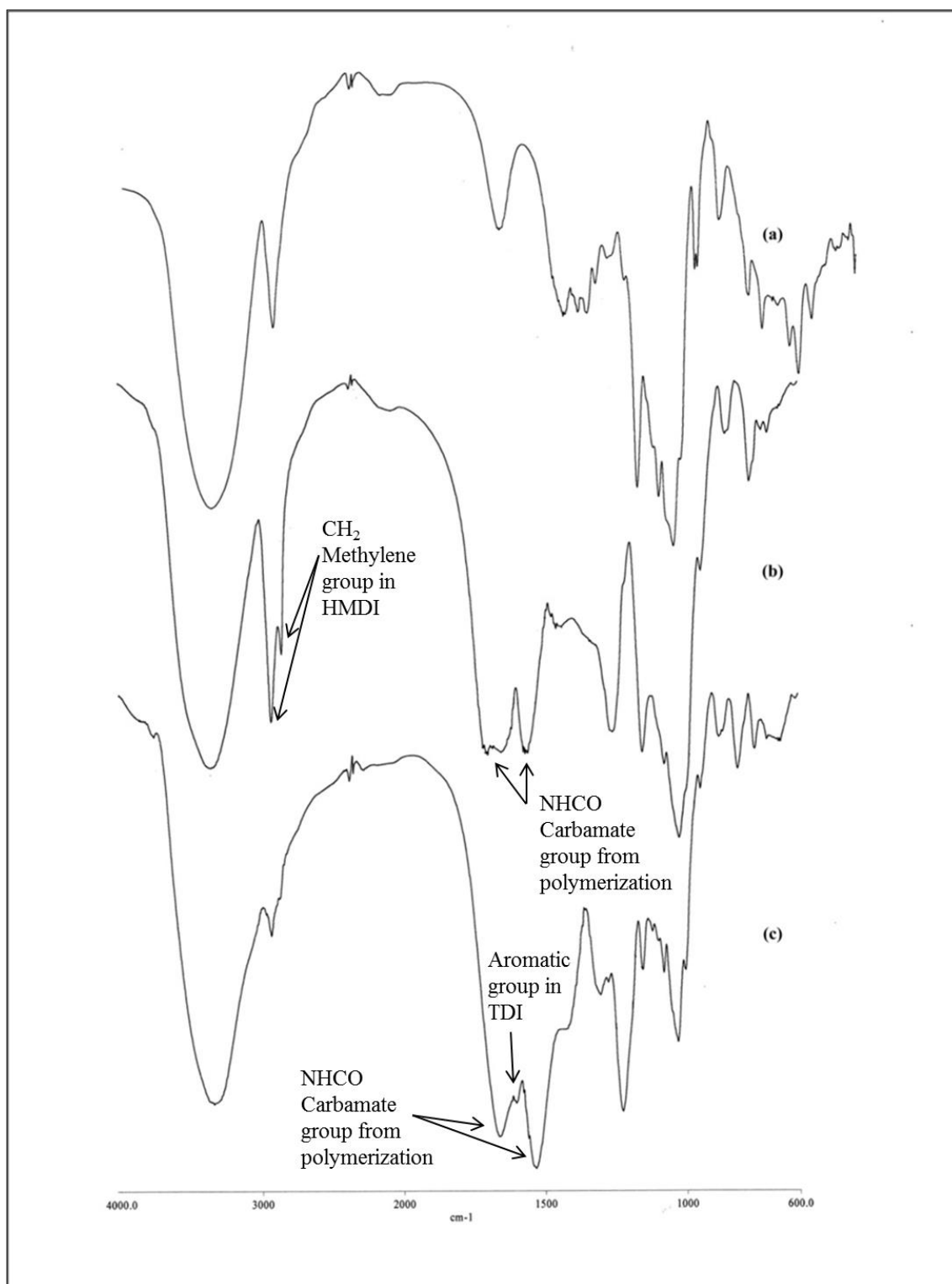


**Figure 4.1: Preparation of (a)  $\beta$ -CD-HMDI and (b)  $\beta$ -CD-TDI cross-linked polymers**

#### 4.1.1 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra for  $\beta$ -CD,  $\beta$ -CD-HMDI and  $\beta$ -CD-TDI are shown in Figure 4.2(a), (b), and (c) respectively. The difference between the three spectra indicates that  $\beta$ -CD cross-linked polymers are formed. Similar spectra were described by Bhaskar et al. Spectra of  $\beta$ -CD polymers are similar to  $\beta$ -CD, showing that  $\beta$ -CD is the main component in  $\beta$ -CD polymers. For Figure 4.2 (b) and (c), the absorption at  $2270\text{ cm}^{-1}$  corresponding to isocyanate group were absent indicating that  $-\text{N}=\text{C}=\text{O}$  group from cross-linker is covalently bonded to  $-\text{OH}$  group from  $\beta$ -CD to form the polymers. The FT-IR spectrum of  $\beta$ -CD-HMDI show characteristic absorption bands that correspond to both of the NH and C=O group ( $3364$  and  $1719\text{ cm}^{-1}$ ). Stretching of NHCO from formation of carbamate group is observed at  $1570\text{ cm}^{-1}$ . In Figure 4.2 (b), strong bands at  $2860$  and  $2934\text{ cm}^{-1}$  correspond to methylene group in HMDI. For  $\beta$ -CD-TDI, the characteristic absorption bands from  $\beta$ -CD were same as observed in  $\beta$ -CD-HMDI spectrum. However, the bands at  $1535$  and  $1603\text{ cm}^{-1}$  in the spectrum show the existence of aromatic group in the polymer. Therefore, we can conclude that polymerization occur and completely between  $\beta$ -CD and both of the cross-linker.





**Figure 4.2: FT-IR spectra for (a) β-CD, (b) β-CD-HMDI, and (c) β-CD-TDI**

#### 4.1.2 CHN Elemental Analysis

Three polymers are chosen for the analysis:  $\beta$ -CD-HMDI(a),  $\beta$ -CD-TDI(a), and  $\beta$ -CD-TDI(b).  $\beta$ -CD-HMDI(a) and  $\beta$ -CD-TDI(b) were chosen because both of them have the highest adsorption towards parabens in their series (Section 4.2). Table 4.1 represents the percentage of composition of various elements in  $\beta$ -CD and these three  $\beta$ -CD polymers.  $\beta$ -CD-TDI(a) is chosen for comparison among these three polymer as  $\beta$ -CD-TDI have same amount of cross-linker used in  $\beta$ -CD-HMDI(a). Percentage of  $\beta$ -CD in the prepared polymer is higher in  $\beta$ -CD-HMDI(a) compared with  $\beta$ -CD-TDI(a). TDI, being an aromatic isocyanate with highly unsaturated bonds is more reactive than HMDI, which is an aliphatic isocyanate (Che et al., 2007; Prabaharan & Mano, 2006; Sekkar et al., 1997). Thus,  $\beta$ -CD-TDI polymers may have more TDI units than expected.

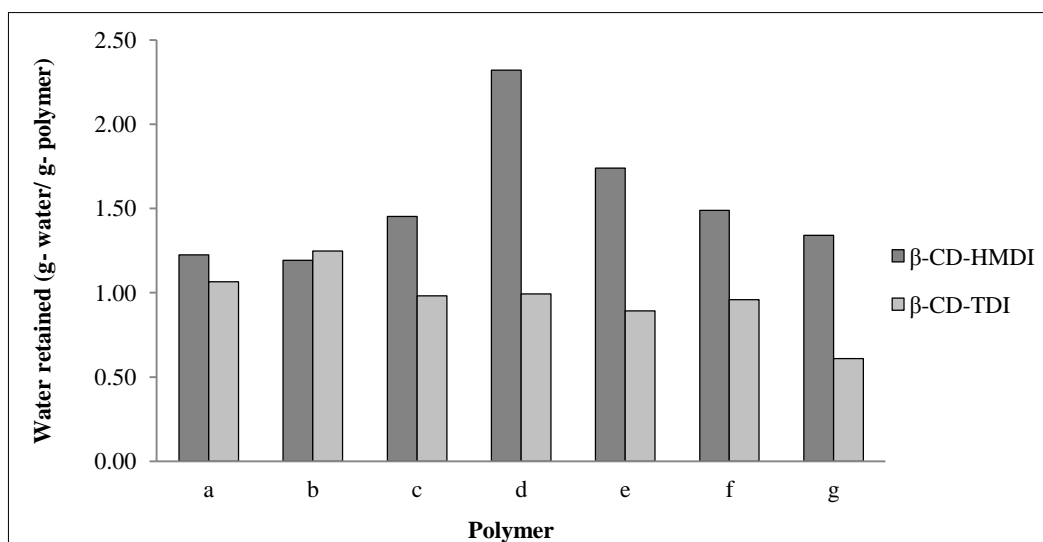
**Table 4.1: Elemental composition analysis for  $\beta$ -CD,  $\beta$ -CD-HMDI(a),  $\beta$ -CD-TDI(a), and  $\beta$ -CD-TDI(b)**

Sample	%C	%H	%N	Amount of $\beta$ -CD		Amount of cross-linker		Ratio of $\beta$ -CD: cross-linker	
				( $10^{-4}$ mol/g)	(%)	( $10^{-4}$ mol/g)	(%)	Expected ratio	Polymer prepared
$\beta$ -CD	38.1	5.9	0.0	-	-	-	-	-	-
$\beta$ -CD-HMDI (a)	46.6	7.3	6.6	4.8	17.0	23.4	83.0	1: 4	1: 5
$\beta$ -CD-TDI (a)	50.5	6.1	8.8	3.3	9.6	31.3	90.4	1: 4	1: 9
$\beta$ -CD-TDI (b)	52.8	5.9	10.8	2.2	5.3	38.6	94.	1: 7	1: 18

#### 4.1.3 Water Adsorption of $\beta$ -CD Polymers

The water adsorption property of all polymer were examined. Figure 4.3 shows that  $\beta$ -CD-HMDI polymers adsorbed more water than  $\beta$ -CD-TDI polymers. This can be explained by number of  $\beta$ -CD units in  $\beta$ -CD-HMDI in the same molar ratio of cross-linker (Table 4.1). Hydrophobic cavity of  $\beta$ -CD can be filled by 11 water molecules

(Dodziuk, 2006), therefore  $\beta$ -CD-HMDI can adsorb more water. When percentage of  $\beta$ -CD units increases, the water adsorption decreases. However, this phenomenon only occurs in  $\beta$ -CD-TDI polymers. Thus, cross-linkers may play a main role in water adsorption. TDI has poor interaction with water because it has an aromatic ring; therefore, polymers that contain TDI are more hydrophobic. This can be simply explained as water adsorption decreases when percentage of TDI increases. Water adsorption in  $\beta$ -CD-HMDI increases with the increasing of HMDI molar ratio since water molecules may be trapped in the polymer network other than enter  $\beta$ -CD cavity. From the elemental analysis results, the cross-linking of  $\beta$ -CD and HMDI is less than  $\beta$ -CD-TDI, therefore, there are much more  $-OH$  group from  $\beta$ -CD that are not cross-linked. These  $-OH$  group may form hydrogen bonding easily with water molecules. When the molar ratio of HMDI increases until 1: 16, water adsorption decreases as the molar ratio of HMDI increases due to the low percentage of  $\beta$ -CD and  $\beta$ -CD units are highly cross-linked.



**Figure 4.3: Water adsorption by  $\beta$ -CD-HMDI and  $\beta$ -CD-TDI polymers (molar ratio of  $\beta$ -CD: cross-linker: 1: 4 (a), 1: 7 (b), 1:10 (c), 1:13 (d), 1:16 (e), 1:19 (f), 1:21 (g))**

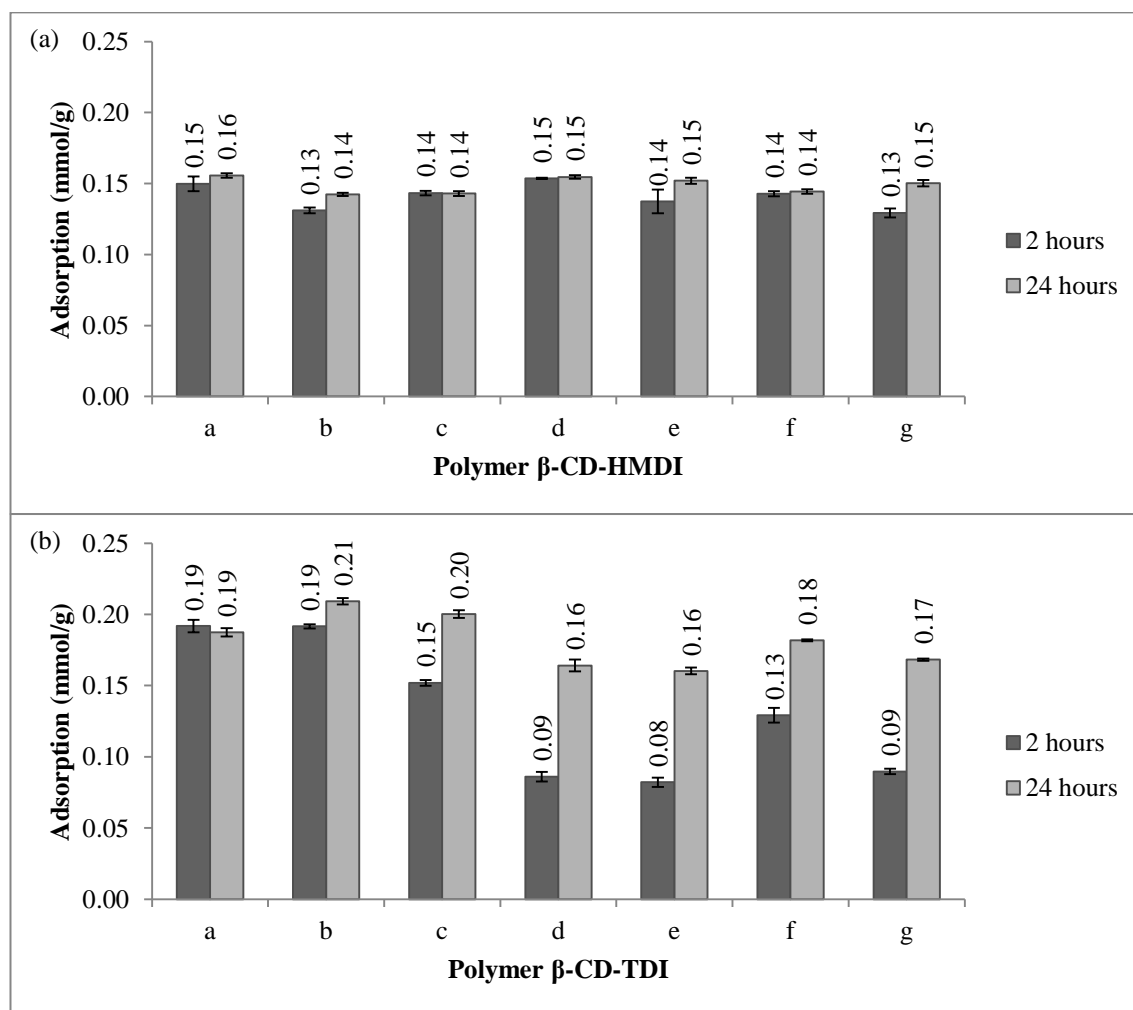
## 4.2 Effect of Types and Amount of Cross-linker

All the polymers prepared were used for adsorption of parabens to evaluate the influence of types and amount of cross-linker. After this study, polymer with the highest adsorption will be chosen for further studies. All  $\beta$ -CD polymers show good adsorption towards parabens as shown in Figure 4.4. For  $\beta$ -CD-HMDI polymers, the different is in amount of HMDI and increase of contact time does not affect the adsorption of parabens very much. However, the adsorptions onto  $\beta$ -CD-TDI have a marked difference with different amount of TDI, and appear to have a bigger difference between the contact time of two and 24 hours (Figure 4.4 (b)). These results show that adsorption of parabens onto  $\beta$ -CD polymers are dependent on the percentage of TDI in the polymers, but not on the amount of HMDI.

Figure 4.4 (b) shows that the adsorption of parabens decreasing when the amount of TDI increase. As discussed in Section 4.1.3,  $\beta$ -CD-TDI polymers are more hydrophobic, therefore, the diffusion of water is less, which makes the swelling of polymer network not enough for big sorbate molecules to penetrate the sorbent linking chains (García-Zubiri et al., 2009). However, penetration of parabens molecules not only depends on water as the 'carrier', but they can move across the polymer network through the cavity of  $\beta$ -CD (García-Zubiri et al., 2009). Hence,  $\beta$ -CD-HMDI with higher percentage of  $\beta$ -CD units shows a faster adsorption rate as compare to  $\beta$ -CD-TDI.

Apart from adsorption rate, Figure 4.4 also shows that the adsorption of parabens on  $\beta$ -CD-TDI polymer is higher than that of the  $\beta$ -CD-HMDI polymer. This is due to the  $\beta$ -CD-TDI has aromatic rings which gives advantage to adsorb parabens since it is more hydrophobic. Other than hydrophobicity,  $\pi$ - $\pi$  interaction derived from the

aromatic rings may also have some effects on the adsorption behaviour (Huang et al., 2007; Pompeua et al., 2010).  $\beta$ -CD-TDI has advantage of forming  $\pi$ - $\pi$  interaction with the parabens molecules. Therefore,  $\beta$ -CD-TDI has better adsorption ability compare to  $\beta$ -CD-HMDI.



**Figure 4.4: Comparison of adsorption (mmol/g) towards parabens by varying (a)  $\beta$ -CD-HMDI and (b)  $\beta$ -CD-TDI polymers. Molar ratio of  $\beta$ -CD: cross-linker - 1:4 (a), 1:7 (b), 1:10 (c), 1:13 (d), 1:16 (e), 1:19 (f), and 1:21 (g)**

Both hydrophobicity interaction and  $\pi$ - $\pi$  interaction are better between  $\beta$ -CD-TDI and parabens molecules compare to  $\beta$ -CD-HMDI.  $\beta$ -CD-TDI(b) is chosen for further studies because it has the highest adsorption toward parabens among all the polymers. This polymer is also economically favoured since it is prepared from lower amount of cross-linker.

### 4.3 Adsorption Behaviour of Polymer towards Parabens

Molecular interactions between solute-adsorbent, solute-solvent, and solvent-adsorbent can explain the adsorption behaviour (Crini et al., 2002). In this study, solutes are parabens, solvent is water, and adsorbent is  $\beta$ -CD-TDI polymer. Comparison of adsorption capacities in two different solutions (single paraben solutions and a mixture of four parabens solution) was examined in order to understand the adsorption behaviour of  $\beta$ -CD-TDI polymer towards parabens. The results are shown in Table 4.2.

**Table 4.2: Adsorption capacities of  $\beta$ -CD-TDI(b) in single paraben solutions and a mixture of four parabens solution**

Paraben	Single paraben solutions		A mixture of four parabens solution	
	Adsorption capacity (mmol/g)	R.S.D.(%) n = 3	Adsorption capacity (mmol/g)	R.S.D.(%) n = 3
<b>MP</b>	0.1019	3.03	0.0324	5.42
<b>EP</b>	0.1286	3.22	0.0508	6.31
<b>PP</b>	0.2551	3.04	0.1150	2.73
<b>BP</b>	0.3699	3.44	0.3570	9.69
		<b>Total</b>	0.5552	

Adsorption capacity of each paraben in single paraben solutions is higher than those of in a mixture of four parabens solution. This is probably because; there is a competition among the four parabens to be adsorbed into a limited cavity in solution containing the mixture of parabens.

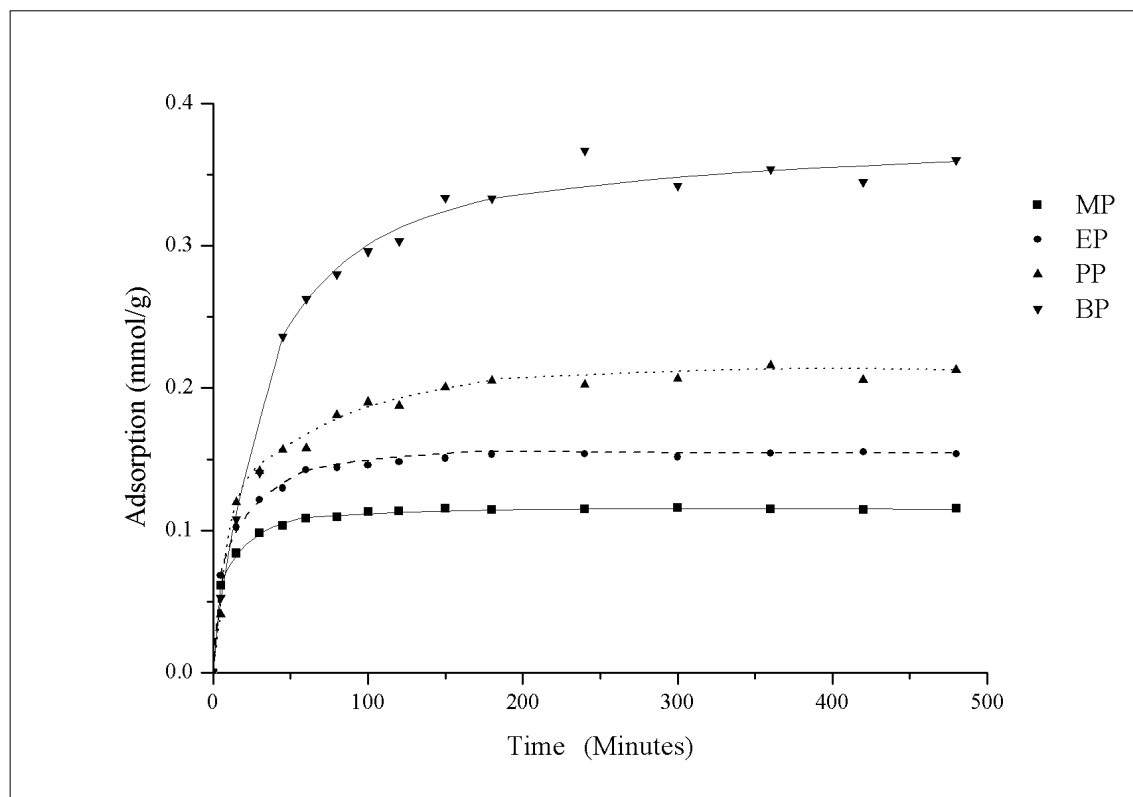
In aqueous solution, the water molecules will fill in to the apolar cyclodextrin's cavity, but, this polar-apolar interaction is energetically unfavourable (Szejtli, 1998). Hence, water molecules will be easily substituted by parabens molecules which are much more apolar. On the other hand, parabens are able to form hydrogen bonding with

water molecules in the solution, but, as the size of paraben molecules increase, the polarity of paraben decreases. Therefore, the interaction between solute-adsorbent will be stronger than solute-solvent as the molecular size increases. The adsorption capacities follows BP>PP>EP>MP. BP shows the highest adsorption either in single paraben solution or a mixture of four parabens solution. This is because the interaction between BP and water is least favourable since BP is least polar with two aromatic rings. BP is the only parabens that has 2 aromatic rings which can have a better interaction with TDI through  $\pi$ - $\pi$  interaction (Huang et al., 2007; Pompeua et al., 2010). Thus, BP is most easily adsorbed due to the weakest solute-solvent interaction and the strongest solute-adsorbent interaction.

#### **4.4 Adsorption Kinetics**

Adsorptions of parabens were measured as a function of contact time (Figure 4.5). Time to reach adsorption equilibrium,  $t_e$  increases as molecular size increases.  $t_e$  for all adsorption are within 100 minutes except adsorption of PP and BP are within 180 minutes as shown in Figure 4.5. Adsorption of parabens is fast at the initial stage as parabens molecules attached to the polymer in a very fast rate, then the adsorption decrease gradually due to the decreasing amount of adsorption sites that is available in the polymer network. After that, the amount of sorbate becomes constant when equilibrium is achieved. The adsorption curves are single, smooth and continuous show the possibility of monolayer coverage of parabens on the surface of polymer. All the results obtained are similar to the work done by Crini et al. (2007). Further calculations were done to confirm the adsorption mechanism and to determine the rate determining stage in the mechanism. Lagergren's pseudo-first-order kinetic model, pseudo-second-order kinetic model, and intraparticle diffusion model were used to test the experimental

data obtained. All the results shown in Sections 4.4.1, 4.4.2, and 4.4.3 are done in single paraben solutions. The results obtained for a mixture of four parabens solution will be discussed in Section 4.4.4.



**Figure 4.5: Adsorption (mmol/g) of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI polymer in single paraben solutions with increasing of time (minutes)**

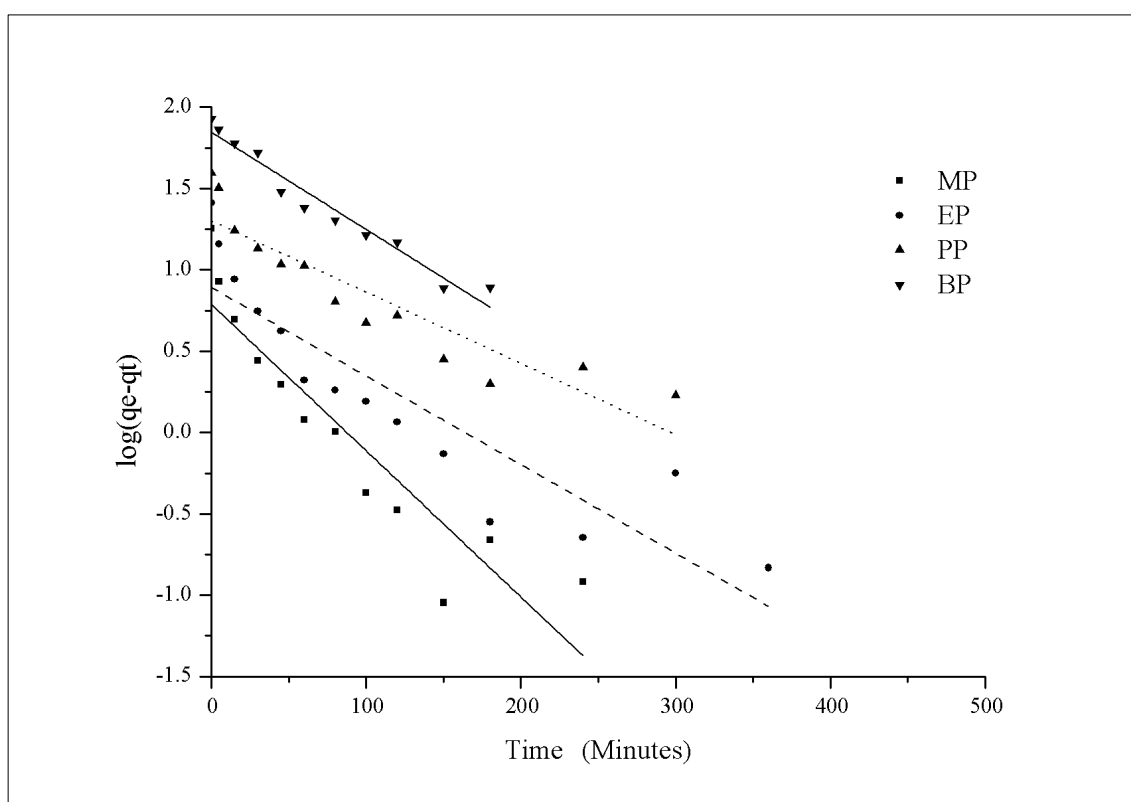
#### 4.4.1 Pseudo-first-order Kinetic Model (Single Paraben Solutions)

Figure 4.6 shows the Lagergren plots for adsorption of parabens onto  $\beta$ -CD-TDI and the details of the plots are shown in Table 4.3. The  $R^2$  values for the plots were in range 0.798 to 0.952 (Table 4.3) and the calculated  $q_e$  values obtained for this kinetic model are much lower than the experimental  $q_e$  values. According to Ho & McKay (1998), if the intercept value for the plots are not equal to  $\log(q_e)$ , the adsorption does not obey pseudo-first-order kinetic model. Therefore, we can conclude that the adsorption of parabens onto  $\beta$ -CD-TDI does not follow Lagergren's kinetic model.



**Table 4.3: Kinetic models' parameters for the adsorption of MP, EP, PP, and BP onto  $\beta$ -CD-TDI(b) in single paraben solutions**

Paraben	$q_e$ , exp (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion		
		$k_1$ ( $\text{min}^{-1}$ )	$q_e$ , cal (mg/g)	$R^2$	$k_2$ ( $\times 10^{-3}$ g/mg min)	$q_e$ , cal (mg/g)	$R^2$	$k_i$ (mg/g min)	C (mg/g)	$R^2$
<b>MP</b>	17.991	0.021	6.138	0.838	9.911	18.349	1.000	0.784	0.052	0.589
<b>EP</b>	25.754	0.013	7.804	0.798	5.006	26.178	1.000	0.904	0.072	0.578
<b>PP</b>	39.457	0.010	20.049	0.832	1.265	40.816	0.998	1.842	0.062	0.755
<b>BP</b>	85.081	0.014	70.243	0.952	0.232	99.010	0.989	5.813	0.023	0.930

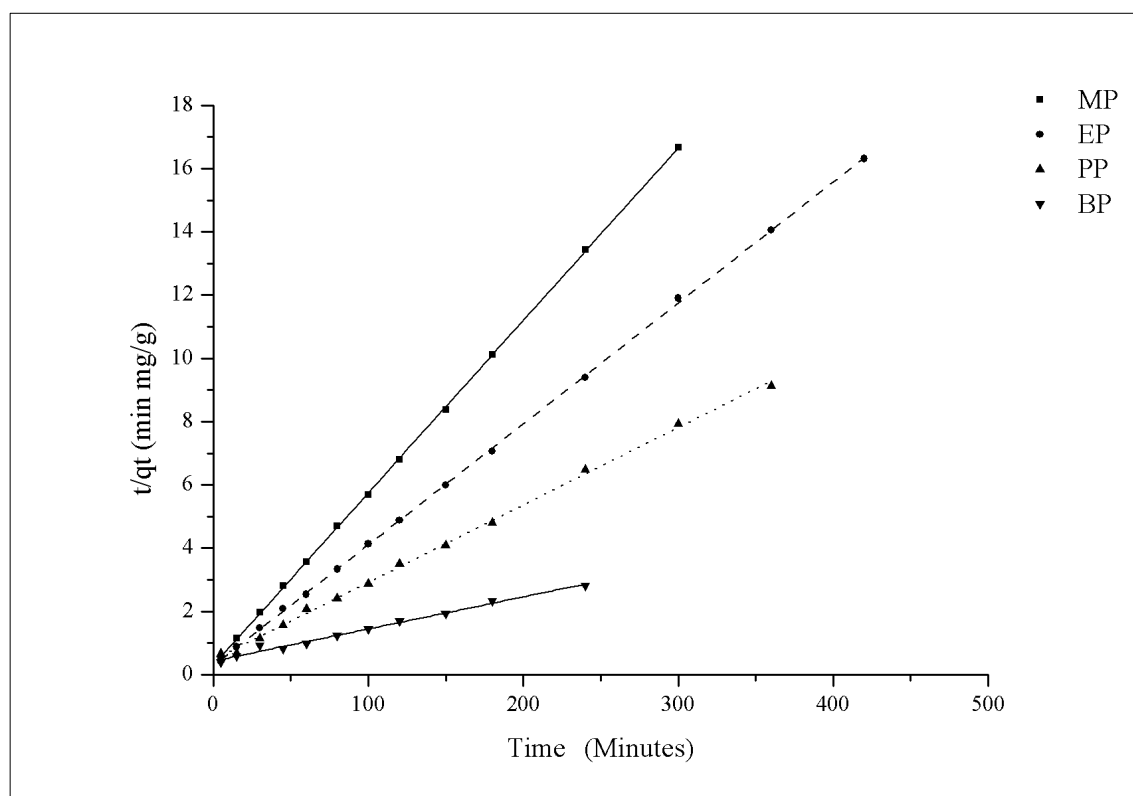


**Figure 4.6: Lagergren plots for adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b) in single paraben solutions**

#### 4.4.2 Pseudo-second-order Kinetic Model (Single Paraben Solutions)

Pseudo-second-order plots for MP, EP, PP, and BP onto  $\beta$ -CD-TDI(b) are shown in Figure 4.7. The  $R^2$  values are from 0.989 to 1.000 and the calculated  $q_e$  values are similar to the experimental  $q_e$  values (Table 4.3). These show the applicability of

pseudo-second-order kinetic and thus, the adsorption rate-determining step is due to chemisorptions. Adsorption of parabens may probably be via surface adsorption until the polymer surface is saturated; then paraben molecules will diffuse into the polymer network. Further interaction and reactions happen as the molecules diffuse into the polymer network, such as, forming inclusion complex, hydrogen bonding and hydrophobic interaction.



**Figure 4.7: Pseudo-second-order plots for adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b) in single paraben solutions**

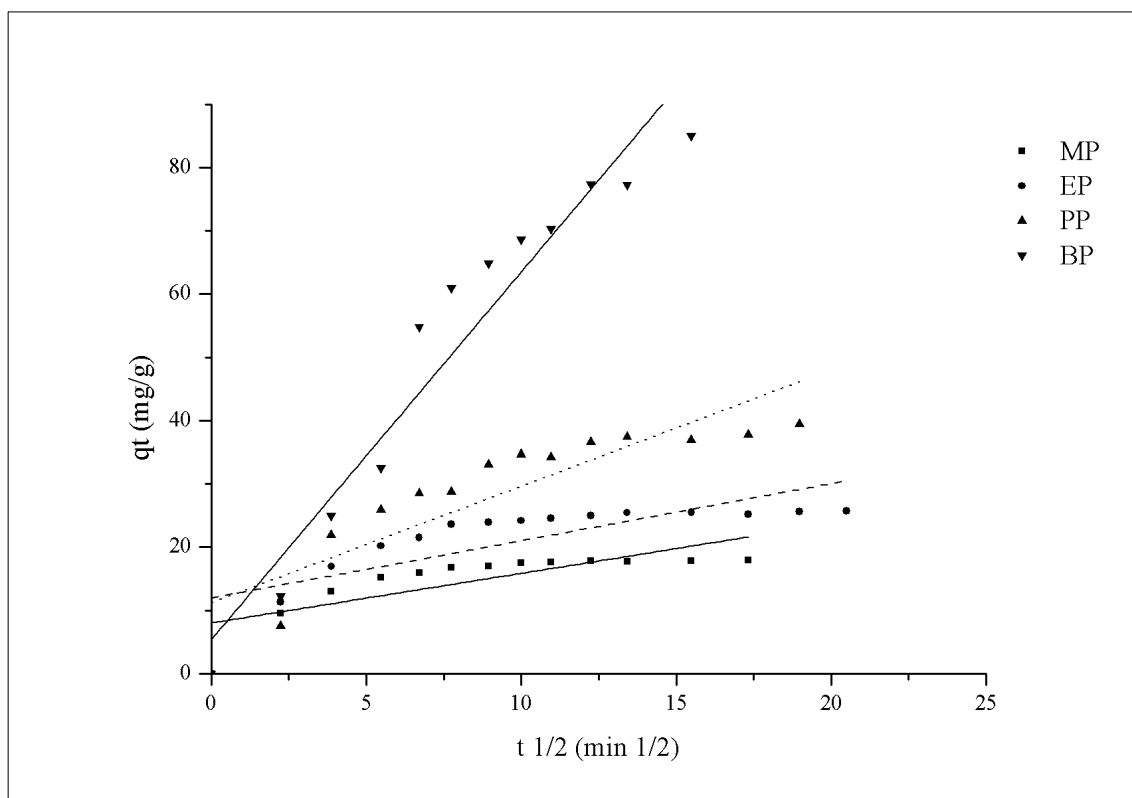
As shown in Table 4.3,  $k_2$  decreases as the size of paraben molecules increases, i.e. bigger molecules being adsorbed in a slower rate. However,  $q_e$  increases as the sorbate molecular size increases. These show that the smaller molecules are mobile in the polymer network but the interaction is weaker. As the molecular size increases, the sorbate molecules are more hydrophobic, therefore the hydrophobic interaction between sorbate-adsorbent are stronger. In addition, smaller paraben molecules have higher

water solubility, hence, the adsorption equilibrium become less since the molecules prefer to stay in water compared to a more hydrophobic paraben molecules.

Thus, adsorption of parabens onto  $\beta$ -CD-TDI follows pseudo-second-order kinetic model. The rate determining step is the chemisorptions. Molecular size and hydrophobicity of the paraben molecules play the main role in the rate of adsorption and adsorption capacity.  $k_2$  decrease as the size of paraben molecules increase (MP>EP>PP>BP) and vice-versa for  $q_e$  (BP>PP>EP>MP).

#### **4.4.3 Intraparticle Diffusion Model (Single Paraben Solutions)**

Figure 4.8 shows the Weber-Morris plots from the experimental results, whereas  $k_i$  and  $R^2$  values are shown in Table 4.3.  $k_i$  value increases as the molecular size increases. The increase in molecular size and molecular hydrophobicity give stronger sorbate-adsorbent interaction which makes the transportation faster. The  $R^2$  value shows that experimental data do not follow the intraparticle diffusion model. The only acceptable  $R^2$  value is 0.930 for BP, indicating that the BP molecule as the only paraben molecule that adsorbed through intraparticle diffusion. This is due to the extra  $\pi$ - $\pi$  interaction from the two aromatic rings compare to the other parabens molecules which only have one aromatic ring. All the plots do not pass through the origin means that intraparticle is not the only step that controlling the adsorption rate.



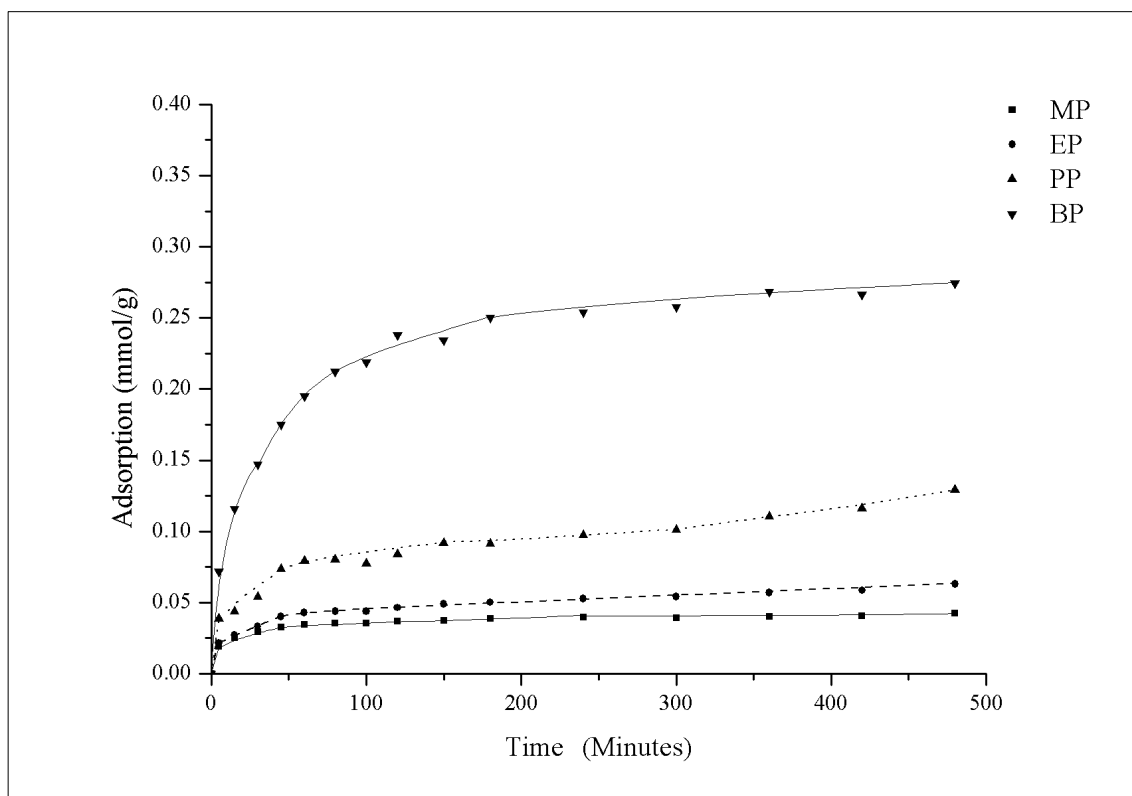
**Figure 4.8: Weber-Morris plots for adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b) in single paraben solutions**

#### 4.4.4 Adsorption in a Mixture of Four Parabens Solution

Competition may exist if four parabens exist in a solution. Different paraben molecules will compete for the limited amount of  $\beta$ -CD cavities. Figure 4.9 shows the adsorption of parabens in parabens mixture solution onto  $\beta$ -CD-TDI and Table 4.4 shows the comparison of  $t_e$  and  $q_e$  between adsorption in single paraben solutions and a mixture of four parabens solutions.

The adsorption capacities for each paraben in a mixture of four parabens solution are lower than the adsorption capacities in single paraben solutions. This shows that different paraben molecules will compete among each other for the same number of  $\beta$ -CD cavities. Among the parabens, the  $q_e$  increases as the hydrophobicity increases as described in Section 4.3.  $t_e$  for adsorption in both solutions are same except for PP, it

achieves equilibrium adsorption in 60 minutes in a mixture of four parabens solution while 180 minutes in single paraben solutions. This may due to the stronger sorbate-sorbate interaction that encourage the adsorption since much more parabens molecules are on the adsorption sites of the polymer in the same period of time as compare to single paraben solutions.

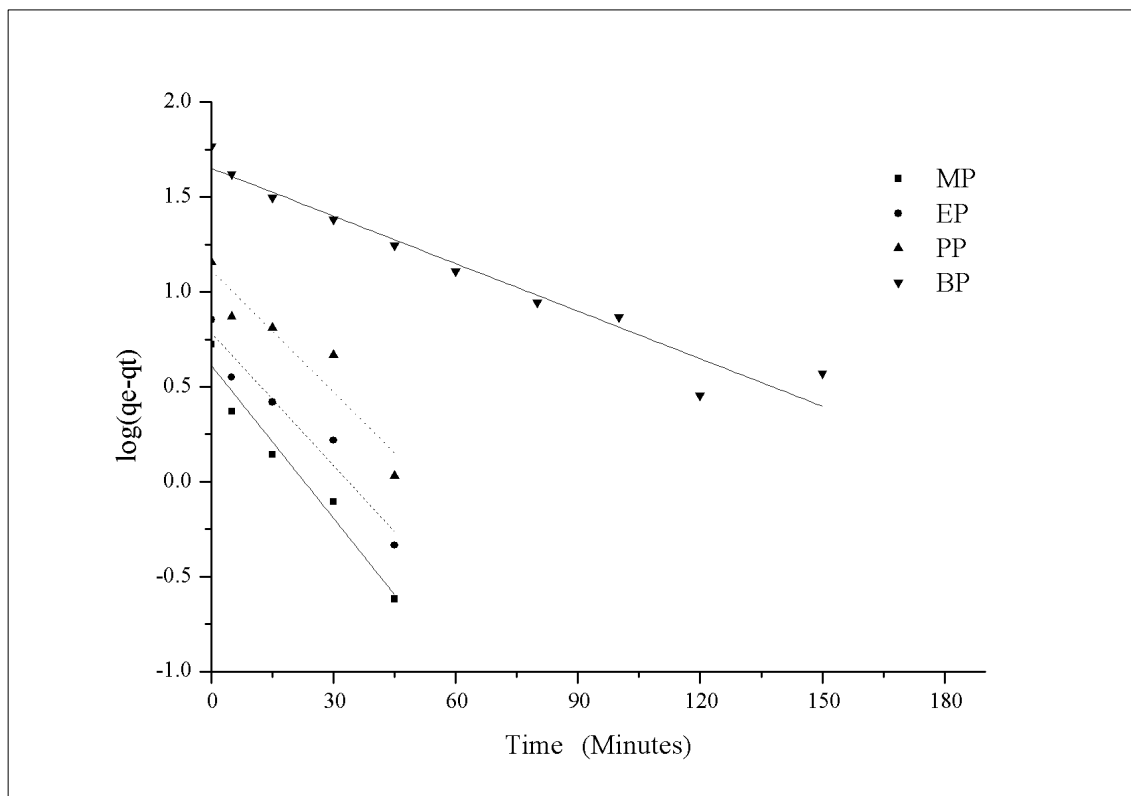


**Figure 4.9: Adsorption (mmol/g) of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b) in a mixture of four parabens solution with increasing of time (minutes)**

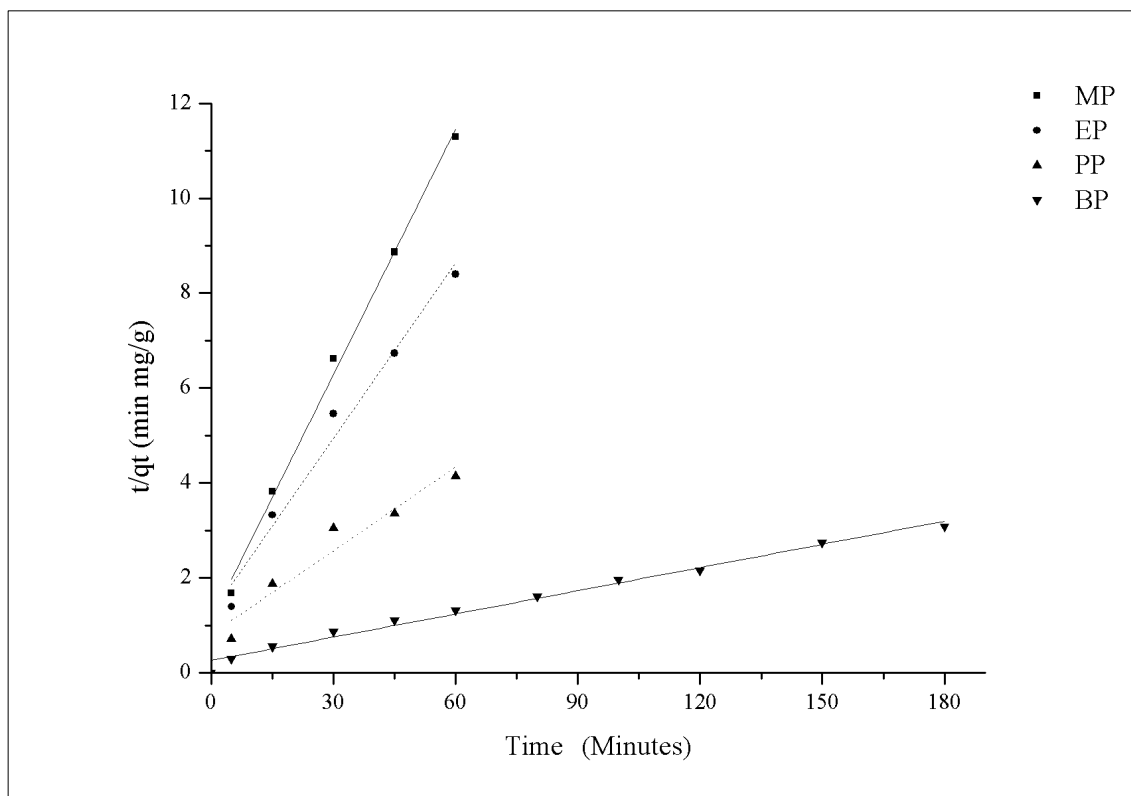
**Table 4.4: Equilibrium time,  $t_e$  (min) and adsorption capacity,  $q_e$  (mmol/g) for adsorption of parabens onto  $\beta$ -CD-TDI(b) in single paraben solutions and a mixture of four parabens solution**

Paraben	Single paraben solutions		A mixture of four parabens solution	
	$t_e$ (min)	$q_e$ (mmol/g)	$t_e$ (min)	$q_e$ (mmol/g)
<b>MP</b>	60	0.108	60	0.034
<b>EP</b>	60	0.142	60	0.043
<b>PP</b>	180	0.205	60	0.080
<b>BP</b>	180	0.333	180	0.250

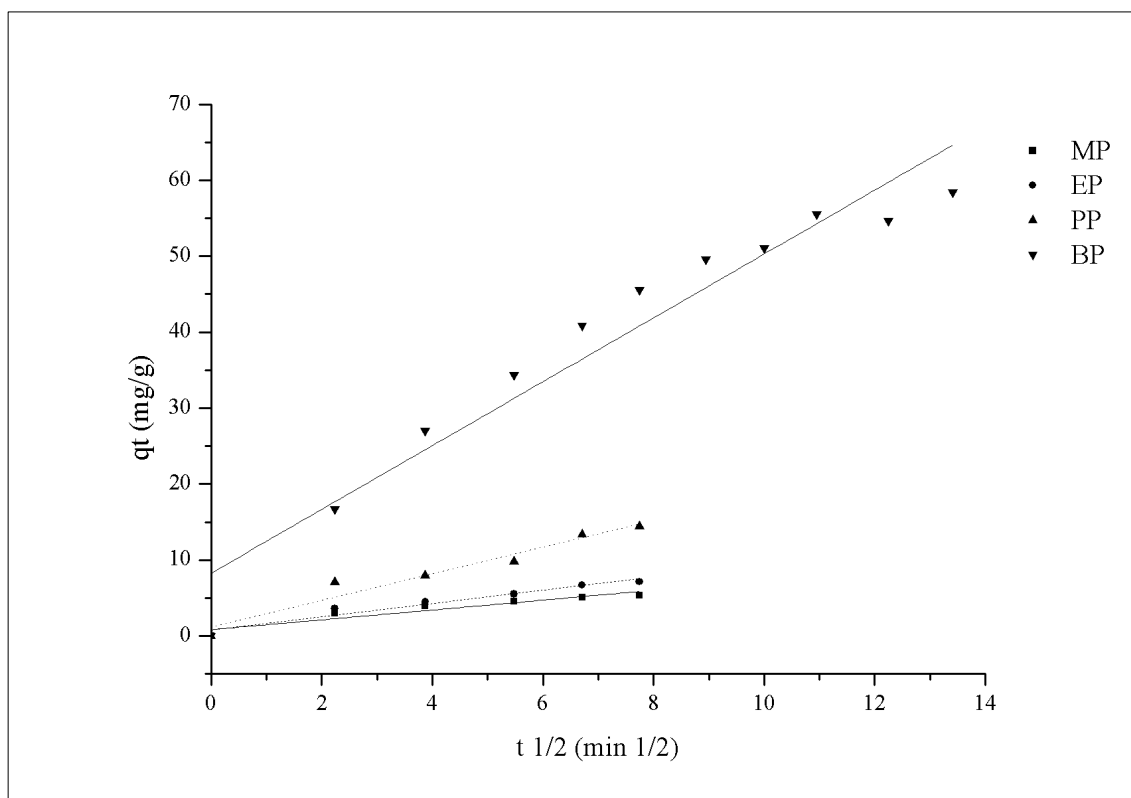
Figures 4.10, 4.11, and 4.12 show Lagergren plots, pseudo-second-order plots and Weber-Morris plots respectively for the adsorption of parabens in a mixture of four parabens solution. Table 4.5 summarizes the details of the plots as shown in Figures 4.10, 4.11, and 4.12. All the kinetic model's parameters have the same trend as in the single paraben solutions. The  $R^2$  values are higher for pseudo-first-order and intraparticle diffusion but lower for pseudo-second-order compare to single paraben solutions. Adsorption in a mixture of four parabens solution also has higher adsorption rate constant for pseudo-first-order and pseudo-second-order kinetic. The intraparticle diffusion rate constant is lower than that of the single parabens solutions. These data show that when competition exists, adsorption process can reach equilibrium at a faster rate following pseudo-second-order kinetic model and transport of sorbate from surface to the interior active sites is more likely to happen.



**Figure 4.10: Lagergren plots for adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b) in a mixture of four parabens solution**



**Figure 4.11: Pseudo-second-order plots for adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b) in a mixture of four parabens solution**



**Figure 4.12: Weber-Morris plots for adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b) in a mixture of four parabens solution**

**Table 4.5: Kinetic models' parameters for the adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b) in a mixture of four parabens solution**

Paraben	$q_e, \text{exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion		
		$k_1$ ( $\text{min}^{-1}$ )	$q_e, \text{cal}$ (mg/g)	$R^2$	$k_2$ ( $\times 10^{-3}$ g/mg min)	$q_e, \text{cal}$ (mg/g)	$R^2$	$k_i$ (mg/g min)	C (mg/g)	$R^2$
MP	5.314	0.060	4.106	0.952	26.860	5.794	0.995	0.648	0.823	0.883
EP	7.142	0.053	6.087	0.930	12.271	8.104	0.974	0.875	0.770	0.940
PP	14.570	0.049	13.026	0.860	4.271	17.007	0.914	1.752	1.176	0.941
BP	58.412	0.018	44.782	0.942	1.006	61.350	0.985	4.204	8.258	0.932



## 4.5 Adsorption Isotherms

Two isotherm models were used to study the equilibrium of the adsorption of parabens molecules onto  $\beta$ -CD-TDI polymer at various temperatures.

### 4.5.1 Langmuir Isotherm

Experimental data were plotted as in Equation 14 (Figure 4.13) and Langmuir parameters calculated from the graph is shown in Table 4.6. The fitting values,  $R^2$  for all the adsorption is from 0.6630 to 0.9963 and will be discussed in Section 4.5.3. On the other hand, both  $q_{\max}$  calculated and  $q_{\max}$  experimental value decrease as the temperature increases. This is probably due to the paraben solubility increases as the temperature is increases. That is, the solute-solvent interaction is greater than sorbate-adsorbent interaction. The  $q_{\max}$  calculated and the  $q_{\max}$  experimental values increase from MP to BP as the adsorption capacity,  $q_e$  shown in Table 4.4. However,  $q_{\max}$ , calculated value deviated from the  $q_{\max}$ , experimental value. Other isotherm model may apply when the molecular size increases.  $K_L$  value does not show a trend as the temperature increases or as the increase of molecular sizes. All the adsorptions are favourable as the  $R_L$  values are between 0.09 and 0.58.

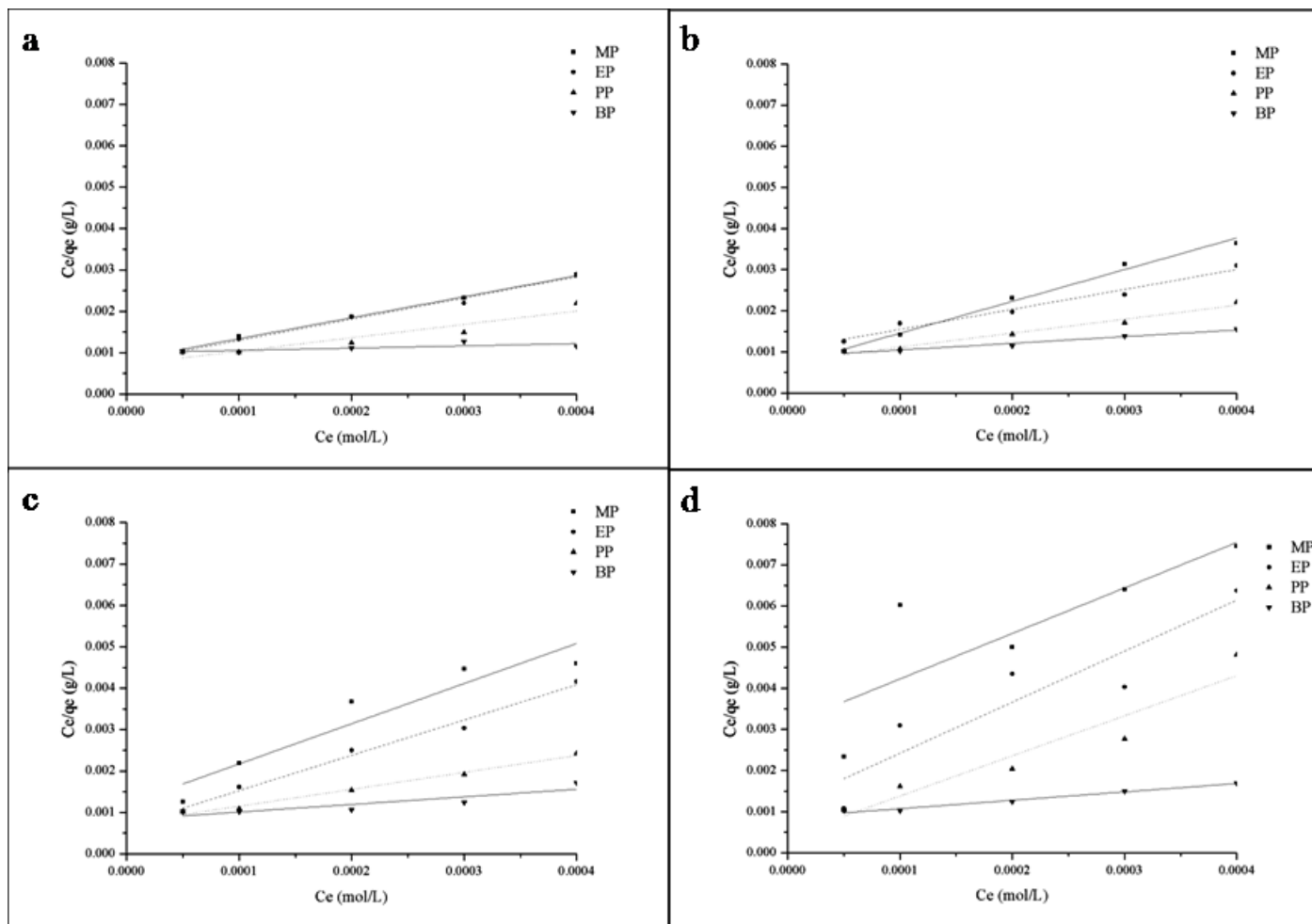


Figure 4.13: Langmuir adsorption isotherms of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI, at temperature (a) 15°C, (b) 30°C, (c) 45°C, and (d) 65°C

**Table 4.6: Langmuir parameters,  $q_{\max}$  cal (mol/g) (calculated adsorption capacity),  $q_{\max}$  exp (mol/g) (experimental adsorption capacity),  $K_L$  (L/mol) (Langmuir isotherm constant),  $R_L$  (Langmuir isotherm constant separation factor), and  $R^2$  (linear fitting value) for adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b)**

Temperature (°C)	Paraben	$q_{\max}$ , cal (mol/g)	$q_{\max}$ , exp (mol/g)	$K_L$ (L/mol)	$R_L$	$R^2$
15	MP	0.20	0.14	6332.50	0.28	0.9963
	EP	0.20	0.14	6403.88	0.28	0.9889
	PP	0.31	0.20	4616.29	0.35	0.8888
	BP	1.81	0.35	5513.00	0.31	0.6067
30	MP	0.13	0.11	11038.71	0.18	0.9906
	EP	0.21	0.13	4414.64	0.36	0.9734
	PP	0.29	0.18	4237.38	0.37	0.9796
	BP	0.62	0.26	1800.44	0.58	0.9652
45	MP	0.10	0.09	8085.83	0.24	0.9024
	EP	0.12	0.10	12172.00	0.17	0.9881
	PP	0.24	0.16	5844.29	0.30	0.9894
	BP	0.54	0.24	2296.50	0.52	0.7967
65	MP	0.09	0.05	3569.03	0.41	0.6630
	EP	0.08	0.07	10342.50	0.19	0.8480
	PP	0.10	0.11	24394.25	0.09	0.9134
	BP	0.49	0.24	2268.11	0.52	0.9788

#### 4.5.2 Freundlich isotherm

Figure 4.14 shows the plots as in Equation 16 and Freundlich isotherm's parameters calculated from the plots are shown in Table 4.7.

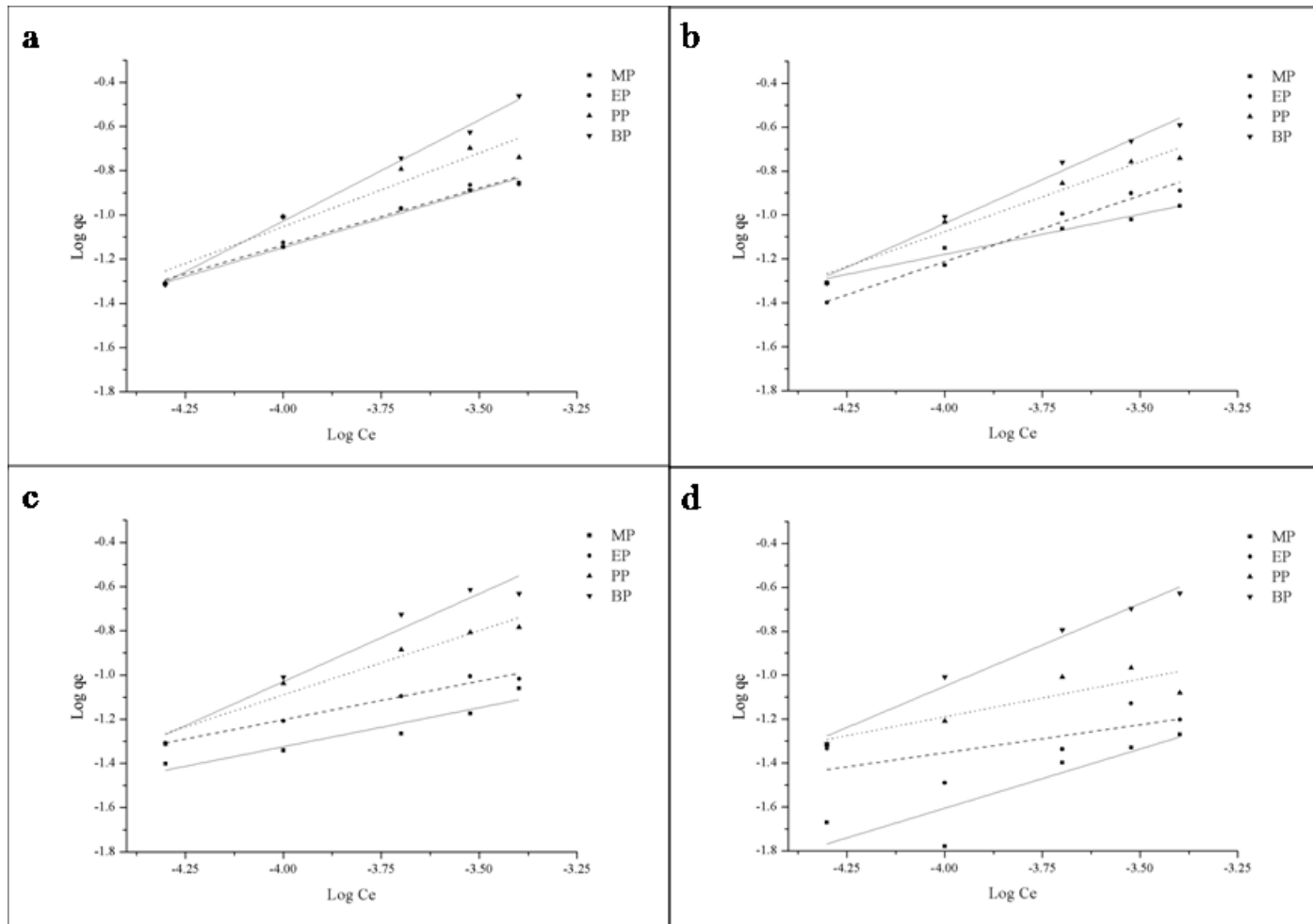


Figure 4.14: Freundlich adsorption isotherms of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI, at temperature (a) 15°C, (b) 30°C, (c) 45°C, and (d) 65°C

**Table 4.7: Freundlich parameters,  $K_F$  (L/g) (Freundlich constant),  $n_F$  (Freundlich isotherm exponent), and  $R^2$  (linear fitting value) for adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b)**

Temperature ( $^{\circ}$ C)	Paraben	$K_F$ (L/g)	$n_F$	$R^2$
<b>15</b>	MP	8.79	1.91	0.9932
	EP	8.56	1.93	0.9839
	PP	40.69	1.50	0.9304
	BP	427.07	1.09	0.9954
<b>30</b>	MP	1.92	2.73	0.9808
	EP	15.75	1.66	0.9811
	PP	29.30	1.57	0.9674
	BP	140.67	1.26	0.9873
<b>45</b>	MP	1.23	2.83	0.9151
	EP	1.56	2.87	0.9767
	PP	17.01	1.72	0.9599
	BP	141.61	1.26	0.9604
<b>65</b>	MP	3.55	1.85	0.7876
	EP	0.47	3.91	0.4525
	PP	1.54	2.90	0.7614
	BP	90.03	1.33	0.9842

Linear,  $R^2$  will be discussed in Section 4.5.3. All the  $n_F$  value are between 1.09 and 3.91 which indicate all the adsorption are favourable physical adsorption.  $K_F$  values increase as the molecular size increases and decreases as the temperature decreases. These results are similar to the adsorption capacity trend; therefore, molecular size and hydrophobicity play the main roles in the adsorption as discussed.

### 4.5.3 Comparison between Isotherm Models

Both Langmuir and Freundlich isotherm models show some degrees of fitting. The linear fitting data are shown in Table 4.8, isotherm model that has better fitting is also listed. Both of the isotherm models do not fit well for some of the adsorption, i.e. adsorption of MP at 45 and 65°C together with adsorption of EP and PP in 65°C.

**Table 4.8: Linear fitting,  $R^2$  Langmuir and Freundlich isotherm model for adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b) polymer**

Temperature (°C)	Paraben	$R^2$		Isotherm model
		Langmuir	Freundlich	
15	MP	0.9963	0.9932	Langmuir
	EP	0.9889	0.9839	Langmuir
	PP	0.8888	0.9304	Freundlich
	BP	0.6067	0.9954	Freundlich
30	MP	0.9906	0.9808	Langmuir
	EP	0.9811	0.9734	Langmuir
	PP	0.9796	0.9674	Langmuir
	BP	0.9652	0.9873	Freundlich
45	MP	0.9151	0.9024	Langmuir
	EP	0.9881	0.9767	Langmuir
	PP	0.9894	0.9599	Langmuir
	BP	0.7967	0.9604	Freundlich
65	MP	0.6630	0.7876	-
	EP	0.8480	0.4525	-
	PP	0.9134	0.7614	-
	BP	0.9788	0.9842	Freundlich

García-Zubiri et al. (2009) have described the adsorption behaviour of  $\beta$ -CD crosslinked polymer. Langmuir isotherm model assumes that adsorption only takes place at specific homogenous sites within the adsorbent and Freundlich isotherm model assumes that there are different adsorption sites acting simultaneously. In this study, Langmuir isotherms describe the adsorption as paraben molecules fill in the  $\beta$ -CD cavity and form inclusion complex. On the other hand, Freundlich isotherm model describes the adsorption of parabens at the  $\beta$ -CD cavity and being entrapped in the polymer crosslinking networks.

**Table 4.9: Isotherm model for adsorption of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben onto  $\beta$ -CD-TDI(b) polymer at 15, 30, 45 and 65°C**

<b>Temperature (°C)</b>	<b>15</b>	<b>30</b>	<b>45</b>
<b>MP</b>	Langmuir	Langmuir	Langmuir
<b>EP</b>	Langmuir	Langmuir	Langmuir
<b>PP</b>	Freundlich	Langmuir	Langmuir
<b>BP</b>	Freundlich	Freundlich	Freundlich

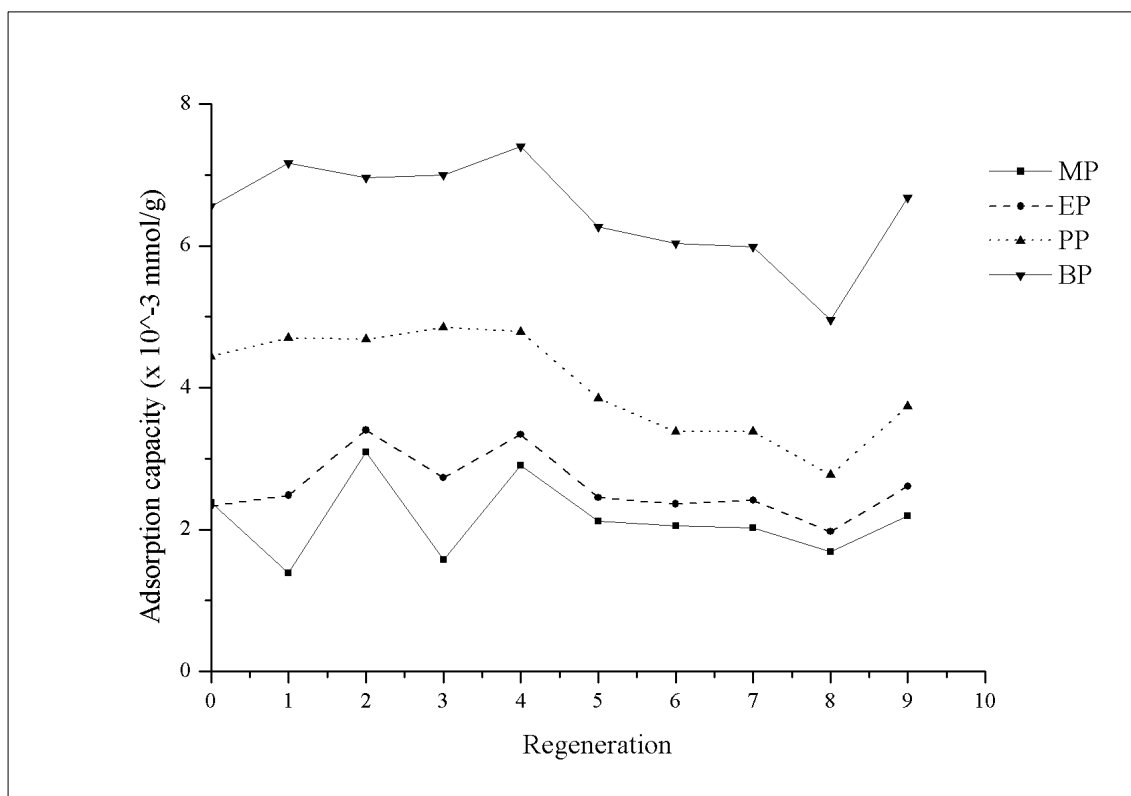
As shown in Table 4.9, data for 65°C cannot be considered as the  $R^2$  fitting for both models because the values are too low. Langmuir isotherm shows a better fitting for the adsorption of MP and EP. MP and EP are the parabens that have the smallest molecular size and most hydrophilic, therefore, they can only form inclusion complex with  $\beta$ -CD but they cannot be entrapped on the polymer crosslinking networks. Adsorption of PP can be described by Freundlich isotherm model at 15°C but Langmuir isotherm model is applied at 30 and 45°C. At a lower temperature, the solubility of PP decreases and the polymer crosslinking networks shrink, therefore, PP can be entrapped in the polymer crosslinking networks but not in higher temperature. Freundlich isotherm

model fit well in all adsorption of BP because it has 2 aromatic rings and it is the most hydrophobic. The low solubility and its bulky structure attributed to the adsorption of BP due to the formation inclusion complex and easy entrapment on the polymer crosslinking networks. Adsorption of BP onto the polymer crosslinking networks also due to the extra  $\pi$ - $\pi$  interaction between BP and TDI. In conclusion, both isotherm models can be used to explain the adsorption mechanism depending on the characteristic of the paraben molecule and adsorption temperature.

#### **4.6 Reusability**

Adsorbent can be the most expensive consumable component in an adsorption system; therefore, its reusability is very important to reduce the cost of adsorption. In addition to the cost, method to regenerate the adsorbent is also important. In this study, small amount of methanol which is a relatively cheap solvent was used to desorb parabens from  $\beta$ -CD polymer after adsorption. Parabens were desorbed from  $\beta$ -CD polymer by eluting 10 mL of methanol. Polymer was used from nine regenerations and its adsorption capacities for all regeneration are shown in Figure 4.15. The adsorption capacities of  $\beta$ -CD-TDI are between 75.6 to 112.8% in the nine regenerations. Hence,  $\beta$ -CD-TDI is suitable to use as adsorbent in an adsorption system as it can be easily regenerated and has high adsorption capacity after regeneration.





**Figure 4.15: Adsorption capacity of regenerated  $\beta$ -CD-TDI(b) towards methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben**

#### 4.7 Application on Real Samples

$\beta$ -CD-TDI was applied on various samples to study the adsorption of parabens in different matrices. From Table 4.10, all the adsorption show positive results especially for PP and BP. Removal of parabens from all water samples gave similar results as standard deionised water. This has shown that chemical species in the real samples do not affect the adsorption. River water and waste water effluent have slightly lower of percentage of removal due to the interference of other chemical species in the samples. BP is not detected by HPLC from solution of Facial cleanser A. This might be due to the existence of the other material in facial cleanser ingredients that can adsorb BP. The removal of other parabens from Facial Cleanser A also shows a relatively lower percentage due to the same reason. However, the interference of other chemical

species and existence of other component in real samples that affecting the adsorption by  $\beta$ -CD polymer was not studied.

**Table 4.10: Removal of methyl paraben, ethyl paraben, propyl paraben, and benzyl paraben from spiked real samples using  $\beta$ -CD-TDI(b) polymer**

Sample	MP		EP		PP		BP	
	Removal (%)	R.S.D. (%)	Removal (%)	R.S.D. (%)	Removal (%)	R.S.D. (%)	Removal (%)	R.S.D. (%)
<b>Deionised water (Standard)</b>	33.56	1.88	51.55	2.62	95.51	1.31	100.00	-
<b>Tap water</b>	29.76	7.37	48.07	11.04	89.98	7.82	100.00	-
<b>Drinking water</b>	32.58	2.76	52.42	0.41	97.93	1.43	100.00	-
<b>Swimming pool water</b>	27.09	0.27	47.35	3.59	93.34	2.89	100.00	-
<b>River water</b>	28.56	5.92	46.28	5.30	88.29	4.31	100.00	-
<b>Waste water effluent</b>	24.24	2.41	38.77	1.61	73.63	2.21	100.00	-
<b>Soy sauce</b>	28.74	6.97	44.49	9.62	85.66	6.15	100.00	-
<b>Mouth rinse</b>	20.87	3.83	44.99	7.74	84.03	6.79	100.00	-
<b>Facial cleanser A</b>	6.81	2.76	17.54	9.99	50.11	1.44	-	-
<b>Facial Cleanser B</b>	13.20	3.65	28.91	6.48	61.19	5.45	84.96	9.29
<b>Lotion</b>	19.11	8.70	39.84	1.79	76.86	8.15	100.00	-

## CHAPTER 5 CONCLUSION

In this study,  $\beta$ -cyclodextrin cross-linked polymers were successfully synthesized, i.e.  $\beta$ -CD-HMDI and  $\beta$ -CD-TDI. These polymers were characterized using fourier transform infrared spectroscopy (FT-IR) and CHN elemental analysis.

Water adsorption of  $\beta$ -CD polymers was studied to understand the interaction between the polymers and water molecules. The effect of types and amount of cross-linker were studied and  $\beta$ -CD-TDI with molar ratio of  $\beta$ -CD : cross-linker is 1:7 being chosen for further studies because it possess the highest adsorption toward parabens among all polymers. Adsorption capacity of the polymers follows BP>PP>EP>MP in both single paraben solutions and a mixture of four parabens solution. Due to the competition among parabens molecules, adsorption capacities for all parabens are slightly lower in a mixture of four parabens solution.

In order to understand the adsorption mechanism, kinetic and isotherm studies were done. In single paraben solutions, time to reach adsorption equilibrium,  $t_e$  are within 100 minutes for MP and EP, whereas for PP and BP are within 180 minutes. Adsorption of parabens onto  $\beta$ -CD-TDI follows pseudo-second-order kinetic model, i.e., rate determining is chemisorptions. Pseudo-second-order rate constant,  $k_2$  decrease as the paraben molecular size increase (MP>EP>PP>BP). Linear fitting value,  $R^2$  values show that the adsorption do not follow pseudo-first-order and intra particle diffusion model except BP, which possess extra  $\pi$ - $\pi$  interaction with the aromatic ring in TDI. In a mixture of four parabens solution,  $t_e$  for MP, EP, and PP are 60 minutes whereas 180 minutes for BP. The adsorptions follow pseudo-second-order and intraparticle diffusion model with faster rate.

Langmuir isotherms and Freundlich isotherms were used to study the equilibrium of adsorption. All Langmuir isotherm constant separation factor,  $R_L$  values are between 0 and 1, i.e. all adsorption are favourable follow Langmuir isotherms. All the Freundlich isotherm exponent,  $n_F$  are more than 1, i.e. adsorptions are favourable physical adsorption. After comparing the  $R^2$  for both isotherm models, adsorption of MP and EP follow Langmuir isotherm, adsorption of PP follows Freundlich isotherm in 15°C but follows Langmuir isotherm in 30°C and 45°C, adsorption of BP follows Freundlich isotherm model. From these results, the adsorption of MP and EP are at homogenous sites ( $\beta$ -CD cavities). At low temperature (15°C), PP can only be adsorbed onto  $\beta$ -CD cavities because cross-linked polymer networks shrink at low temperature. BP is easily adsorbed onto  $\beta$ -cavities and cross-linked polymer networks due to its large molecular size and extra  $\pi$ - $\pi$  interaction between BP and TDI.

$\beta$ -CD-TDI polymer has high reusability and simple regeneration procedure. The adsorption capacities are between 75.6 to 112.8% for nine regenerations. The polymer was applied on 10 different real aqueous samples and all shows positive results. Hence, this study has shown that  $\beta$ -CD cross-linked polymer ( $\beta$ -CD-TDI) can be used to remove parabens in aqueous solutions with high efficiency and reusability.

A few recommendations for future studies:

- Thermodynamic study for better understanding of the adsorption mechanism.
- Modify the  $\beta$ -CD cross-linked polymers to improve the adsorption performance and to lower the cost of preparation.
- Polymer degradation study for health and environmental concerns.

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## PUBLICATION

Chin, Y. P., Mohamad, S., & Abas, M.R. (2010). Removal of parabens from aqueous solution using  $\beta$ -cyclodextrin cross-linked polymer. *International Journal of Molecular Science*, 11, 3459-3471.

## SEMINARS

1. Removal of parabens by using  $\beta$ -cyclodextrin as adsorbent. 10th Asian Conference on Analytical Sciences (ASIANALYSIS X) 2009, August 2009, Putra World Trade Center, Kuala Lumpur.
2. Adsorption of parabens from aqueous solution using  $\beta$ -cyclodextrin cross-linked polymer. 16th Malaysian Chemical Congress (16MCC), October 2010, Putra World Trade Center, Kuala Lumpur.
3. Adsorption of parabens from aqueous solution using  $\beta$ -cyclodextrin cross-linked polymer. Symposium "Emerging Trends in Chemistry", October 2010, University of Malaya.
4. Adsorption of parabens from aqueous solution using  $\beta$ -cyclodextrin cross-linked polymer. 6th Mathematics and Physical Science Graduate Congress (MPSGC), December 2010, University of Malaya.