CHAPTER 4

RESULT AND DISCUSSION

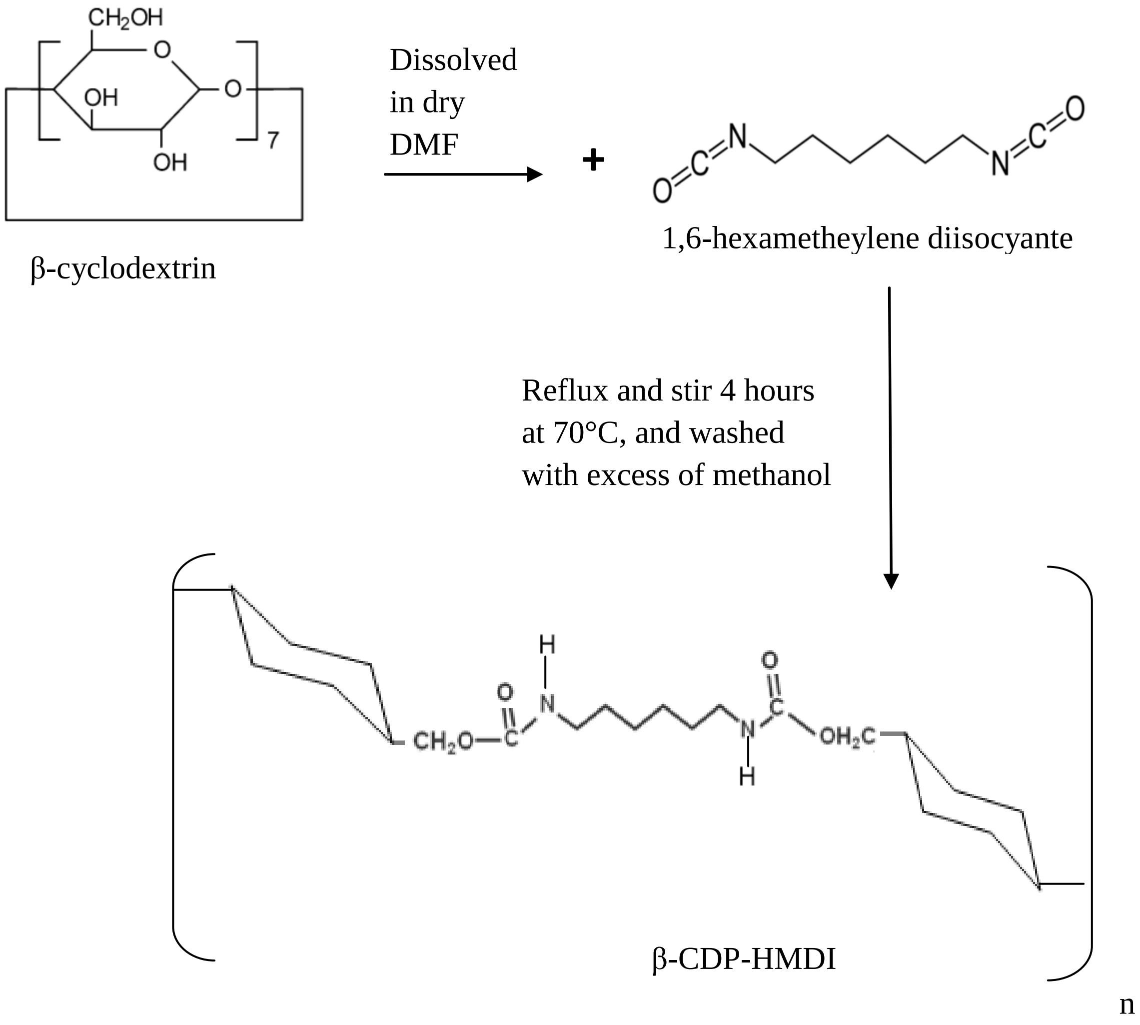
4.1 SYNTHESIS AND CHARACTERIZATION OF β-CYCLODEXTRIN-BASED AS AN ADSORBENT

4.1.1 Synthesis of β-CD polymer

In this study, 1,6-hexamethylene diisocyanate (HMDI) and toluene-2,4-diisocyanate (TDI) were used as crosslinker which is aliphatic and aromatic bifunctional of isocyanate group respectively and generally utilized as a strong cross linker of amino or hydroxyl group since it possesses two isocyanate groups (-N=C=O) (Jianfei *et al.*, 2007). TDI is more reactive than HMDI to hydroxyls because it has highly unsaturated bonds and two isocyanate groups (-N=C=O) having different activities to hydroxyls groups. Isocyanate group at para position is more reactive than ortho position of isocyanate. During reaction, an electrophilic attack at the hydroxyl group from β-CD reacts with an isocyanate to form a urethane product (-NH-CO-O) due to the transfer of proton from hydroxyl to nitrogen atom to isocyanate (Prabaharan and Mano, 2006; Crini, 2006; Jianfei *et al.*, 2007).

i) Synthesis of β-CDP-HMDI

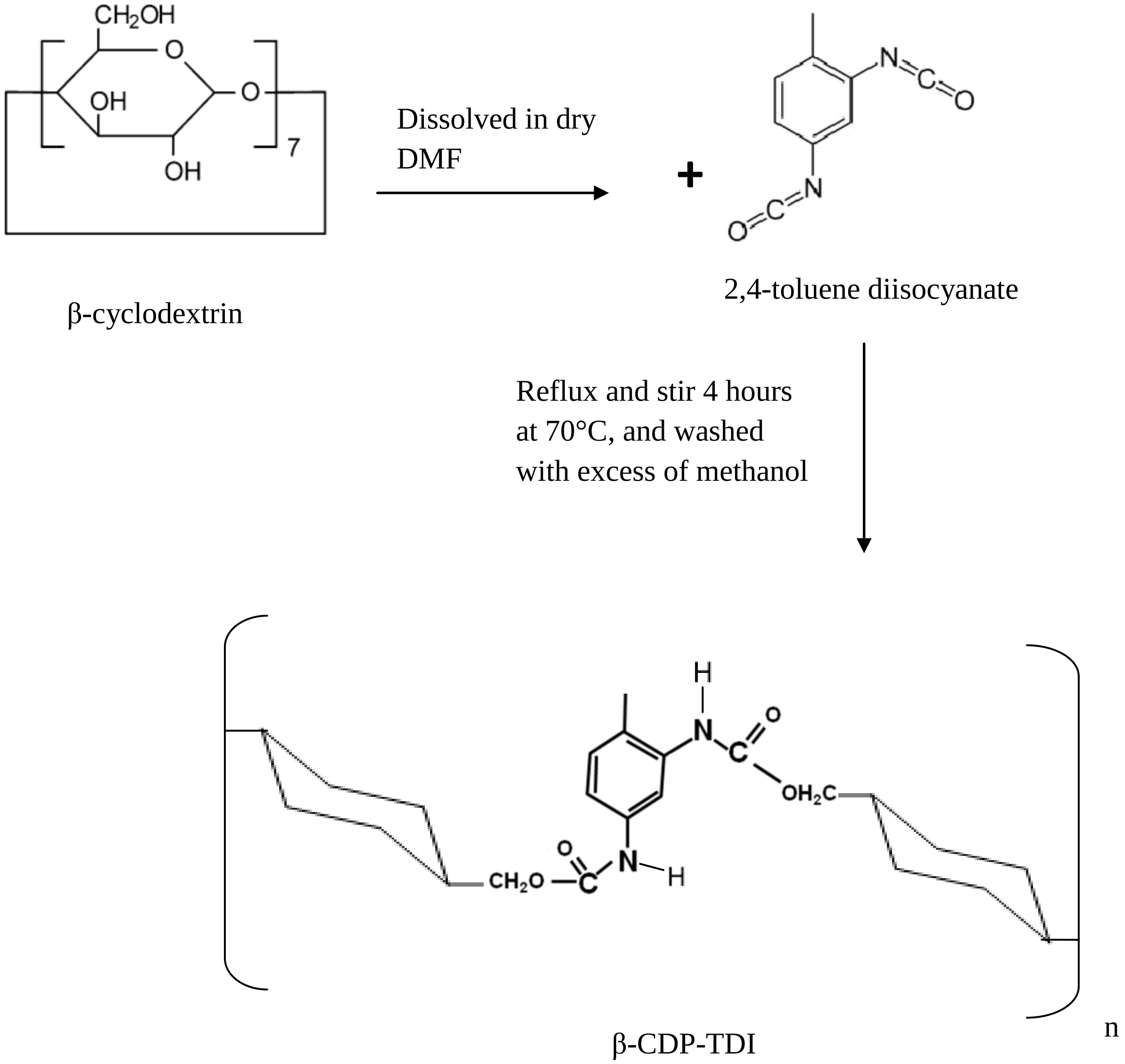
Scheme 4.1 shows the synthesis route for preparing poly-cyclodextrin using 1,6-hexamethylene diisocyanate (HMDI) as a crosslinker.



Scheme 4.1: Schematic diagram of the synthesis route used for preparing β-CDP-HMDI

ii) Synthesis of β-CDP-TDI

Scheme 4.2 shows the synthesis route for preparing poly-cyclodextrin using toluene-2,4-diisocyanate (TDI) as a crosslinker.



Scheme 4.2: Schematic diagram of the synthesis route used for preparing β-CDP-TDI

β-CD, β-CDP-HMDI, β-CDP-TDI has been characterized using Fourier Transform Infrared Spectroscopy (FT-IR) and Thermal Gravimetric Analysis-Derivative Thermal Analysis (TGA-DTA).

Figure 4.1 (a-c) shows the FT-IR spectra for β-CD, β-CDP-HMDI and β-CDP-TDI respectively. The band assignments related to the FT-IR analyses of the β-CD, β-CDP-HMDI and β-CDP-TDI are regrouped in Table 4.1. Figure 4.1 (b) shows the bands at 2925 cm^{-1}, 2933 cm^{-1} corresponding to CH_2 asymmetric stretching vibration from methylene crosslinker. Absence of peak 2270 cm^{-1} (corresponding to isocyanate group) shows that the reaction is complete. The bands at 1602 cm^{-1} and 1457 cm^{-1} in Figure 4.1 (c) represent the aromatic group in TDI. The adsorption band at 1253 cm^{-1} in Figure 4.1 (b) could be attributed to the C=O characteristics vibrations of aliphatic polyurethane. The band at 856 cm^{-1} is considering for α-(1,4) glucopyranose from β-CD (Bhaskar *et al.*, 2004; Jianfei *et al.*, 2007 and Chin *et al.*, 2010)

4.1.2 Characterization of β-cyclodextrin polymer (β-CDP-HMDI and β-CDP-TDI)

(a) FT-IR analysis

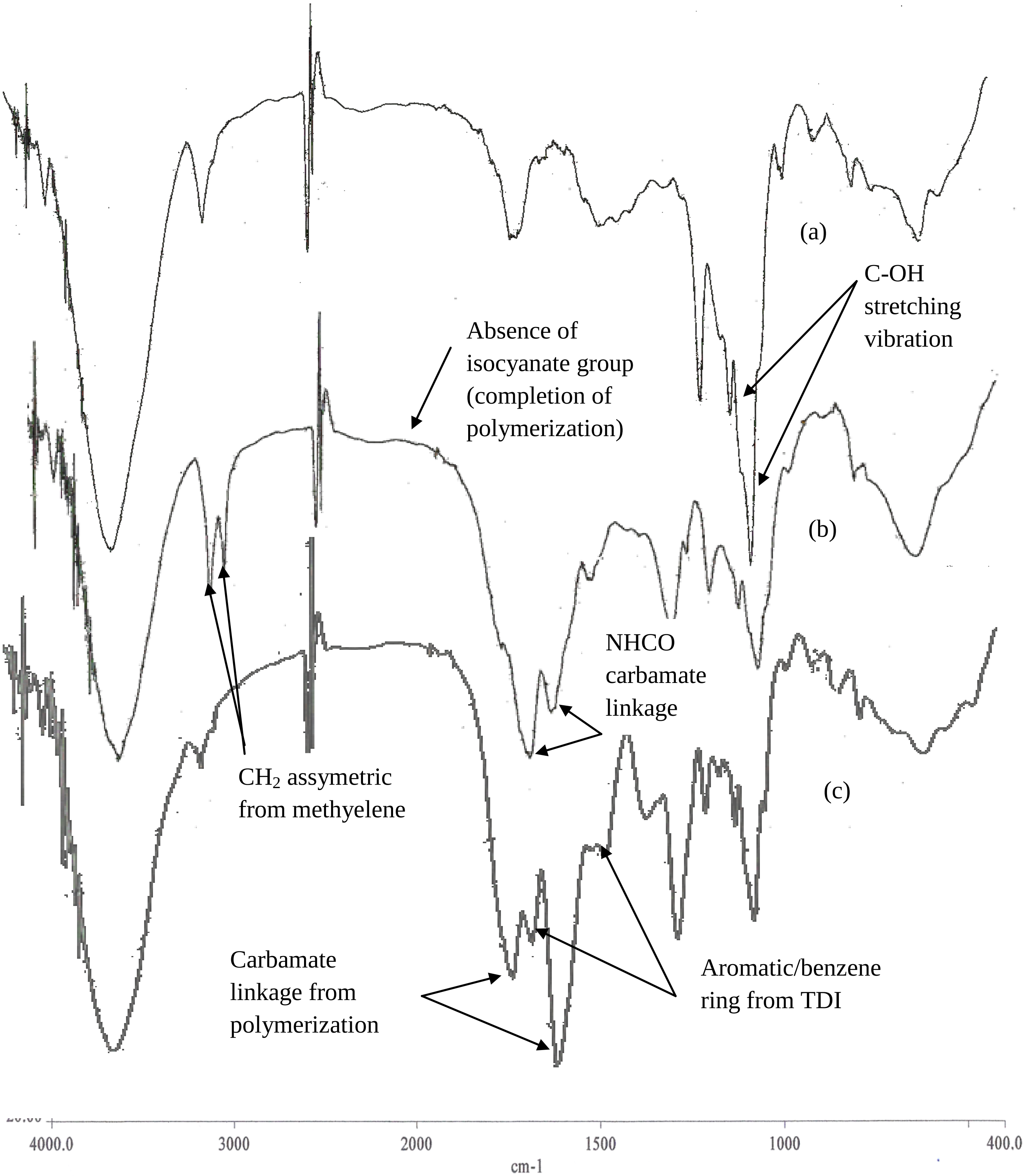


Figure 4.1: FT-IR Spectra for a) β-CD, b) β-CDP-HMDI and c) β-CDP-TDI

Table 4.1 : Main IR frequencies with assignments

Samples	**wavelength (cm^{-1})**	**Assignments**
β-CD	856	α-(1,4)glucopyranose
	1029,1100	C-OH stretching vibration
β-CDP-HMDI	1253	C=O vibrations of aliphatic polyurethane
	1569	NHCO, carbamate linkage
	3420, 1700	NH and C=O
	2270	Absence of isocyanate group (completion of reaction polymerization)
	2925, 2933	CH_2 asymmetric stretching vibration from methylene crosslinker
β-CDP-TDI	1227	C=O vibration of aromatic polyurethane
	1602, 1457	aromatic group in TDI
	1541, 1655	NHCO, carbamate linkage
	3393, 1700	NH and C=O
	2270	Absence of isocyanate group (completion of reaction polymerization)

(b) TGA-DTA analysis

All adsorbents were characterized using Thermal Gravimetric Analysis-Derivative Thermal Analysis (TGA-DTA). Figure 4.2-4.4 shows the TGA-DTA analysis of β-CD, β-CDP-HMDI and β-CDP-TDI, respectively. Figure 4.2 shows that the weight loss of β-CD is due to the oxidative degradation and it starts to decompose at 310 ºC and completes at 650ºC. For thermogram of β-CDP-HMDI in Figure 4.3, there are two stages of decomposition, which are at 300-380ºC and 380-510ºC. At the first stage, it shows the decomposition of β-CD, while at second stage is due to the linker of HMDI. The enhanced thermal stability of β-CD polymer is attributed to the crosslinked nature, since it is well-known that cross-linking leads to thermal stability (Bhaskar *et al*., 2004). For thermogram of β-CDP-TDI in Figure 4.4, it shows that the weight loss of polymer at stage 260-380ºC and 380-700ºC. The presences of two exothermic peaks at DTA curve (Figure 4.4) at 310ºC and 350ºC are due to the linkage of TDI and decomposition of β-CD, respectively.

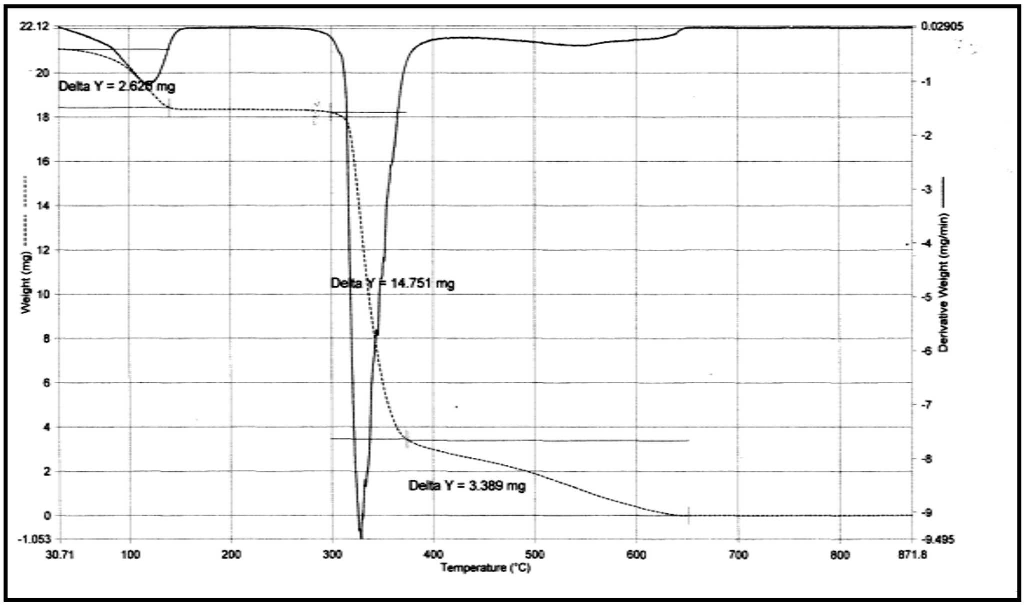


Figure 4.2 : TGA-DTA analysis of beta cyclodextrin

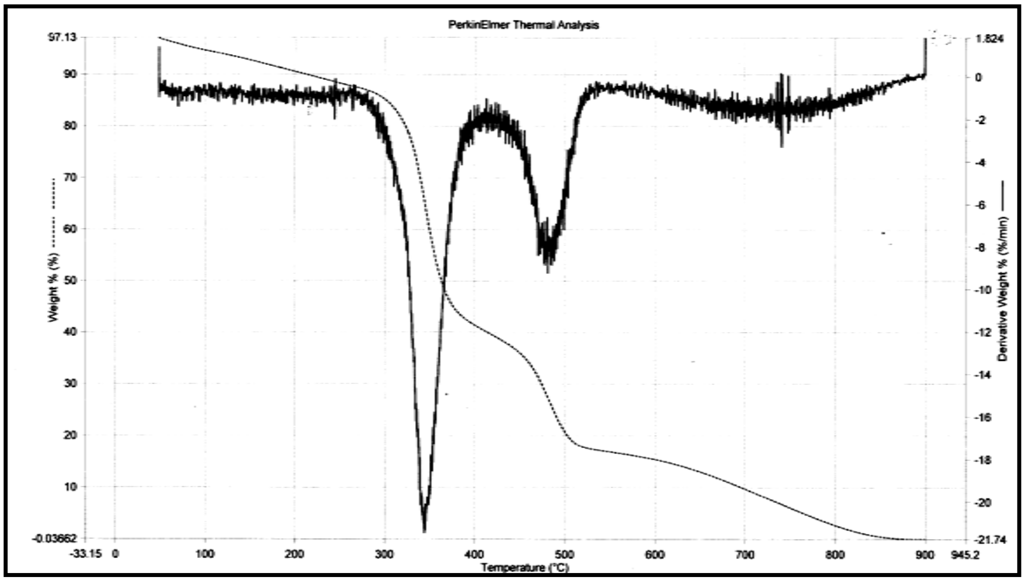


Figure 4.3 : TGA-DTA analysis of β-CDP-HMDI

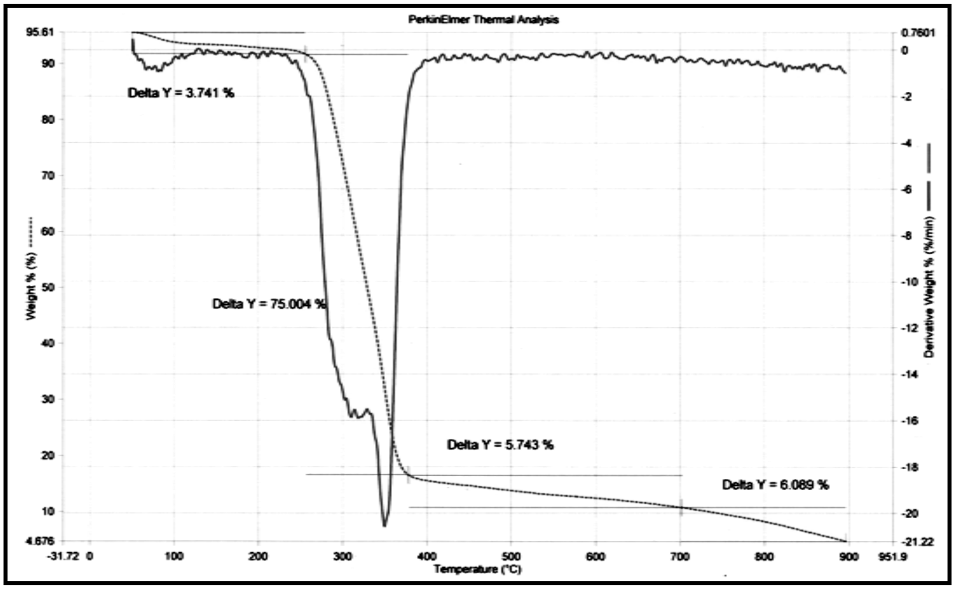


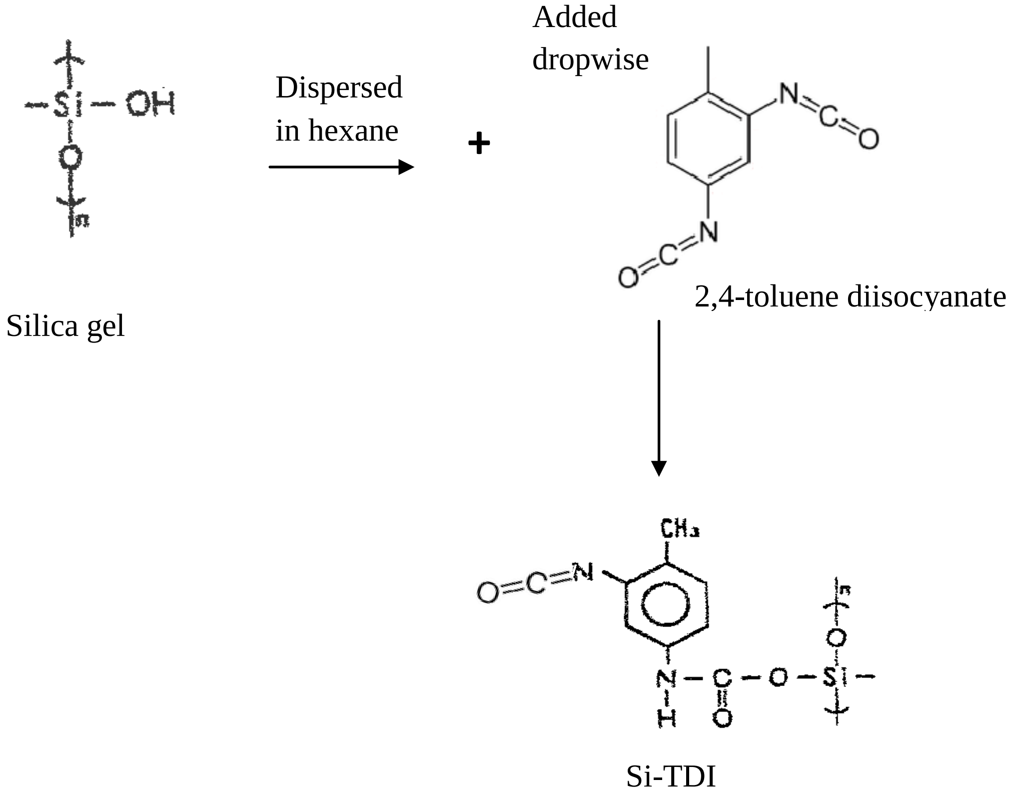
Figure 4.4 : TGA-DTA analysis of β-CDP-TDI

4.1.3 Immobilization of cyclodextrin on silica (Si-TDI-β-CD)

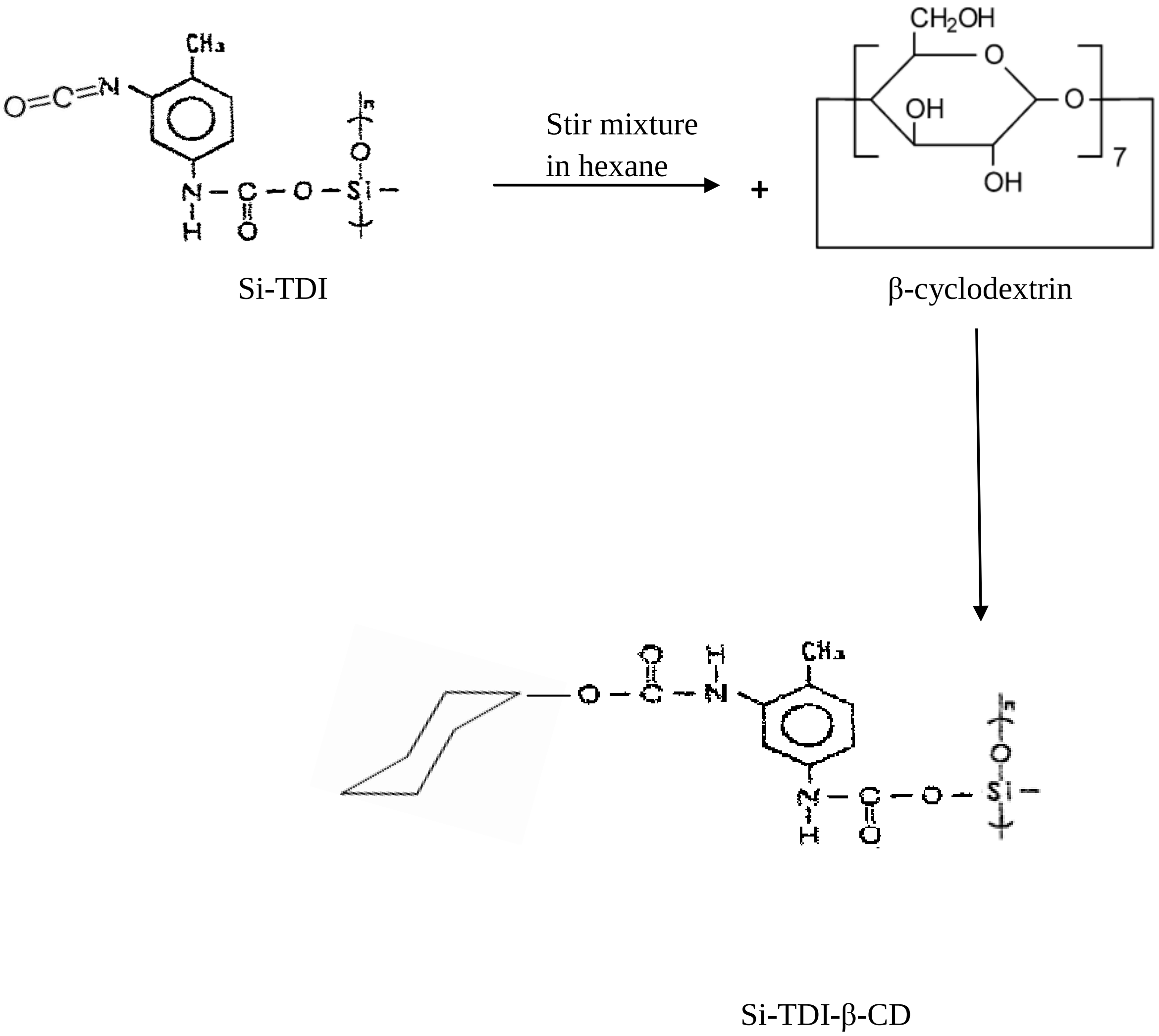
Silica is the most frequently used for producing functionalized materials, because of their high physical strength and chemical inertness. Silica particles manifest a hydrophilic surface due to the presence of silanol groups. The strongest interaction with the silica surface was proposed through hydrogen bonding onto the surface silanol.

Scheme 4.3 shows the synthesis route for preparing Si-TDI-β-CD. There are two steps that need to prepare Si-TDI-β-CD. In the first step, silanol groups from silica surface reacted with isocyanate group in para position to form urethane (-NH-CO-O), and some isocyano groups in ortho position were reserved. In the second step, the reserved isocyanate group will react with hydroxyl group from cyclodextrin.

Step I: Introduction of isocyanate group onto silica surfaces.



Step II: Immobilization of cyclodextrin on Silica-TDI.



Scheme 4.3: Schematic diagram for the synthesis route used for preparing Si-TDI-β-CD.

SiO_2, Silica-TDI and Si-TDI-β-CD have been characterized using Fourier Transform Infrared Spectroscopy (FT-IR).

The IR spectra of SiO_2, Si-TDI and Si-TDI-β-CD are shown in Figure 4.5. The band assignments related to the FT-IR analyses of the SiO_2, Si-TDI and Si-TDI-β-CD are regrouped in Table 4.2. Figure 4.5(b) shows the peaks at 1601 cm^{-1} and 1421 cm^{-1} are represented the stretching vibration of the aromatic ring from TDI while the NCO stretch at around 2270 cm^{-1} could be observed. These indicate that some isocyanate groups reacted with the hydroxyls on the SiO_2 surface and some isocyanate groups were reserved. The absence of peaks 2270 cm^{-1} in Figure 4.5(c) which is refer to isocyanate group reveals that all the reserved isocyanate groups were reacts with hydroxyl groups from cyclodextrin. It shows that cyclodextrin successfully immobilized on silica. Figure 4.5(c) shows that the peaks at 468.08 cm^{-1} represented to Si-O bond rocking where as 855 cm^{-1} is referred to the peak considered for α-(1,4) glucopyranose from β-CD (Jianfei *et al.*, 2007).

4.1.4 Characterization of Silica, Silica-TDI and Si-TDI-β-CD

(a) FT-IR analysis

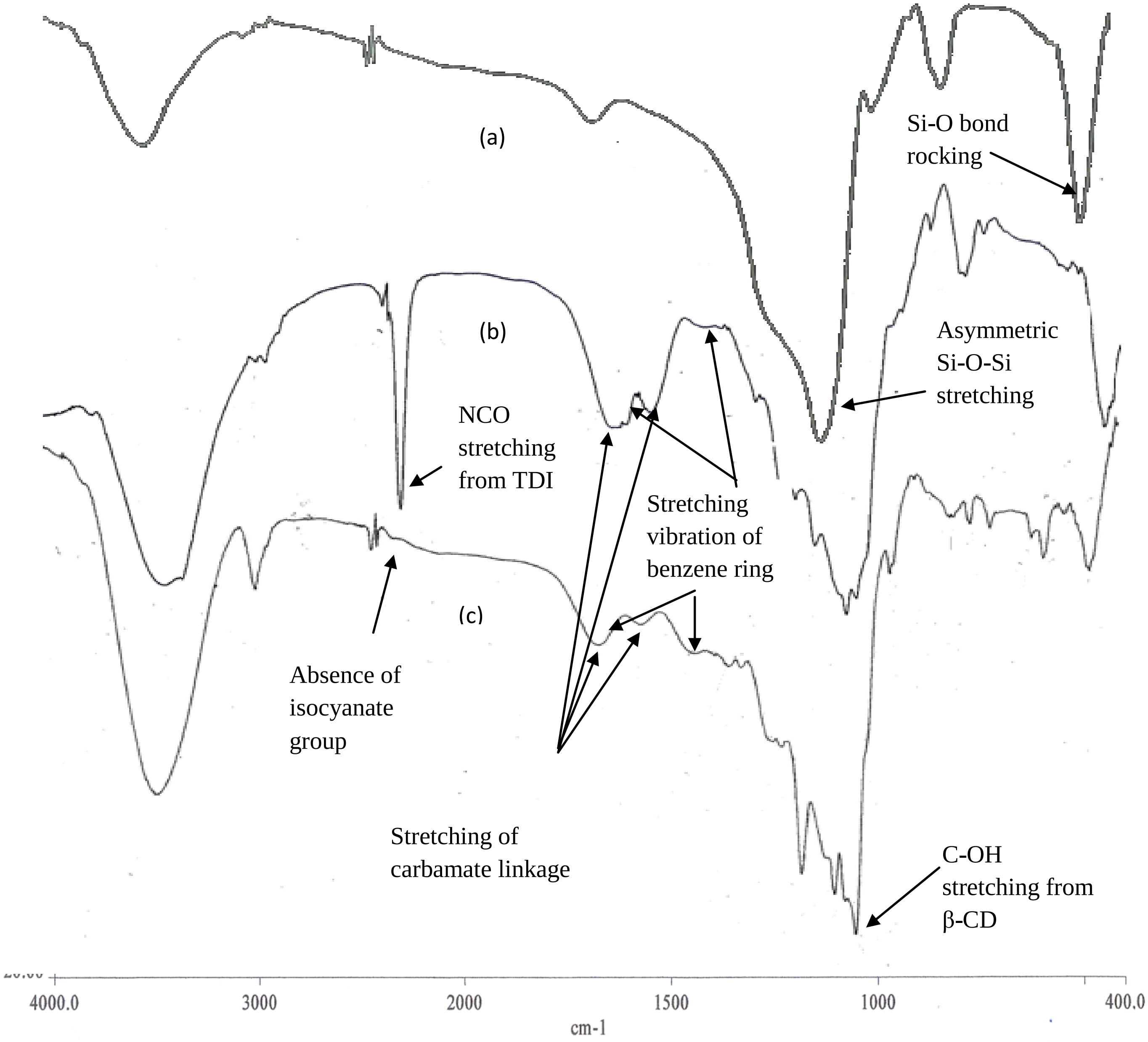


Figure 4.5 : IR spectra of (a) SiO_2 , (b) Si-TDI and (c) SI-TDI-β-CD

Table 4.2 : Main IR frequencies with assignments

Samples	**wavelength (cm^{-1})**	**Assignments**
SiO_2	1093	asymmetric Si-O-Si stretching
	472	Si-O bond rocking
Silica-TDI	1630, 1541	stretching vibration of carbamate
	1585,1415	stretching vibration of aromatic ring
	2270	NCO stretch
Si-TDI-β-CD	1645, 1547	stretching vibration of carbamate
	1585,1415	stretching vibration of aromatic ring
	1029	C-OH stretching vibration from β-CD
	855	α-(1,4) glucopyranose in β-CD

(b) TGA-DTA analysis

Figure 4.6 and Figure 4.7 show TGA-DTA analysis of Si-TDI and Si-TDI-β-CD, respectively. At figure 4.6, the peak at 230-300°C is due to the decomposition of carbamate group, while Figure 4.7, the peak at 300-350°C is due to the decomposition of β-CD. From the result of thermogram, it shows that β-CD successfully immobilized on Si-TDI.

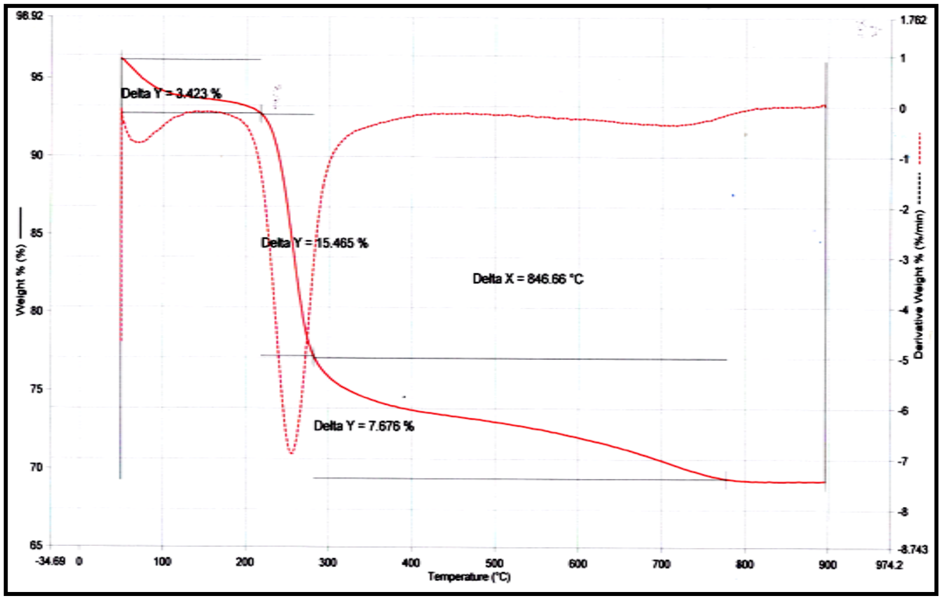


Figure 4.6: TGA-DTA analysis of Si-TDI

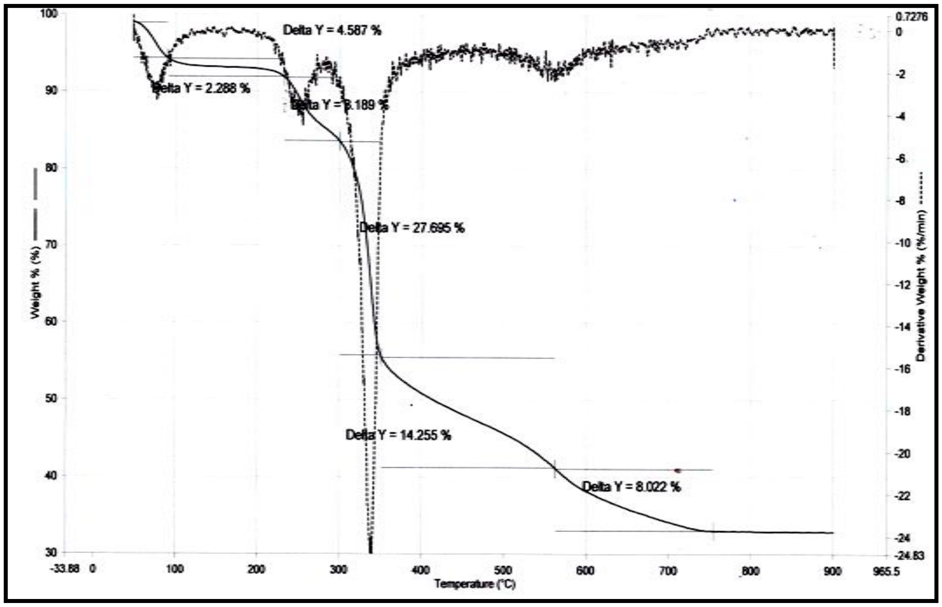


Figure 4.7: TGA-DTA analysis of Si-TDI-β-CD

4.2 OPTIMIZATION OF CR(VI)-DPC COMPLEX

4.2.1 Effect of acidity

The formation and stability of the Cr-complex with DPC were affected by acidity. The concentration of H_2SO_4 was investigated between a range of 0.007-0.015 mol/L in 100 mL of volumetric flask. The maximum capacity of Cr-complex with DPC was observed at 0.008 mol/L of H_2SO_4 (Figure 4.8). So, 0.008 mol/L of H_2SO_4 was chosen for further study.

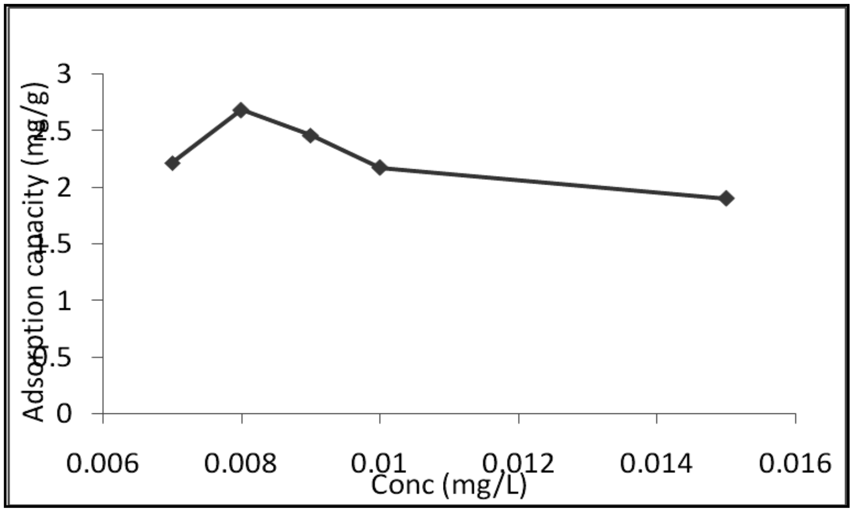


Figure 4.8 : Graph effect of acidity in ranges molarity 0.007-0.015 mol/L.

4.2.2 Effect of concentration of 1,5-diphenylcarbazide (DPC) as chelating reagent.

The concentration of DPC was investigated between range of 0.001-0.015 mol/L in 100 mL volumetric flask. It was shown that the highest capacity for adsorption of Cr-complex with DPC was achieved at 0.0025 mol/L of DPC. The concentration of DPC at 0.0025 mol/L was used for further study.

4.3 SORPTION ISOTHERM STUDIES

Adsorption equilibrium data which express the relationship between mass of adsorbate per unit weight of adsorbent and liquid phase equilibrium concentration of adsorbate are presented by adsorption isotherms and provide important data for adsorption system. Adsorption isotherm also plays a crucial role in the predictive modeling procedures for the analysis and design of an adsorption system. Therefore, the Langmuir and Freundlich isotherm are the most frequently used equations to plot data corresponding to adsorption from solution measurements (Crini *et al.*, 2007; Aydin *et al.*, 2009). Several isotherm equations have been used for the equilibrium modeling of adsorption systems. The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the regression: i.e the isotherm giving an R^2 value close to unity is deemed to provide the best fit (Benguella and Benaissa, 2002).

a) Langmuir isotherm

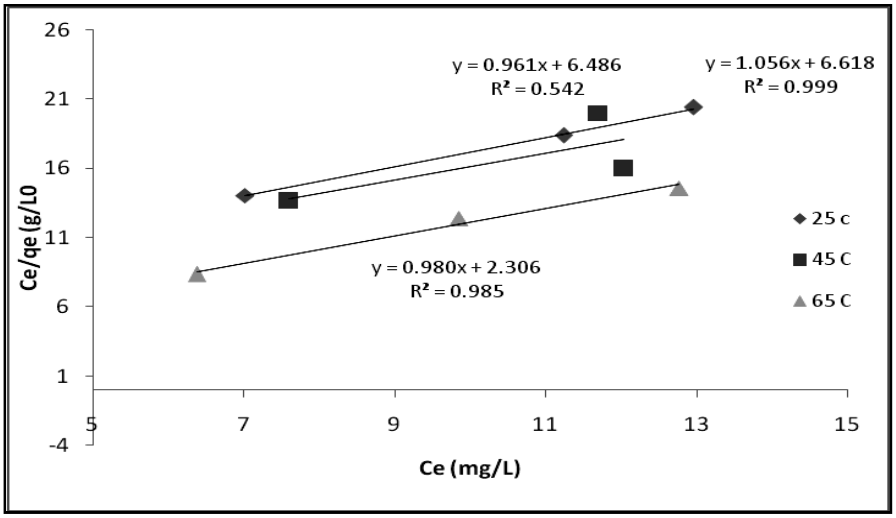
Langmuir equation is probably the most widely applied model for isotherm adsorption, it is considered that the adsorption energy of each molecule is the same, independently of the surface material, the adsorption takes place only on some sites and there is no interaction between the molecules (Granados-Correa and Jimenez-Becerril, 2009). The Langmuir equation is applicable to homogeneous adsorption, where the adsorption of each molecule onto surface has equal adsorption activation energy and no transmigration of adsorbate in the plane of the surface (Monika *et al.,* 2009; Pehlivan and Cetin, 2009).

Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \qquad [2]$$

where C_e is the equilibrium concentration (mg/L), q_e the amount of chromium sorbed at equilibrium (mg/g), q_m is amount of chromium sorbed for a complete monolayer (mg/g), b is a constant related to the energy or net enthalpy of sorption (L/mg). The graph plots of Langmuir model at different temperature are exhibited at Figure 4.9 (a-c).

(a)



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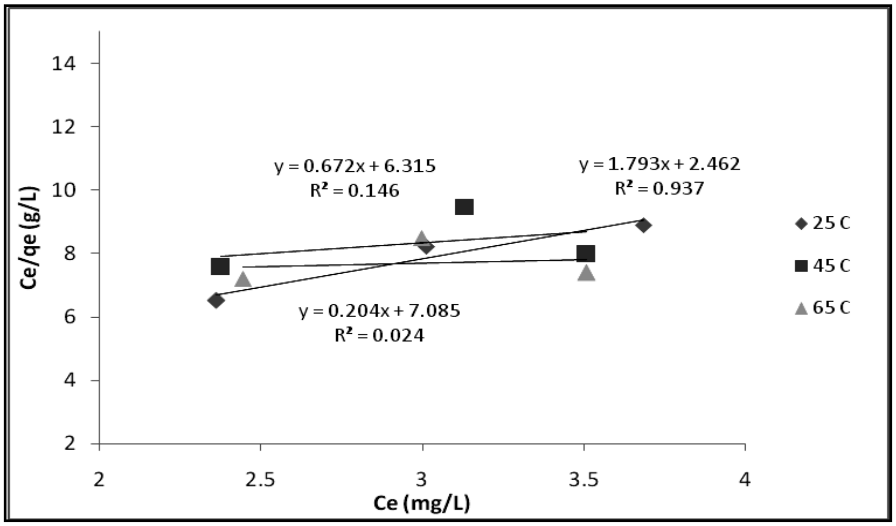


(c)

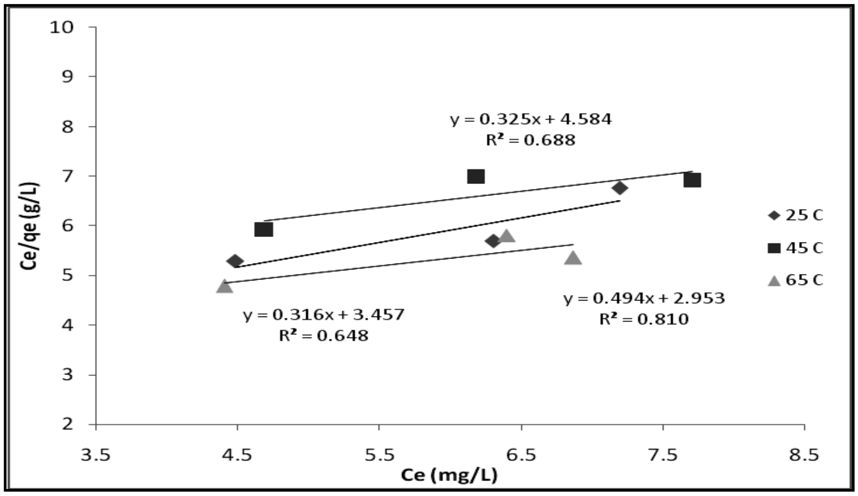


Figure 4.9 (a-c): Langmuir isotherm at different temperature for (a) β-CDP-HMDI, (b) β-CDP-TDI and (c) Si-TDI-β-CD.

b) Freundlich isotherm model :

The Freundlich isotherm assumes that the uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with increase concentration (Karthikiyen *et al.*, 2005). Its application suggests that adsorption energy decreases exponentially on completion of the adsorption centre of an adsorbent. From the Freundlich isotherm of metal ion it could be assumed that the stronger binding sites are occupied first, and then the binding strength decreased with increasing degree site occupation (Pehlivan *et al.*, 2009).

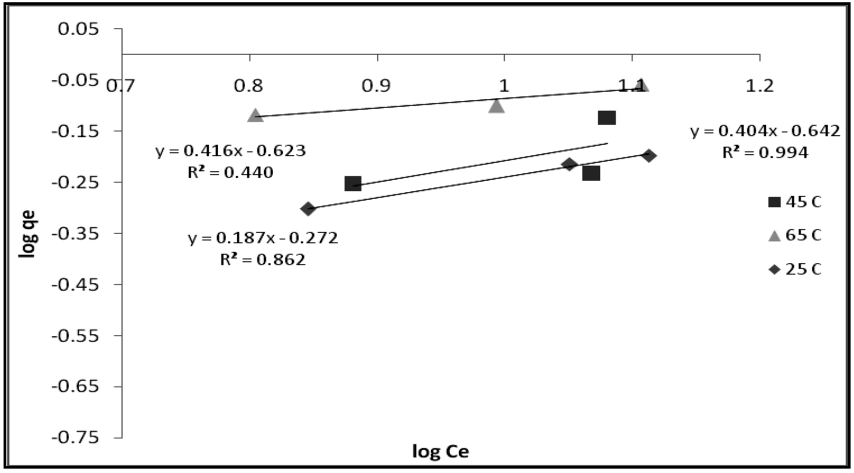
Freundlich isotherm model:

$$\log q_e = \log K_f \ + \frac{1}{n} \log C_e \qquad [3]$$

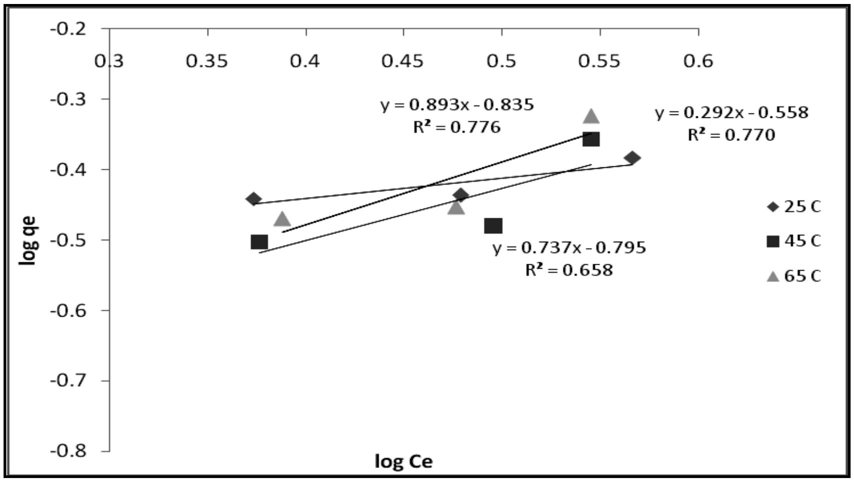
where K_f indicate adsorption capacity (mg/g) and 1/n is an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent, q_e is amount of chromium sorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L).

The graph plots of Freundlich model at different temperature are exhibited at Figure 4.10 (a-c).

(a)



(b)



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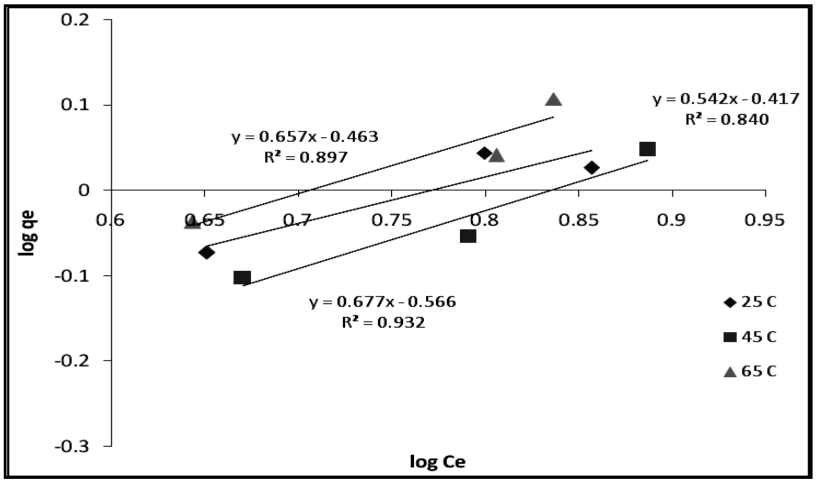


Figure 4.10 (a-c) : Freundlich isotherm at different temperature for (a) β-CDP-HMDI, (b) β-CDP-TDI and (c) Si-TDI-β-CD

The Langmuir and Freundlich adsorption constants are evaluated from the isotherms equations and also presented in Table 4.3. It can be seen from the correlation coefficient (R^2) that the Langmuir model fits well for β-CDP-HMDI, suggesting the monolayer coverage of Cr-complex with DPC onto particles and also the homogeneous distribution of active sites on the material. The adsorption phenomenon on β-CDP-HMDI seems to be caused by inclusion of Cr-complex with DPC into β-CDP-HMDI.

However, Freundlich isotherm model fits well for β-CDP-TDI and Si-TDI-β-CD. It can be seen from correlation coefficient suggesting the multi layer coverage of Cr-complex with DPC onto the particle and also heterogeneous distribution of active sites on the adsorbent. From the results, it show that the type of bifunctional isocyanate linker play important role to control the behavior of adsorbate during adsorption process.

Table 4.3 shows the value of q_m is increased when the temperature increases from 25ºC to 65ºC. The increase in adsorption capacity with rise temperature may be is due to the increase in chemical interaction between adsorbate and sorbent surface (Das *et al.*, 2000). This reveals the endothermic nature ongoing process.

Table 4.3 shows that β-CDP-TDI has the highest adsorption capacity while β-CDP-HMDI has the lowest adsorption capacity. The trend of adsorption capacity can be summarizing as follow: β-CDP-TDI > Si-TDI-β-CD > β-CDP-HMDI. This order is due to the behavior of adsorbent itself. β-CDP-TDI and Si-TDI-β-CD consist of aromatic ring and able to entrap Cr-complex with DPC in polymer network due to the π-π interaction between TDI and DPC. Therefore, the capacity of β-CDP-TDI and Si-TDI-β-CD are higher than β-CDP-HMDI. While the capacity of Si-TDI-β-CD is lower than β-CDP-TDI probably due to the unit of cyclodextrin is less in Si-TDI-β-CD compared to β-CDP-TDI.

1/n represented to the empirical parameter which is related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range of $0.1 < 1/n < 1$, the adsorption is favorable. The greater the value of 1/n is better which suggests more favorability of adsorption (Karthikiyen *et al.*, 2005). It was shown from Table 4.3, the trend of favorability of adsorption can be summarizing as follows: β-CDP-TDI > Si-TDI-β-CD > β-CDP-HMDI.

Table 4.3 : Parameters of Langmuir and Freundlich isotherm for sorption Cr-complex with DPC upon different types of adsorbents and temperature.

Adsorbent	Temp	Langmuir			Freundlich		
		b (L/mg)	q_m (mg/g)	R^2	K_f	1/n	R^2
β-CDP-HMDI	25 ° C	0.9469	0.1596	0.9990	0.2276	0.4042	0.9942
	45 ° C	0.9239	1.0403	0.5422	0.2379	0.4165	0.4406
	65 ° C	0.4250	1.0202	0.9855	0.5336	0.1870	0.8620
β-CDP-TDI	25 ° C	0.7279	0.5574	0.9376	0.2767	0.2920	0.7705
	45 ° C	0.1065	1.4872	0.1460	0.1602	0.7379	0.6581
	65 ° C	0.0289	4.8800	0.0242	0.1461	0.8936	0.7762
Si-TDI-β-CD	25 ° C	0.1674	2.0218	0.8103	0.3821	0.5425	0.8404
	45 ° C	0.0711	3.0694	0.6882	0.2715	0.6778	0.9320
	65 ° C	0.1315	2.4402	0.4081	0.3896	0.5668	0.6106

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant equilibrium parameter, R_L that is used to predict if an adsorption system is ‘”favorable” or “unfavorable”. Thus, R_L is a positive number whose magnitude determines the feasibility of the adsorption process. The equilibrium parameter R_L was calculated using constant b values from the following formula (Malkoc and Nuhoglu, 2007) (a & b) as given below:

$$R_L = \frac{1}{(1+bC_0)} \qquad [4]$$

where C_o is the initial Cr(VI) concentration (mg/L) and b is the Langmuir adsorption equilibrium constant (L/g). The isotherm is unfavorable when $R_L>1$, the isotherm is linear when $R_L=1$, the isotherm is favorable when $R_L<1$ and the isotherm is irreversible when $R_L=0$. The R_L values at different temperature relating to the initial Cr(VI) ion concentration are given in Table 4.4.

Table 4.4: Values of R_L for three adsorbents at different temperature and initial concentration of Cr-complex with DPC.

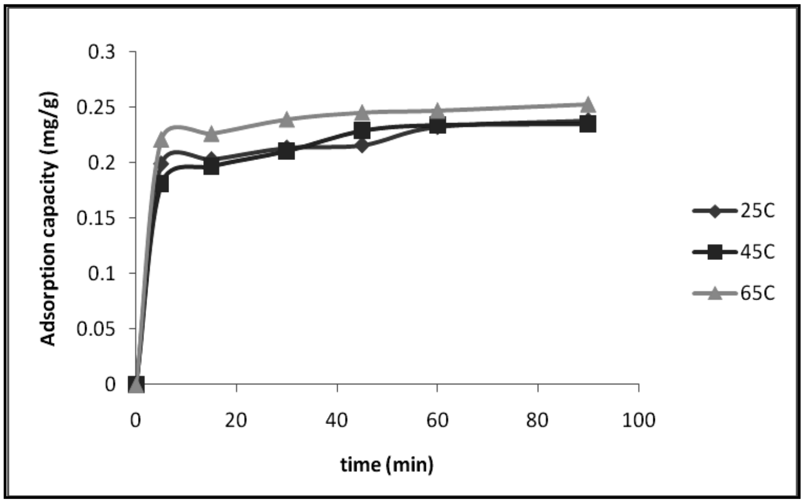
	β-CDP-HMDI			β-CDP-TDI			Si-TDI-β-CD		
C_o(mg/L)	25°C	45°C	65°C	25°C	45°C	65°C	25°C	45°C	65°C
10	0.096	0.098	0.191	0.121	0.484	0.776	0.374	0.585	0.432
15	0.066	0.067	0.136	0.084	0.385	0.698	0.285	0.484	0.336
20	0.050	0.051	0.105	0.064	0.320	0.634	0.230	0.413	0.276
25	0.041	0.042	0.086	0.052	0.273	0.581	0.193	0.360	0.233
30	0.034	0.035	0.073	0.044	0.238	0.536	0.166	0.319	0.202

The values of R_L for adsorption of Cr-complex with DPC for all adsorbents were studied at different initial concentration, temperatures and the values between 0 and 1, which indicates favorable adsorption of Cr-complex with DPC on β-CDP-HMDI, β-CDP-TDI and SI-TDI-β-CD. The R_L values increased with increasing temperature, this indicates that sorption is more favorable at high temperature except for SI-TDI-β-CD at 65°C. In addition, the R_L values decreased with increasing initial Cr(VI) ion concentration at all studied temperature indicating that sorption is more favorable at low concentration (Mittal *et al.*, 2007; Aydin and Aksoy, 2009). From the values of R_L in Table 4.4, we can conclude that the adsorption of Cr-complex with DPC in β-CDP-TDI is more favorable than Si-TDI-β-CD and β-CDP-HMDI.

4.4 SORPTION KINETIC STUDIES

The adsorption kinetic process of β-CDP-HMDI, β-CDP-TDI, Si-TDI-β-CD with 5 mg/L of Cr-complex with DPC at different temperature; 25°C, 45°C and 65°C was investigated and shown in Figure 4.11 (a-c). The sorption increase instantly at initial stages may be due to rapid attachment of Cr-complex with DPC to the surface of the adsorbent and then keeps increasing gradually until equilibrium is reached and remains constant. The kinetics result indicated that the sorption process is very fast because of the largest amount of Cr-complex with DPC adsorbed to the adsorbent within 5 minutes and equilibrium reached within 60 min.

(a)



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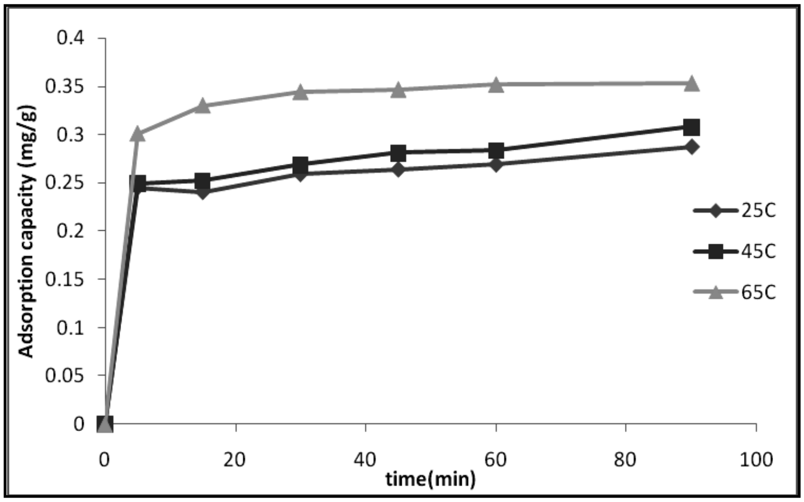


(c)

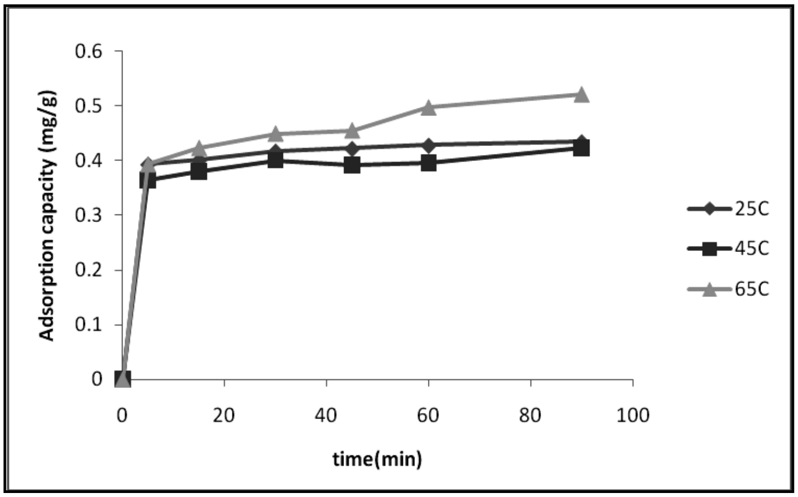


Figure 4.11(a-c) : Sorption kinetic of Cr-complex with DPC at different temperature on (a) β-CDP-HMDI, (b) β-CDP-TDI, and (c) Si-TDI-β-CD

Kinetic analysis is required to get an insight of the rate of adsorption and the rate limiting step of the transport mechanism, which are primarily used in the modelling and design of the process (Yasar and Aksoy, 2009). The adsorption kinetic data of chromium are analyzed using the pseudo-first order kinetic and pseudo-second order kinetic equation (Malkoc and Nuhoglu, 2007)(a & b).

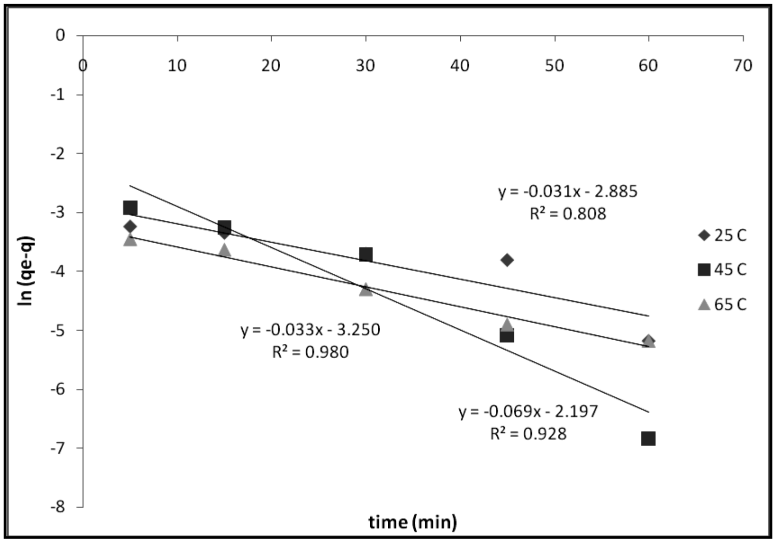
The equation of pseudo-first order kinetic model is given as:

$$\ln(q_{e-}q_t) = \ln q_e - k_1 t \qquad [5]$$

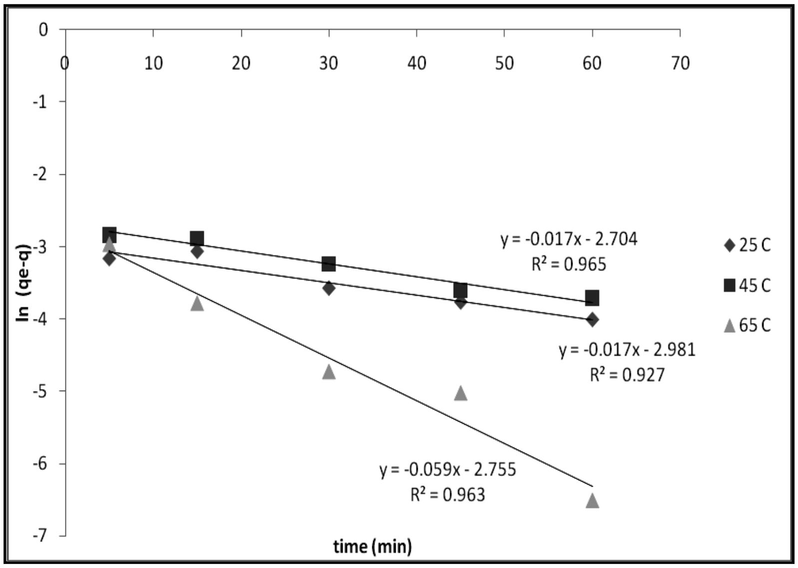
where k_1 (min $^{-1}$) is the rate constant of first order sorption, q_t denotes the amount of chromium sorption (mg/g) at time, t (min) and, q_e denotes the amounts of chromium sorption (mg/g) at equilibrium. Values of q_e and k_1 were calculated from the slope of the plots of $\log(q_e\text{-}q_t)$ against t.

The graph plot of pseudo-first order kinetic model are shown in Figure 4.12 (a-c).

(a)



(b)



(c)

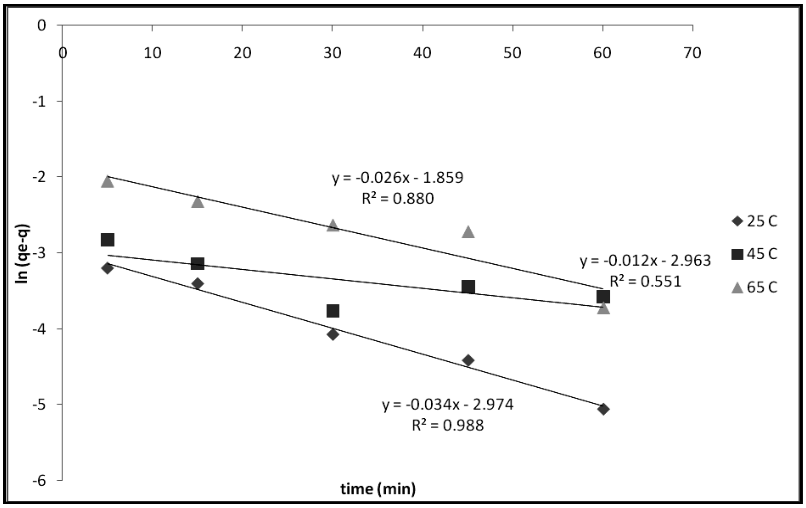


Figure 4.12 (a-c) : Plot for pseudo-first order kinetic model for adsorption Cr-complex with DPC on (a) β-CDP-HMDI, (b) β-CDP-TDI and (c) Si-TDI-β-CD.

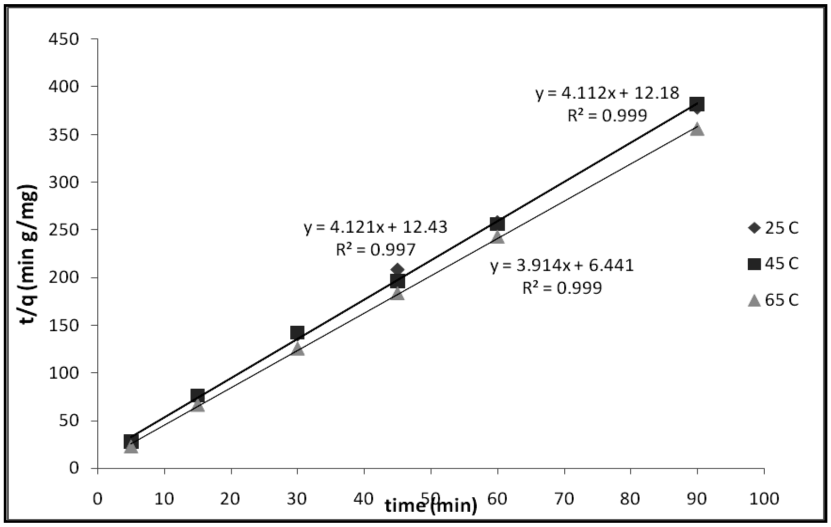
The equation of second order kinetic model is given as :

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \qquad \textbf{[6]}$$

where k_2 is the equilibrium rate constant of second order adsorption (g mg^{-1} min^{-1}). Values of k_2 and q_e were calculated from the plot of t/q against t.

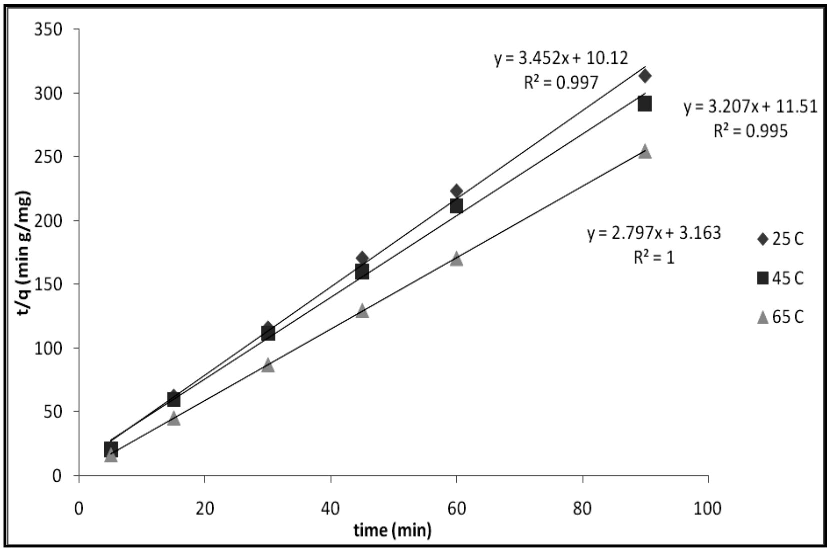
The graph plot of psuedo-second order kinetic model are exhibited in Figure 4.13 (a-c) for adsorption of Cr-complex with DPC on β-CDP-HMDI, β-CDP-TDI, Si-TDI-β-CD respectively.

(a)



t/q (min g/mg)
450
400
350
300
250
200
150
100
50
0
0
10
20
30
40
50
60
70
80
90
100
time (min)
y = 4.112x + 12.18
R² = 0.999
y = 4.121x + 12.43
R² = 0.997
y = 3.914x + 6.441
R² = 0.999
◆ 25 C
■ 45 C
▲ 65 C

(b)



t/q (min g/mg)
350
300
250
200
150
100
50
0
0
20
40
60
80
100
time (min)
y = 3.452x + 10.12
R² = 0.997
y = 3.207x + 11.51
R² = 0.995
y = 2.797x + 3.163
R² = 1
◆ 25 C
■ 45 C
▲ 65 C

(c)

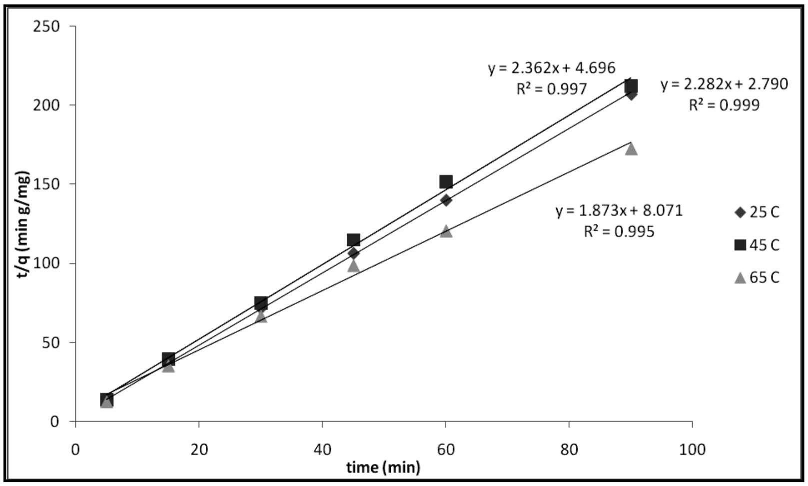


Figure 4.13(a-c) : Plot for pseudo-second order kinetic model for adsorption Cr-complex with DPC on (a) β-CDP-HMDI, (b) β-CDP-TDI, and (c) Si-TDI-β-CD

The straight line plots of pseudo-first order and pseudo-second order kinetic have been tested to obtain the kinetic parameters which are given in Table 4.5. It can be seen from correlation coefficents (R^2) that the adsorption for β-CDP-HMDI, β-CDP-TDI, and Si-TDI-β-CD follow pseudo-second order model. The calculated q_e values agree very well with the experimental data, indicating that the sorption system belongs to second order kinetic model. The rate constant for psuedo-second order increase with increasing temperature for adsorbent β-CDP-HMDI and β-CDP-TDI, while, rate constant for Si-TDI-β-CD for this adsorbent decrease with increasing of temperature.

From Table 4.5, the order of trend rate constant as follows: Si-TDI-β-CD > β-CDP-HMDI > β-CDP-TDI. β-CDP-TDI have lower rate constant than β-CDP-HMDI, this is due to the presence of aromatic group in TDI causing β-CDP-TDI to be more hydrophobic than β-CDP-HMDI. As the polymer is more hydrophobic, the diffusion of water is less, and hence the contact between polymer and solute become slower (Chin *et al.*, 2010).

While, Si-TDI-β-CD has the highest rate constant, it is might be due to the residual silanol groups on the silica, as solid support make the adsorbent more hydrophilic. Therefore, the rate constant is faster than β-CD polymer (Belyakov *et al.*, 2005).

Table 4.5 : Kinetic parameters for pseudo-first order and pseudo-second order kinetic.

Type of adsorbent	Temperature		First order kinetic			Second order kinetic		
		qe^{exp} (mg/g)	K_1 x 10^{-2} (min^{-1})	Qe^{cal} (mg/g)	R^2	K_2 x 10^{-2} (g/mg min)	qe^{cal} (mg/g)	R^2
β-CDP-HMDI	25°C	0.238	3.10	0.056	0.808	136.64	0.243	0.997
	45°C	0.235	6.90	0.111	0.928	138.80	0.245	0.999
	65°C	0.252	3.30	0.039	0.980	237.80	0.256	0.999
β-CDP-TDI	25°C	0.287	1.70	0.051	0.927	117.75	0.290	0.997
	45°C	0.308	1.70	0.067	0.965	89.35	0.312	0.995
	65°C	0.353	5.90	0.064	0.963	247.34	0.368	1.000
Si-TDI-β-CD	25°C	0.434	3.40	0.051	0.988	186.88	0.439	0.999
	45°C	0.424	1.20	0.052	0.551	118.80	0.423	0.997
	65°C	0.521	2.60	0.156	0.880	43.46	0.534	0.995

4.5 DETERMINATION THERMODYNAMIC

Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy (ΔS°) can be estimated using equilibrium constants changing with temperature. The standard free energy change of the sorption reaction is given by the following equation (Kumar *et al.*, 2006; Malkoc and Nuhoglu, 2007 (a & b)).

$$\Delta G^{\circ} = -RT\ lnK_d \qquad [7]$$

where R is the ideal gas constant (8.314 $Jmol^{-1}K^{-1}$) and T is the temperature (K).

The apparent equlibrium constant (K_d) of the adsorption is defined as :

$$K_d = \frac{C_{ad,eq}}{C_{eq}} \qquad [8]$$

where $C_{ad,eq}$ and C_{eq} are the concentration of Cr(VI)-DPC complex on the adsorbent and residual Cr-complex with DPC concentration at equlibrium, respectively. In this case, the activity should be instead of concentration in order to obtain the standard thermodynamic equlibrium constant (K_d) of the adsorption system.

$$\ln K_d = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad [9]$$

Figure 4.14 shows the graph plot of ln K_d vurses 1/T. The value of ΔH° and ΔS° can be calculated from the slope and intercept, respectively. The value of parameters of thermodynamic are shown in Table 4.6.

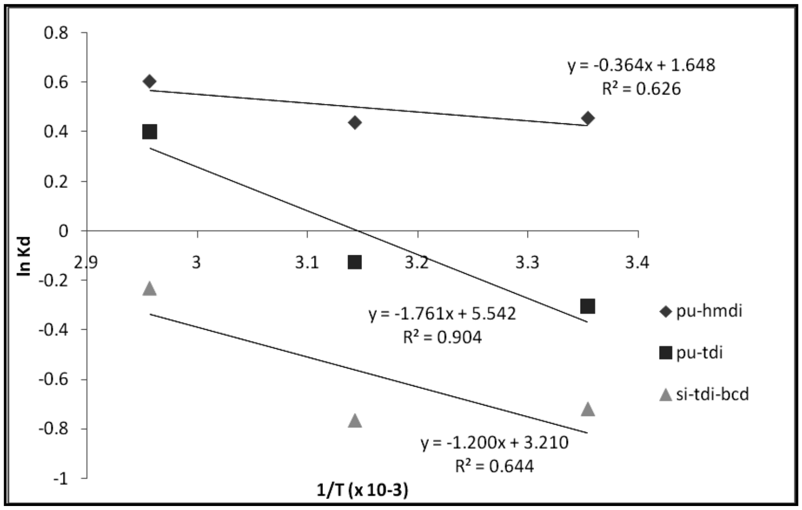


Figure 4.14 : Plot graph of ln Kd vs 1/T for three of adsorbents.

Table 4.6: Thermodynamic parameters of adsorbent

Type of adsorbent	Temperature	Enthalpy **ΔH°(kJ/mol)**	Entropy **ΔS°(J/Kmol)**	**Gibbs energy, ΔG° (J/mol) x 10^3**
β-CDP-HMDI	25°C	3.026	13.709	-4.084
	45°C			-4.358
	65°C			-4.636
β-CDP-TDI	25°C	14.649	46.076	-13.723
	45°C			-14.645
	65°C			-15.566
Si-TDI-β-CD	25°C	9.977	26.688	-7.947
	45°C			-8.841
	65°C			-9.015

The negative values of free energy change (ΔG°) at all temperature indicates thermodynamically feasible and spontaneous nature of the adsorption of Cr-complex with DPC on all adsorbents. The values of ΔG° varied in the range of -15.566 to -4.084 kJ/mol. The change of the standard free energy decreases with increasing temperature regardless of the nature of adsorbent, suggesting the more adsorbable of Cr-complex with DPC with increasing temperature and also shows a decrease in feasibility of adsorption at higher temperature (Karagozoglu *et al.,* 2007; Sari and Tuzen, 2008). The trends of ΔG° values follows as: β-CDP-TDI > Si-TDI-β-CD > β-CDP-HMDI, with β-CDP-TDI is more absorbable of Cr-complex with DPC than β-CDP-HMDI.

The values of ΔH° varied in the range of 3.03-9.98 kJ/mol,which the positive value of ΔH° suggests the endothemic nature of adsorption. In addition, the low values of ΔH° indicates that there was loose of bonding between the adsorbate molecules and adsorbent surface (Singh, 2000; Ozcan, 2006). From the values of ΔH° and compared with the three of adsorbents, we can make the trend and order of increasing the value of ΔH°; β-CDP-TDI > Si-TDI-β-CD > β-CDP-HMDI. Table 4.6 shows that β-CDP-TDI has the highest value of ΔH° and it reveals that β-CDP-TDI have strong chemical bond with Cr-complex with DPC. The magnitude heat of adsorption, ΔH° value gives an indication on the type of adsorption, which can either physical or chemical sorption. The heat of adsorption, ranging from 0.5 to 5 kcal/mol (2.1-20.9 kJ/mol), is said to be physical adsorption, and the heat of adsorption ranging from 5-100 kcal/mol (20.9-418.4 kJ/mol), is said to be chemical sorption (Deng *et al.*, 2007; Sari and Tuzen, 2008). The values of ΔH°for all adsorbents were in range of 3.03-9.98 kJ/mol, indicating the type of adsorption is physiosorption.

The values of entropy for all adsorbents were in range of 13.71-46.08 kJ/K mol. The positive of ΔS° shows that the increased randomness at the solid/solution interface during the adsorption process, which suggests that Cr-complex with DPC ions replace some water molecules from the solution previously adsorbed on the surface of adsorbent. These displaced molecules gain more translation entropy than is lost by the absorbate ions, thus allowing the prevalence of randomness in the system (Vinod *et al.*, 1999; Malkoc and Nuhoglu, 2007 (a)). In addition, the positive of entropy of adsorption reflects the affinity of the adsorbent material towards Cr-complex with DPC (Chegrouche *et al.*, 2009). From the values of entropy in Table 4.6, it shows that β-CDP-TDI has the highest affinity of the adsorbent material towards the Cr-complex with DPC than Si-TDI-β-CD and β-CDP-HMDI.

CHAPTER 5

CONCLUSION

In this study, adsorbents containing β-cyclodextrin were successfully synthesized with two methods, polymerization and immobilization processes. The adsorbents are β-CDP-HMDI, β-CDP-TDI and Si-TDI-β-CD. Al these adsorbents were characterized using FT-IR and TGA-DTA analysis. The adsorbents were used for adsorption of Cr-complex with DPC.

The adsorption isotherm and kinetics of all adsorbents were studied. It shows that the Langmuir isotherm model is better fitting for adsorbent β-CDP-HMDI, while Freundlich isotherm model is better fitting for adsorbent β-CDP-TDI and Si-TDI-β-CD. The order of adsorbent for adsorption capacity can be summarized as follows: β-CDP-TDI > β-CDP-HMDI > Si-TDI-β-CD.

In order to analyze the kinetics data, two kinetic models, pseudo-first order and pseudo-second order were applied. It was found that the adsorption processes for all adsorbents follow second order kinetic. The pseudo-second order rate constant is increased with increasing temperature for adsorbent β-CDP-HMDI and β-CDP-TDI, while rate constant for Si-TDI-β-CD decreases with increasing temperature.

Thermodynamic parameters for the sorption have been evaluated. The thermodynamic study for enthalpy ($\Delta H°$) value is positive suggesting an endothermic nature of the adsorption. The magnitude heat of adsorption , $\Delta H°$ falls into the heat range of physiosorption.

The negative value of free energy (ΔG°) for all adsorbents decrease with increasing temperature, indicating that the thermodynamically feasible and and spontaneous nature of the adsorption of Cr-complex with DPC. β-CDP-TDI has the highest value of free energy than Si-TDI-β-CD and β-CDP-HMDI.

The positive value of ΔS° shows that the increased randomness at the solid/solution interface during the adsorption process. In addition, more positive value of entropy suggesting that the adsorption reflects the affinity of the adsorbent material towards the Cr-complex with DPC. The order of ΔS° value are : β-CDP-TDI > Si-TDI-β-CD > β-CDP-HMDI. It shows that, β-CDP-TDI has a good affinity of adsorbent material towards Cr-complex with DPC than Si-TDI-β-CD and β-CDP-HMDI.

From the trends of parameter of adsorption capacity, rate constant and thermodynamic parameter, it reveals that there are two main factors contributing in the adsorption process. The factors are the types of crosslinker and the matrix of adsorbent. In this study, TDI which consist aromatic group enhance the adsorption process due to the π-π interaction between TDI and DPC. This aromatic group also decreased the rate of uptake since it is more hydrophobic compared to the aliphatic crosslinker, HMDI. In addition, the matrix of adsorbent need to be considered. The immobilization of cyclodextrin on silica gel has highest rate of uptake compared to the poly-cyclodextrin. It is due to presence of residual silanol groups on the surface of silica gel which make the adsorbent more hydrophilic. Recommendation for future studies;-

- To apply these adsorbents for speciation study;
- To apply these adsorbents for extraction for organic components