



Effect of Bifunctional Isocyanate Linker on Adsorption of Chromium(VI) Diphenylcarbazide Complex onto β -Cyclodextrin

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Two polymers has been synthesized using bifunctional reagents of isocyanate group as crosslinking agent, which are β -cyclodextrin polymer crosslinked hexamethylene diisocyanate (β -CDP-HMDI) and β -cyclodextrin polymer crosslinked toluene-2,4-diisocyanate (β -CDP-TDI). The adsorption of Cr(VI) ions from aqueous solution by β -cyclodextrin polymer (β -CDP) as an adsorbent was studied in batch adsorption experiments. The method was based on the complex of Cr(VI) with 1,5-diphenylcarbazide (DPC) in acidic solution loaded on β -CDP-HMDI and β -CDP-TDI adsorbents. The adsorbents were characterized using Fourier transform infrared spectroscopy. The adsorption isotherm and kinetics of Cr(VI)-DPC complex onto both of β -cyclodextrin polymer were studied. It showed that the Langmuir isotherm is better fit described the adsorption process for β -CDP-HMDI, while Freundlich isotherm is better fit for β -CDP-TDI. The pseudo second order kinetic model represented the adsorption process for both of β -cyclodextrin polymer adsorbents. However, the rate constant of adsorption by β -CDP-TDI was lower than β -CDP-HMDI. The thermodynamic study showed that the enthalpy (ΔH°) value of β -CDP-TDI was higher than β -CDP-HMDI, indicated that β -CDP-TDI has strong chemical bond with Cr(VI)-DPC. Furthermore, the value of free energy (ΔG°) and entropy (ΔS°) showed that β -CDP-TDI was more absorbable of Cr(IV)-DPC complexes than β -CDP-HMDI. From these results, it was revealed that cross-linking agent is the main factor that contribute in the adsorption process of Cr(VI)-DPC complex onto β -cyclodextrin polymer.

Key Words: β -Cyclodextrin, Bifunctional cross-linking agent, Isocyanate, Adsorption, Cr(VI).

INTRODUCTION

Chromium is one of the toxic heavy metals and is a major pollutant in wastewater. The chromium is originates from wide-spread use in various industries such as metallurgical, refractory and chemical. Chromium exists in two stable oxidation states, Cr(III) and Cr(VI). Both of them have drastically different charge, physicochemical properties as well as chemical and biochemical reactivity¹. Cr(VI) exerts toxic effects on biological systems and exposure to hexavalent Cr compounds leads variety of clinical problem. It can cause perforation of the nasal septum, asthma and bronchitis. It also causes health disorders, such as vomiting and hemorrhage². It is known to be carcinogenic and mutagenic which induces dermatitis. The maximum level permitted in wastewater is 5 ppm for Cr(III) and 0.05 ppm for Cr(VI)^{3,4}. Due to the extreme toxicity of Cr(VI), its selective determination and removal from wastewater is of particular concern.

Several methods have been developed for removal of Cr(VI) from aqueous solution such as chemical precipitation,

chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology and evaporation recovery⁵. However, these technology processes have considerable disadvantages including incomplete metal removal, necessity for expensive equipment and monitoring system, high reagent, energy requirement or generation of toxic sludge or other waste products that require disposal⁶. Compared with several methods, adsorption is one of the most economically favourable and a technically easy method, more effective and widely used technique⁷ for water treatment in terms of flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants⁸. It is a physicochemical wastewater treatment process, which is gaining prominence as a means of producing high quality effluents, which are low in metal ion concentrations.

Many different types of adsorbents were used for selective determination and removal of chromium species from water samples in adsorption technique includes activated carbon⁹⁻¹¹, industrial by-products¹², biomass¹³, clays¹⁴ and agricultural

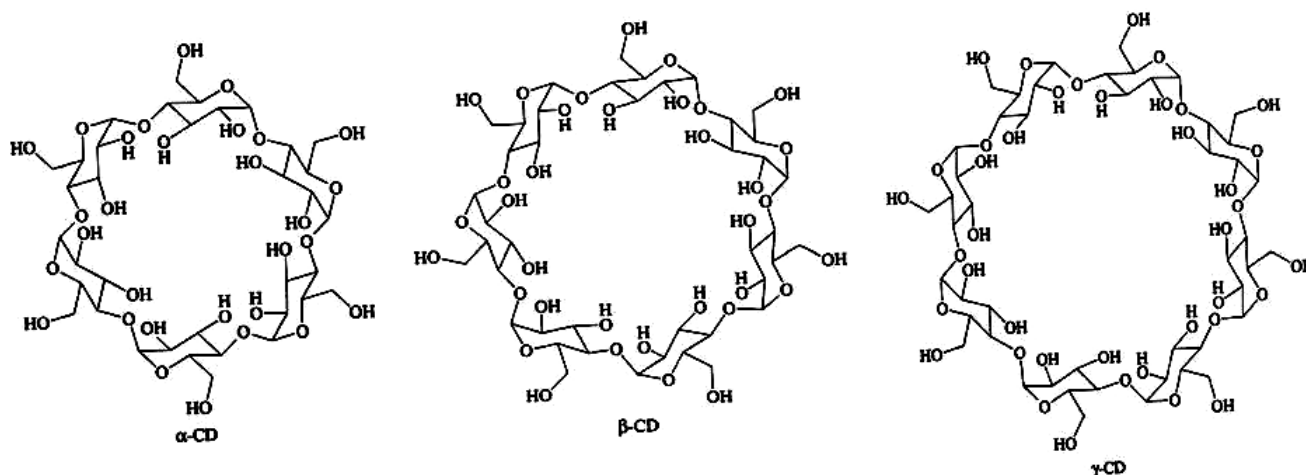


Fig. 1. Chemical structure of types of cyclodextrins²¹

waste^{5,15-17}. Recently, much attention has been focused on biopolymers and natural molecules^{18,19} such as chitosan²⁰, starch or β -cyclodextrin (β -CD) as adsorbents.

Cyclodextrins are a family of cyclic oligosaccharides composed of α -(1,4) linked glucopyranose subunits. There are three main types of cyclodextrin; α -, β - and γ -cyclodextrin, which contain 6, 7 and 8 of glucopyranose unit, respectively (Fig. 1). They possess a cage-like supramolecular structure, which is the same as the structure formed from cryptands, calixarenes, cyclophanes, spherands and crown ethers²¹. It is a torus-shaped cyclic oligosaccharide made up of seven α -1,4-linked-D-glucopyranose units. The C-2-OH group of one glucopyranose unit can form a hydrogen bond with the C-3-OH of the adjacent glucopyranose unit²². Among these three types, β -cyclodextrin is most accessible and low-priced²³. However, its solubility in water makes it inconvenient to use as adsorbent²⁴, therefore, β -cyclodextrin polymer may offer better alternatives.

There are many several application of β -cyclodextrin polymer as adsorbent is applied to adsorb pollutants such as removal of dyes²⁵⁻²⁹ and aromatic compounds³⁰⁻³⁷. The β -cyclodextrin can be cross-linked by a reaction between the hydroxyl groups of the chains with a coupling agent to form water-insoluble cross-linked network^{28,37}. The general method for synthesis of water-insoluble β -cyclodextrin polymer is by crosslinking the hydroxyl groups of β -cyclodextrins with bi- or multi-functional molecules to form a stable crosslinked network. The bi- or multi-functional molecules used are normally called crosslinking agents. Epichlorohydrin³⁸⁻⁴², diisocyanates⁴³⁻⁴⁵, polycarboxylic acids⁴⁶⁻⁴⁹ and anhydrides^{50,51} have been reported to be effective crosslinking agents.

In this study, two β -cyclodextrin polymer adsorbents which are β -cyclodextrin polymer cross-linked with 1,6-hexamethylene diisocyanate (β -CDP-HMDI) and β -cyclodextrin polymer cross-linked with toluene-2,4-diisocyanate (β -CDP-TDI) has been used as sorbents for removal of Cr(VI) where the method is based on the complex reaction of 1,5-diphenylcarbazide (DPC) (Fig. 2) with Cr(VI) produces diphenylcarbazide complex-chromium at acidic condition. The sorption behaviours of the two polymers were compared through experimental investigations. The influence

of several operating parameters such as initial concentration and contact time was also investigated. The adsorption isotherm and kinetics of Cr(VI)-DPC complex onto both of β -cyclodextrin polymer were studied to identify the possible mechanism of the sorption process. The aim of the present work was to investigate the effect of bifunctional isocyanate linker on adsorption of chromium (VI)- diphenylcarbazide complex onto β -cyclodextrin polymer.

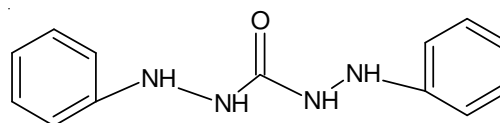


Fig. 2. 1,5-Diphenylcarbazide

EXPERIMENTAL

A model analyst 400 (Perkin Elmer, Germany) flame atomic absorption spectrometry equipped with an air acetylene burner and chromium electrodeless discharge lamp was used for the determination of chromium. The pH measurements were performed with Eutech model (Singapore) of pH meter. FTIR spectra of the polymers were recorded using FTIR spectrophotometer (Perkin Elmer, United Kingdom) in KBr pellets.

1,5-Diphenylcarbazide (Acros) solution was prepared daily by dissolving appropriate amount of 1,5-diphenylcarbazide (Sigma) in 25 mL of acetone (Fisher). Cr(VI) stock solutions (1000 mg/L) were prepared from K_2CrO_4 (Merck), H_2SO_4 (37 %) (Fisher) were used. β -cyclodextrin (Acros), 1,6-hexamethylene diisocyanate (HMDI) (Sigma), toluene-2,4-diisocyanate (TDI), dimethylformamide, acetone were purchased from Acros and all other chemicals used were analytical grade. The ultra pure water was used during experiment.

Synthesis of β -cyclodextrin polymer (β -CDP-HMDI and β -CDP-TDI): β -Cyclodextrin polymer was synthesized according to the method of Baskhar *et al.*⁵², 5 g β -cyclodextrin was dissolved with 15 mL of dimethylformamide in 500 mL of round bottom flask at room temperature. A calculated amount of cross-linker 1,6-hexamethylene diisocyanate or toluene-2,4-diisocyanate was added drop wise into the mixture.

The mixture of β -cyclodextrin and 1,6-hexamethylene diisocyanate or toluene-2,4-diisocyanate was prepared in ratio 1:10 and 1:7 mmol, respectively. The mixture solution was stirred at 70 °C for 4 h. Finally, the polymer was precipitated when added and washed with large excess of methanol. The polymer was filter off by suction and dried at oven overnight at 80 °C. The polymers were characterized using FT-IR with a KBr pellet technique.

Cr(VI)-1,5-diphenylcarbazine complex solution preparation: The formation of Cr(VI)-DPC complex was prepared by adding 20 mL of known concentration of Cr(VI) in acidic medium of H₂SO₄ 0.008 mol/L into 3 mL of 1,5-diphenylcarbazine (0.0025 M). It was left for about 10 minutes to make sure the formation of complex reaction was complete.

Adsorption experiments: Adsorption capacities and kinetics were conducted using the batch method. Experimental data were obtained at of 25, 45 and 65 °C by varying the concentration of Cr(VI)-DPC complex in aqueous solution from 10 to 30 mg/L. In each experiment, a series of 20 mL of Cr(VI)-DPC complex was added to 0.05 g of β -CDP-HMDI or β -CDP-TDI at a known initial concentration. The mixture was then stirred in a water bath on a constant agitation speed of 180 rpm continuously at different temperatures. Studies were conducted at various time intervals to determine when adsorption equilibrium was reached. The solid phase was separated by filtration. The suspension was subjected and the final concentration of filtrate was determined by flame atomic absorption spectrometry.

Adsorption capacity of adsorbent was calculated from the equation given by:

$$Q = \frac{(C_o - C_f)V}{m} \quad (1)$$

where, Q is the adsorption capacity of adsorbent (mg/g), C_o and C_f are the initial and final concentration of the chromium(VI) solution (mg/L) respectively and m is the mass of β -CDP-HMDI or β -CDP-TDI (g).

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy: β -Cyclodextrin, β -CDP-HMDI, β -CDP-TDI has been characterized using Fourier transform infrared spectroscopy. The band assignments related to the FT-IR analyses of the β -cyclodextrin, β -CDP-HMDI and β -CDP-TDI are given in Table-1. Absence of peak at 2270 cm⁻¹ (corresponding to isocyanate group) shows that completion of reaction. The bands at 2925 cm⁻¹ and 2933 cm⁻¹ correspond to the methylene group in 1,6-hexamethylene diisocyanate, while the bands at 1602 cm⁻¹ and 1457 cm⁻¹ are represent the aromatic group in toluene-2,4-diisocyanate. The adsorption band at 1253 cm⁻¹ could be attributed to the C=O characteristics vibrations of aliphatic polyurethane. The 856 cm⁻¹ peak considered for α -(1,4) glucopyranose in β -cyclodextrin.

Adsorption experiments: Adsorption isotherm expresses the relationship between mass of adsorbate per unit weight of adsorbent and liquid phase equilibrium concentrations of adsorbate. Langmuir and Freundlich isotherm are the most frequently used equations to plot data corresponding to adsorption from solution measurements^{20,27}. 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 R² value close to unity is deemed to provide the best fit⁶.

TABLE-1
KEY IR FREQUENCIES WITH ASSIGNMENTS

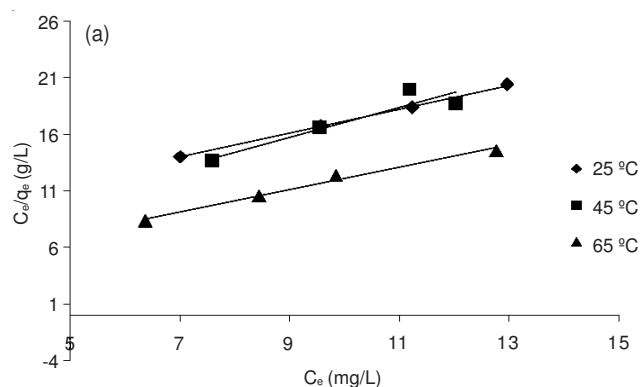
Samples	Wavelength (cm ⁻¹)	Assignments
β -cyclodextrin	856	α -(1,4)glucopyranose
	1029, 1100	C-OH stretching vibration
β -CDP-HMDI	1253	C=O vibrations of aliphatic polyurethane
	1569	NHCO, carbamate linkage
	3420, 1700	NH and C=O
	2270	Absence of isocyanate group (completion of reaction polymerization)
	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)

Langmuir isotherm: Langmuir equation is consider 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 molecules⁵³. 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^{4,54}.

Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m} \quad (2)$$

where, C_e is the equilibrium concentration (mg/L), q_e the amount of Cr sorbed at equilibrium (mg/g), q_m is amount of Cr 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 presented in Fig. 3a and 3b.



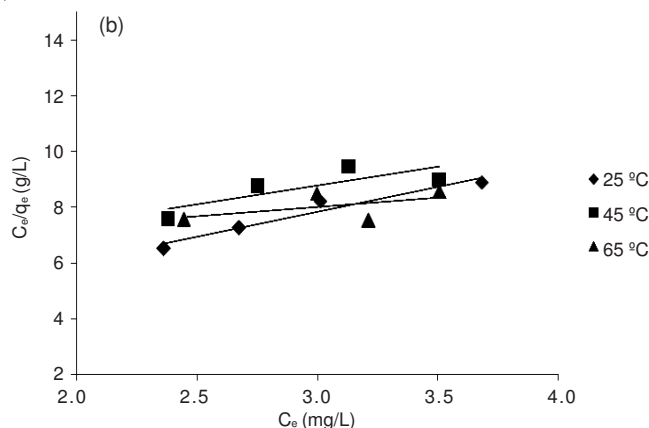


Fig. 3. Langmuir isotherm at different temperature for (a) β -CDP-HMDI, (b) β -CDP-TDI

Freundlich isotherm: Freundlich isotherm assumes that the uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption and the amount of adsorbate adsorbed increases infinitely with an increase concentration¹¹. Its application suggests that adsorption energy exponentially decreases 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 is decreased with increasing degree site occupation⁵⁵.

Freundlich isotherm model:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

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 shown in Fig. 4a and 4b.

From Table-2 it can be seen from the correlation coefficient (R^2) that the Langmuir model is fitting well for β -CDP-HMDI, suggesting the monolayer coverage of Cr(VI)-DPC complex 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(VI)-DPC complex into β -CDP-HMDI. However, Freundlich isotherm model is fitting well for β -CDP-TDI. It can be seen from correlation coefficient and suggesting the multilayer coverage of Cr(VI)-DPC complex onto the particle and also heterogeneous distribution of active sites on the adsorbent. From the result, it shows that the type of bifunctional isocyanate linker plays important role to control the behaviour of adsorbate during adsorption process.

The value of q_m increases with increase of the temperature from 25 to 65 °C. The increase in adsorption capacity with rise temperature may be is due to the increase in chemical interaction between adsorbate and sorbent surface¹⁰. This reveals the endothermic nature of the ongoing process.

Table-2 also showed that β -CDP-TDI has the higher adsorption capacity while β -CDP-HMDI has the lower

adsorption capacity. β -CDP-TDI consists of aromatic ring and able to entrap Cr(VI)-DPC complex in polymer network due to the π - π interaction between toluene-2,4-diisocyanate and 1,5-diphenylcarbazide. Therefore, the capacity of β -CDP-TDI is higher than β -CDP-HMDI.

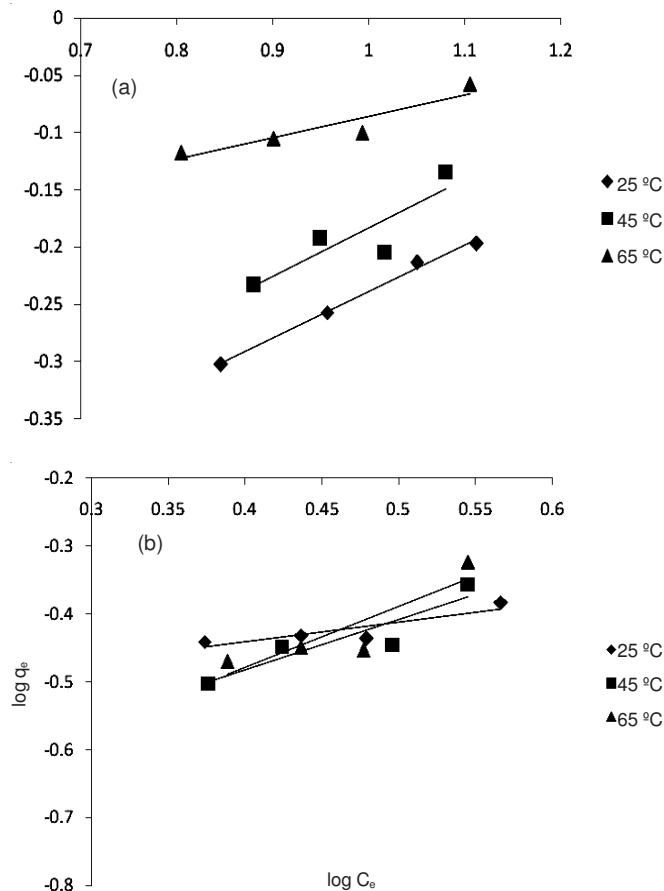


Fig. 4. Freundlich isotherm at different temperature for (a) β -CDP-HMDI, (b) β -CDP-TDI

Adsorbent	Temp. (°C)	Langmuir			Freundlich		
		b (L/mg)	q_m (mg/g)	R^2	K_f	$1/n$	R^2
β -CDP-HMDI	25	0.9469	0.1596	0.9990	0.2275	0.4042	0.9942
	45	0.7564	0.3424	0.8640	0.2460	0.4260	0.773
	65	0.4250	1.0202	0.9855	0.5333	0.1870	0.8700
β -CDP-TDI	25	0.7273	0.5577	0.9430	0.2766	0.2920	0.7800
	45	0.1065	0.7500	0.6320	0.1671	0.7379	0.8350
	65	0.037	3.6363	0.0820	0.1452	0.8990	0.7890

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 favourable or unfavourable. 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 eqn. 4:

$$R_L = \frac{1}{(1 + bC_o)} \quad (4)$$

where, C_0 is the initial Cr(VI) concentration (mg/L) and b is the Langmuir adsorption equilibrium constant (L/g). The isotherm is unfavourable when $R_L > 1$, the isotherm is linear when $R_L = 1$, the isotherm is favourable 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-3.

C_0 (mg/L)	β -CDP-HMDI			β -CDP-TDI		
	25 °C	45 °C	65 °C	25 °C	45 °C	65 °C
10	0.0955	0.1168	0.1905	0.1209	0.2638	0.4593
15	0.0658	0.0810	0.1356	0.0840	0.1928	0.3616
20	0.0502	0.0620	0.1053	0.0643	0.1519	0.2982
25	0.0405	0.0502	0.0860	0.0521	0.1254	0.2536
30	0.0340	0.0422	0.0727	0.0438	0.1067	0.2207

The values of R_L for adsorption of Cr(VI)-DPC complex for both adsorbents studied at different initial concentration, temperatures and the values between 0 and 1, which indicates favourable adsorption of Cr(VI)-DPC complex on β -CDP-HMDI and β -CDP-TDI. The R_L values increase with increasing temperature. This indicates that sorption is more favourable at high temperature. In addition, the R_L values decrease with increasing initial Cr(VI) ion concentration at all studied temperature indicates that sorption is more favourable at low concentration^{20,56}. From values of R_L (Table-3), it is concluded that the adsorption of Cr(VI)-DPC complex in β -CDP-TDI is more favourable than β -CDP-HMDI.

Sorption kinetic studies: The adsorption kinetic process of β -CDP-HMDI and β -CDP-TDI with 5 mg/L of Cr(VI)-DPC complex at different temperature (25 °C, 45 °C and 65 °C) is investigated and showed in Fig. 5a and 5b. The sorption increases instantly at initial stages. It may be due to rapid attachment of Cr(VI)-DPC complex to the surface of the adsorbent and then increase gradually until equilibrium is reached and remains constant. The kinetic result indicates that the sorption process is very fast because of the largest amount of Cr(VI)-DPC complex adsorb to the adsorbent within 5 min and equilibrium reached within 60 min.

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 process⁵⁷. The adsorption kinetic data of chromium are analyzed using the pseudo-first order kinetic and pseudo-second order kinetic equation⁵⁸.

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

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where, k_1 (min^{-1}) is the rate constant of pseudo 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 $\log(q_e - q_t)$ against t . The graph plot of pseudo-first order kinetic model is shown in Fig. 6a and 6b.

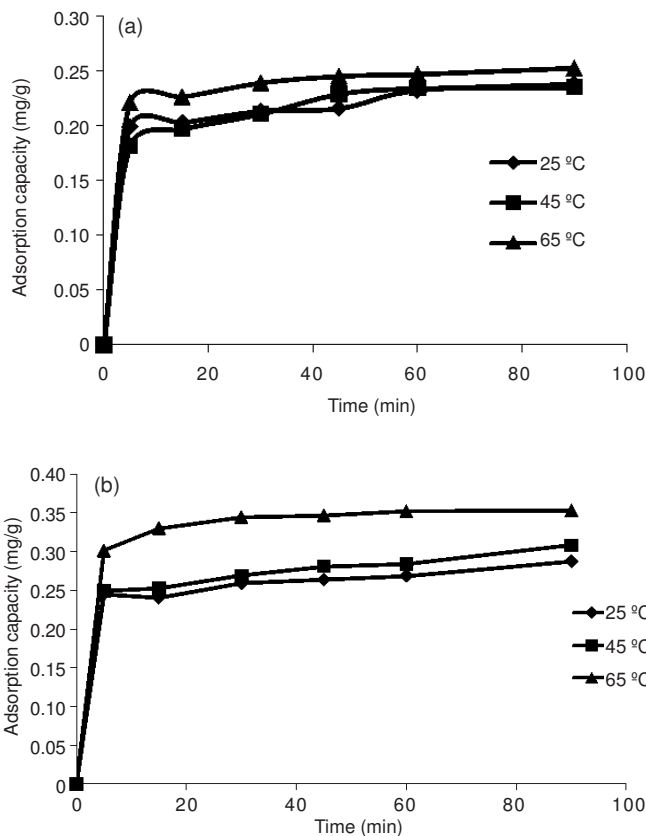


Fig. 5. Sorption kinetic of Cr(VI)-DPC complex at different temperature on (a) β -CDP-HMDI, (b) β -CDP-TDI

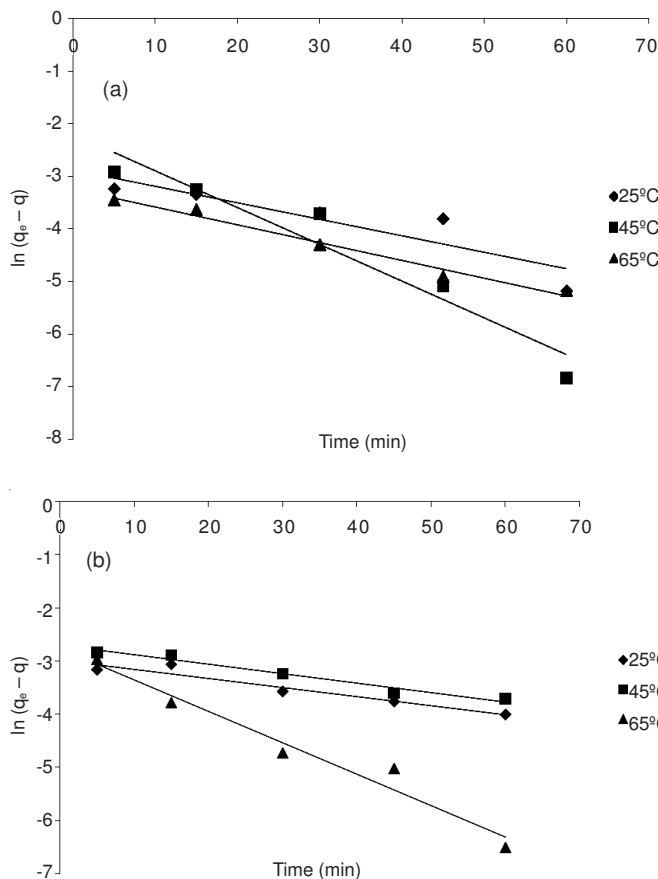


Fig. 6. Plot for pseudo-first order kinetic model for adsorption Cr(VI)-DPC complex on (a) β -CDP-HMDI and (b) β -CDP-TDI

The equation of pseudo second order kinetic model given as follows:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{t}{q_e} \right) \quad (6)$$

where, k_2 is the equilibrium rate constant of pseudo second order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). Values of k_2 and q_e were calculated from the plot of t/q against t . The graph of pseudo-second order kinetic model are exhibited in Fig. 7a and 7b for adsorption of Cr(VI)-DPC complex on β -CDP-HMDI and β -CDP-TDI, respectively.

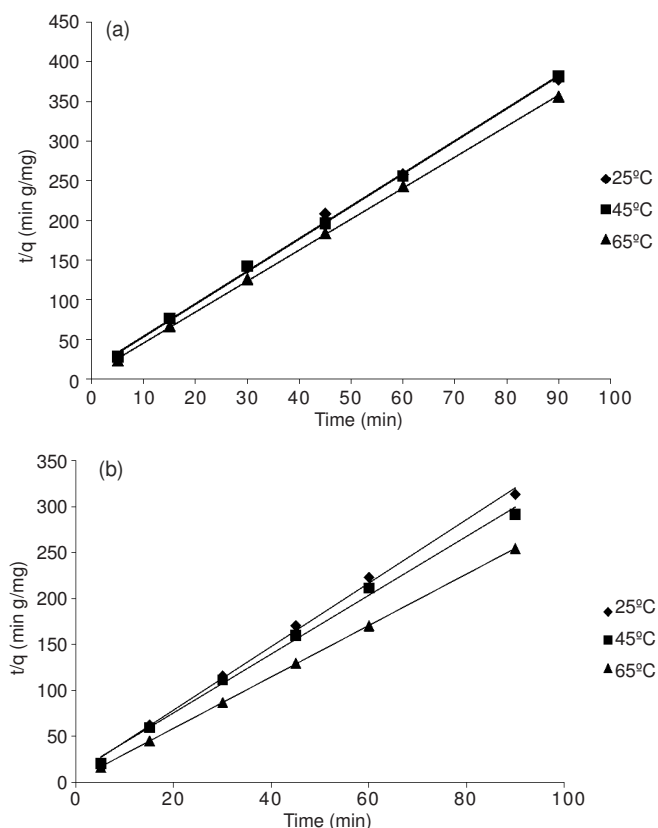


Fig. 7. Plot for pseudo-second order kinetic model for adsorption Cr(VI)-DPC complex on (a) β -CDP-HMDI and (b) β -CDP-TDI

The straight line plots of pseudo-first order and pseudo-second order kinetic have been tested to obtain the kinetic parameters (Table-4). It can be seen from the correlation coefficients (R^2) that the adsorption for β -CDP-HMDI and β -CDP-TDI follow pseudo-second order model. The calculated q_e values agree very well with the experimental data,

indicates that the sorption system belongs to pseudo second order kinetic model. The rate constant for pseudo-second order increases with increasing temperature for both of adsorbents.

The β -CDP-TDI have lower rate constant than β -CDP-HMDI. This is due to the presence of aromatic group in toluene-2,4-diisocyanate. The β -CDP-TDI is more hydrophobic than β -CDP-HMDI. As polymer in behaviour more hydrophobic, the diffusion of water is less and hence the contact between polymer and solute become slower³⁷.

Adsorption thermodynamic parameters: 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 equation⁵.

$$\Delta G^\circ = -RT \ln K_d \quad (7)$$

where, R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$) and T is the temperature (K).

In this case, the activity should be instead of concentration in order to obtain the standard thermodynamic equilibrium constant (K_d) of the adsorption system.

$$\ln K_d = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

Fig. 8 shows the graph of $\ln K_d$ vs. $1/T$. The value of ΔH° and ΔS° can be calculated from the slope and intercept, respectively. The value of parameters of thermodynamic is shown in Table-5.

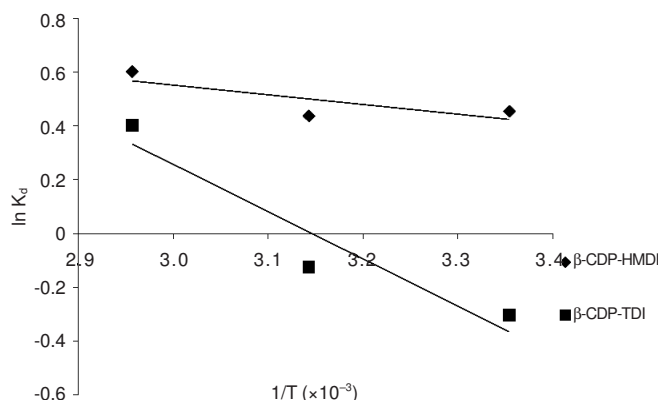


Fig. 8. Plot of $\ln K_d$ vs. $1/T$ for both of adsorbents

The negative values of free energy change (ΔG°) at all temperature indicates thermodynamically feasible and

TABLE-4
KINETIC PARAMETERS FOR PSEUDO-FIRST ORDER AND PSEUDO-SECOND ORDER KINETIC

Adsorbent	Temperature (°C)	q_e exp (mg/g)	Pseudo first order kinetic model			Pseudo second order kinetic model		
			$k_1 \times 10^{-2}$ (min ⁻¹)	q_e cal (mg/g)	R^2	$k_2 \times 10^{-2}$ (g/mg min)	q_e cal (mg/g)	R^2
β -CDP-HMDI	25	0.2380	3.1000	0.0560	0.8080	136.6400	0.2430	0.9970
	45	0.2350	6.9000	0.1110	0.9280	138.8000	0.2450	0.9990
	65	0.2520	3.3000	0.0390	0.9800	237.8000	0.2560	0.9990
β -CDP-TDI	25	0.2870	1.7000	0.0510	0.9270	117.7500	0.2900	0.9970
	45	0.3080	1.7000	0.0670	0.9650	89.3500	0.3120	0.9950
	65	0.3530	5.9000	0.0640	0.9630	247.3400	0.3680	1.0000

spontaneous nature of the adsorption of Cr(VI)-DPC complex on all adsorbents. The values of ΔG° varied in range of -15.566 to -4.084 kJ/mol. The change of the standard free energy decreases with increasing temperature, suggests due to the more absorbable of Cr(VI)-DPC complexes with increases temperature and also shows a decrease in feasibility of adsorption at higher temperature^{59,60}. β -CDP-TDI is more absorbable of Cr(VI)-DPC complexes than β -CDP-HMDI. The positive values of ΔH° varied in the range of 3.03-9.98 kJ/mol, suggests the endothermic nature of adsorption.

TABLE-5
THERMODYNAMIC PARAMETERS OF ADSORBENT

Adsorbent	Temp. (°C)	Enthalpy (ΔH°) (kJ/mol)	Entropy (ΔS°) (J/Kmol)	Gibbs energy (ΔG°) (J/mol) $\times 10^3$
β -CDP-HMDI	25	3.026	13.709	-4.084
	45			-4.358
	65			-4.636
β -CDP-TDI	25	14.649	46.079	-13.723
	45			-14.645
	65			-15.566

In addition, the low values of ΔH° indicate that there was loose of bonding between the adsorbate molecules and adsorbent surface^{61,62}. Table-5 shows that β -CDP-TDI has the highest value of ΔH° and it reveals the presence of strong chemical bond with Cr(VI)-DPC complex. The heat of adsorption, which ranging from 0.5 to 5 kcal/mol (2.1-20.9 kJ/mol), represent a physical adsorption and the heat of adsorption ranging from 5-100 kcal/mol (20.9-418.4 kJ/mol), represent a chemical sorption⁶³. The values of ΔH° for both adsorbents within the range 3.03-9.98 kJ/mol, indicating the type of adsorption is physisorption.

The positive values of ΔS° for both adsorbents are in range of 13.71-46.08 kJ/K mol. It shows the increasing randomness at the solid/solution interface during the adsorption process. It suggests that Cr(VI) 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 adsorbate ions, thus allowing the prevalence of randomness in the system^{58,64}. In addition, the positive entropy of adsorption reflects the affinity of the adsorbent material towards Cr(VI)-DPC complex⁶⁵. From the values of entropy, it shows that β -CDP-TDI has the highest affinity of the adsorbent material towards the Cr(VI)-DPC complex than β -CDP-HMDI.

Conclusion

In this study, β -CDP adsorbents were used for adsorption of Cr(VI)-DPC complex. The adsorption isotherm and kinetics of both adsorbents were studied. From the trends of parameter of adsorption capacity, rate constant and thermodynamic parameter, it reveals that the type of crosslinker is main factor contributes in the adsorption process. In this study, toluene-2,4-diisocyanate which consist aromatic group enhance the adsorption process due to the π - π interaction between toluene-2,4-diisocyanate and 1,5-diphenylcarbazide. This aromatic group also decrease the rate of uptake since it is more hydrophobic compared to the aliphatic crosslinker, 1,6-hexamethylene diisocyanate.

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