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Insights into kinetics and equilibrium of methylene blue adsorption onto β-cyclodextrin polymers

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Abstract: The exclusive properties of β-cyclodextrin (β-CD) combined with its harmless characters making it as an interesting and potential carbon adsorbent for water pollutants removal via adsorption. This work was aimed at evaluating the kinetics and isotherm parameters of methylene blue dye adsorption onto β-CD polymers. The carbon polymers were prepared by citric acid cross-linking, followed by post-treatment with sodium p-toluenesulfinate. The adsorbents were characterized using TGA, BET and FTIR. The adsorption of methylene blue was studied at varying concentrations (5–300 mg/L) and contact times (10–2880 min), and the kinetics and isotherm models were employed to describe the adsorption data. The post-treated carbon polymer exhibits a greater specific surface of 16.6 m^2/g. The maximum adsorption of methylene blue by cross-linked and post-treated β-CD adsorbents are 263 and 227 mg/g, respectively. The kinetics data fitted well into pseudo-first order model, indicating physical adsorption. The Boyd's model showed that film diffusion may be the controlling mechanism. The equilibrium data of methylene blue adsorption for the two β-CD polymers obeyed Langmuir model. To conclude, β-CD is a promising adsorbent candidate for the treatment of dye wastewater.

Keywords: β-cyclodextrin; adsorbent; adsorption; methylene blue; wastewater treatment.

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1 Introduction

Water pollution from textile industries has become a global concern due to its long-term potential risk to ecosystems and harmful effects on human health. The presence of dyes in water blocks the penetration of sunlight, hence impeding the photosynthesis of the aquatic plants. The decrease of dissolved oxygen supply in water may result in the mortality of aquatic creatures (Ming-Twang et al. 2015). Methylene blue is among the commonly used dyes in textile industries. Generally, dyes are chemically stable and hazardous, and can cause mental confusion, profuse sweating, and nausea (Zaini et al. 2014).

Numerous techniques have been applied for the removal of dye in water, of which adsorption supersedes the others because of it is simple, easy to operate, economical and efficient. Adsorption is a process whereby the solute or molecule of interest is adhered onto the solid surface through various mechanisms such as π-π interaction, ion exchange, pore filling, and complex formation (Ming-Twang et al. 2015). Activated carbon is a commonly used adsorbent in wastewater treatment. However, the quest for low-cost and effective adsorbent has continued to improvise the equilibrium and kinetics of dye adsorption. Among others, β-cyclodextrin (β-CD) polymer is a promising adsorbent candidate for water pollutants removal (Amran and Zaini 2022; Duan et al. 2020).

β-CD is a cyclic oligosaccharide containing seven glucopyranose of hydrophilic exteriors and hydrophobic internal cavity to encapsulate the target molecules by forming host-guest complexes. The reactive hydroxyl groups (–OH) around the outer rim of β-CD are feasible to be modified by various functional groups to provide β-CD with specific properties. The exclusive properties of β-CD combined with its harmless characters making it as a

promising alternative for dye adsorption. Nonetheless, β-CD is soluble in water (18.5 g/L), thus a modification is required to insolubilize the polymer via cross-linking using citric acid (Huang et al. 2018). Sodium p-toluenesulfinate, an alkylating agent was used to eliminate the hydrophilic exterior to form a carbon-rich β-CD polymer in post-treatment (Mohamad-Ariff and Ahmad-Zaini 2020). Previous works recorded a somewhat superficial removal of dyes despite the distinct mechanisms depending on the charge carriers (Mohamad-Ariff and Ahmad-Zaini 2020; Sulaiman, Zaini, and Arsad 2021). Therefore, the present work was aimed at elevating the capacity of methylene blue by cross-linked β-CD and post-treated β-CD. The effects of contact time and initial concentration were studied and analyzed using various kinetics and equilibrium models, respectively. The possible mechanisms governing the dye adsorption by β-CD polymers were proposed and discussed.

2 Materials and methods

2.1 Materials

β-cyclodextrin (β-CD, $(C_6H_{10}O_5)_7$, mw = 1135 g/mol) was obtained from Jiangsy Ogo Biotech Co. Ltd., China. Citric acid ($C_6H_8O_7$, mw = 192.13 g/mol) and potassium dihydrogen phosphate (KH_2PO_4, mw = 136.09 g/mol) were purchased from Systerm Chemicals, Malaysia. Sodium p-toluenesulfinate ($C_7H_7NaO_2S$, mw = 178.18 g/mol) was purchased from Acros Organics, Belgium. Methylene blue ($C_{16}H_{18}ClN_3S$, mw = 319.85 g/mol, assay 99%) was supplied by HmBG Chemicals, Germany. All materials are of analytical reagent grade.

2.2 Preparation and characterization of β-CD polymers

A 6 g of β-CD, 3 g of anhydrous citric acid, 1.5 g of KH_2PO_4 and 135 mL of distilled water were mixed in a 500 mL beaker and stirred to achieve homogeneity (Huang et al. 2018). The mixture was heated in an oven at 140 °C for 24 h. The material was washed using distilled water and dried at 50 °C. The insoluble β-CD was stored at room temperature in dry environment. This sample was referred to as cross-linked β-CD.

A 3.26 g of cross-linked β-CD was added into 3.21 g of $C_7H_7NaO_2S$ in 500 mL of distilled water. The mixture was kept under reflux at 110 °C for 24 h with continuous stirring. After that, the excess solvent was removed and the product was washed using distilled water, and refluxed at 100 °C for 48 h. After washing, the product was finally dried in an oven at 110 °C for 24 h. The material was stored at room temperature in dry environment. This sample was referred to as post-treated β-CD.

The profile of thermal degradation was obtained using a TGA 4000 (Perkin Elmer) under N_2 flow at heating rate of 10 °C/min from room temperature to 900 °C. The textural properties of β-CD polymers were determined by N_2 gas adsorption at 77 K using a Quantachrome NOVA-touch (LH4, USA). The FTIR spectrum in the range of 400–4000 cm^{-1} to indicate surface functionalities was obtained using a Spectrum One (Perkin Elmer, USA). β-CD char prepared by heating in air at 300 °C for 2 h was employed for comparison.

2.3 Adsorption studies

Methylene blue (MB) dye was used to investigate the adsorption profiles of β-CD polymers in water. The solution pH was left unadjusted, and the natural pH was recorded as 5.8 ± 0.3. A 0.03 g adsorbent was added into a Beatson bottle containing 30 mL of MB dye solution of specified concentrations of 5 mg/L and 25 mg/L. The residual concentration was measured at different time intervals for 48 h. The adsorption capacity at time, t, q_t (mg/g) was computed as $q_t = (C_o - C_t)V/m$, where V (L) is the volume of solution, m (g) is the mass of adsorbent, C_o (mg/L) is the initial concentration, C_t (mg/L) is the concentration measured at time, t. The residual concentration was measured using a UV-Vis spectrophotometer (Spectrumlab 752 Pro) at a wavelength of 620 nm. The correlation is given as a.u. = $0.0892 \times C_o$ for $0 \le C_o \le 25$ mg/L with $R^2 = 0.999$. The kinetics data were analyzed using intraparticle diffusion, pseudo-first-order, pseudo-second-order and Boyd's models, and the respective constants were determined accordingly.

A 0.03 g of adsorbent was added into Beatson bottles containing 30 mL of MB solution of different concentrations (5–300 mg/L). The bottles were sealed and the mixtures were allowed to equilibrate for 5 days. The amount adsorbed at equilibrium was computed as $q_e = (C_o - C_e)V/m$, where C_e (mg/L) is the equilibrium concentration. The removal performance (%) was calculated as $100 \times (C_o - C_e)/C_o$. The equilibrium data were interpreted using four isotherm models, i.e., Dubinin-Radushkevich, Freundlich, Langmuir and Redlich-Peterson models. Table 1 summarizes the kinetics and isotherm models used in this work. The constants were solved by non-linear regression using *Solver*-add in of MS Excel.

3 Results and discussion

3.1 Characteristics of β-CD polymers

Figure 1 shows the thermogravimetric profiles of β-CD polymers. All β-CD materials exhibit a common peak at 76 °C, signifying the release of moisture under N_2 environment. It corresponds to about 5–7% moisture content. The cross-

Table 1: Kinetic and isotherm models (Hock and Zaini 2022).

Kinetics	
Pseudo-first-order	$q_t = q_e[1 - \exp(-k_1 t)]$
Pseudo-second-order	$q_t = k_2 q_e^2 t/(1 + k_2 q_e t)$
Intraparticle diffusion	$q_t = k_d t^{1/2} + C$
Boyd's	$B_t = -0.4977 - \ln(1 - F)$ for $F > 0.85$ $B_t = \left(\sqrt{\pi} - \sqrt{\pi - \left(\frac{\pi^2 F}{3}\right)}\right)^2$ for $F < 0.85$
Isotherm	
Langmuir	$q_e = (q_m b C_e)/(1 + b C_e)$
Freundlich	$q_e = K_F(C_e)^{\frac{1}{n}}$
Dubinin-Radushkevich	$q_e = Q_s \exp(-K_{ad}\epsilon^2)$
Redlich-Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$

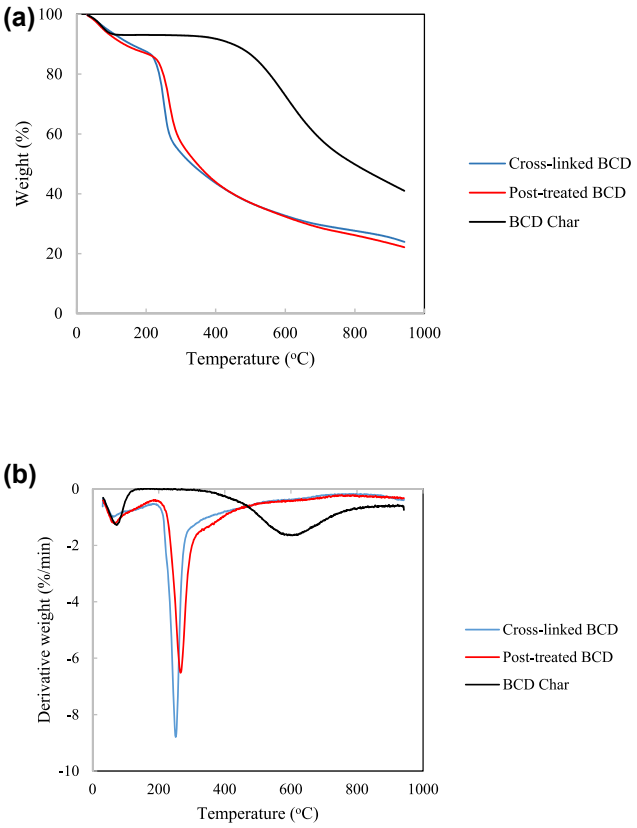

Figure 1: Thermal degradation profiles of β-CD polymers, (a) TGA and (b) DTG curves.

linked β-CD displays a lower moisture content because hydroxyl groups at the edges of β-CD molecule might inhibit the transport of water vapour from the surrounding. It should be noted that hydroxyl groups are easily liberated at 250 °C as can be visualized by the sharp peaks at the designated temperature. The post-treated β-CD contains less hydroxyl groups upon the post-treatment procedure. It can be explained by a lower intensity of the corresponding peak as compared to that of cross-linked β-CD. Furthermore, a slight shift to 266 °C indicates that the remaining hydroxyl groups are relatively more stable to temperature.

In Figure 1, β-CD char demonstrates a thermally stable character, whereby the considerable weight loss is only observed from 400 °C, that corresponds to a broad DTG peak at 600 °C. β-CD char has undergone a structural deformation as compared to its pristine material when it was prepared at 300 °C. Often, the material possesses rudimentary pores to entrap moisture. Also, the amorphous graphitic structure of coke-like char is believed to withstand the material from decomposition at high temperature (Zaini, Amano, and Machida 2010).

Figure 2 depicts the N_2 adsorption-desorption of post-treated β-CD, and the textural properties are summarized in

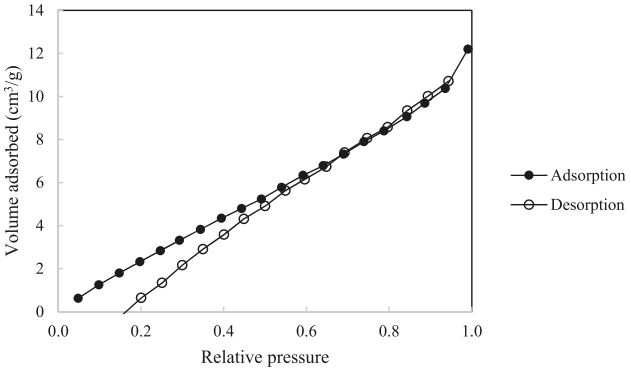

Figure 2: N_2 adsorption-desorption isotherm of post-treated β-CD polymer.

Table 2. According to IUPAC classification, the isotherm falls under Type III that implies the non-porous and microporous nature of post-treated β-CD (Sing et al. 1985). The specific surface of the adsorbent is also small. From Figure 2, a lower desorption branch than that of adsorption suggests that the capillary condensation has not fully completed. Nonetheless, there is an increase of specific surface from almost zero (cross-linked β-CD) to 16.6 m^2/g upon the post-treatment of cross-linked β-CD. From Table 2, the texture of post-treated β-CD exhibits the average pore size of 1.9 nm.

Figure 3 shows the FTIR spectra of β-CD polymers. All materials display comparable peaks, suggesting the inherent functionalities remain unchanged. The broad band at 3420 cm^{-1} is assigned to physisorbed moisture and O–H

Table 2: Textural properties of post-treated β-CD polymer.

Specific surface (m^2/g)	16.6
Micropore area (m^2/g)	0.443
Total pore volume (cm^3/g)	0.0166
Micropore volume (cm^3/g)	0
Mesoporosity (%)	100
Average pore size (nm)	1.9

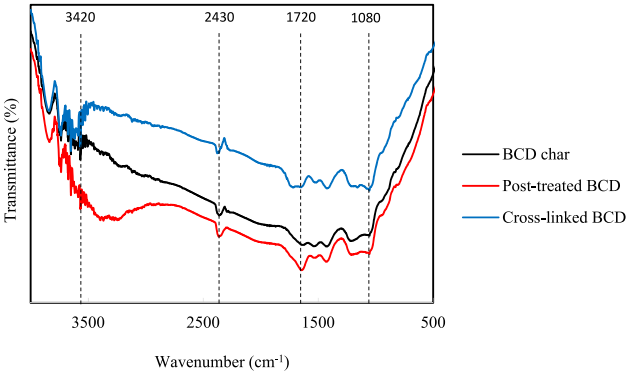

Figure 3: FTIR spectra of β-CD polymers.

stretching vibrations of hydroxyl and carboxyl groups, wherein the post-treated β-CD endows a higher moisture content. The absorption band at 1720 cm^{-1} represents stretching vibrations of C=O carboxyl and C–O–C ester groups, suggesting the esterification of hydroxyl groups of β-CD with carboxyl groups of citric acid to form insoluble adsorbent. A peak at 2430 cm^{-1} is designated to CH_2 asymmetric stretching vibration. The bands at 1150 cm^{-1} and 1080 cm^{-1} are attributed to C–O–C stretches and intense C–O stretch (Mohamad-Ariff and Ahmad-Zaini 2020; Sulaiman, Zaini, and Arsad 2021).

3.2 Adsorption kinetics

The effect of contact time on the adsorption of MB by carbon polymers at different dye concentrations is shown in Figure 4. Generally, the dye adsorption increases with contact time towards a point of equilibrium. The rate of adsorption for post-treated β-CD is faster than that of cross-linked β-CD. This could be attributed to the high specific surface of post-treated β-CD that allows methylene blue molecules to diffuse and interact with the adsorbent. A sharp increment of slope signifies a high affinity of adsorption towards dye molecules that could be associated with the liberation of functional groups that negate the restriction for host-guest formation. Consequently, post-treated β-CD exhibits a relatively faster equilibrium than cross-linked β-CD. As concentration increases, a longer time is required to attain the equilibrium because of the accumulation of dye molecules in bulk to compete to lodge on active sites. At equilibrium, both β-CD polymers achieved ~98% removal of MB at concentrations studied. A better performance at higher concentration could result from the concentration gradient that offers a driving force for adsorption (Hock and Zaini 2022).

The pseudo-kinetic models were used to describe the rate of MB adsorption, while the intraparticle diffusion model was used to interpret whether the intraparticle diffusion is the sole rate-limiting step, where the boundary layer diffusion or film diffusion is negligible (Maksin et al. 2012). The Boyd's model was used to further understand the transport mechanisms of MB adsorption. Table 3 summarizes the constants of kinetic models. The kinetics data of MB removal fitted well into pseudo-first-order model, with R^2 in the range of 0.961–0.997 and close agreement with the experimental values, suggesting that the process is governed by physical adsorption via hydrophobic host-guest complex interactions and/or weak electrostatic interactions at the hydrophilic exterior (Sulaiman, Zaini, and Arsad 2021). The torus-shaped of β-CD prompts the hydrophobic-hydrophobic interaction with MB molecules for host-guest complexation to take place, while the presence of hydroxyl groups at the edges of β-CD reduces the interior hydrophobicity, thus decreasing the adsorption affinity of cross-linked β-CD. The constant C in intraparticle diffusion model signifies the thickness of boundary layer. For both β-CD polymers, the magnitude of C increased with increasing concentration, away from the origin. As the concentration increases, the intraparticle diffusion is no longer the only rate-controlling step, where some other mechanisms may also involve. A high C value indicates a thicker film, which increases the influence of film rate-limiting effect towards the adsorption (Arivoli et al. 2009; Chen et al. 2013).

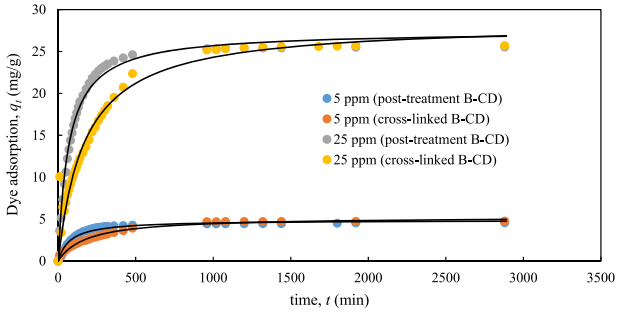

Figure 4: Kinetics of MB adsorption onto β-CD polymers.

Table 3: Constants of kinetic models for MB adsorption by β-CD polymers.

	Cross-linked β-CD		Post-treated β-CD	
C_o (mg/L)	5.0	25.0	5.0	25.0
$q_{e,exp}$ (mg/g)	4.8	25.0	4.6	25.0
Pseudo-first-order				
k_1 (min^{-1})	0.0045	0.0047	0.0095	0.0104
q_e (mg/g)	4.6	25.2	4.4	24.9
R^2	0.980	0.961	0.997	0.996
Pseudo-second-order				
k_2 (g/mg min)	0.001	0.0002	0.0027	0.0005
q_e (mg/g)	5.3	28.5	4.9	27.5
R^2	0.989	0.962	0.981	0.990
Intraparticle diffusion				
k_d (mg/g min)	0.102	0.519	0.0786	0.439
C	0.940	5.971	1.81	10.9
R^2	0.867	0.850	0.603	0.602
Boyd's				
B	0.186	0.198	0.132	0.210
R^2	0.94	0.991	0.883	0.947
D_i (cm^2/s)	1.48×10^{-4}	1.58×10^{-4}	1.05×10^{-4}	1.67×10^{-4}

Furthermore, the positive C suggests a rapid adsorption and certain controlling degree of film diffusion (Wu, Tseng, and Juang 2009). The adsorption process can either be driven by film diffusion or particle diffusion, and this was determined through the linearity test of B_t versus t (Karthikeyan, Sivakumar, and Sivakumar 2010). The Boyd's plots for β-CD polymers are not linear and drift from the origin, showing that the rate-limiting step is film diffusion. In addition, the effective diffusion coefficient, D_i is within the range of film diffusion coefficient, D_f, 1.67×10^{-4} to 1.05×10^{-4} cm^2/s.

3.3 Equilibrium adsorption

The effect of concentration on MB adsorption is shown in Figure 5. The β-CD polymers exhibit a strong intensity (steep gradient) at low concentration that signifies a favourable adsorption. As the equilibrium concentration increases, the removal of MB by post-treated β-CD began to level off at a capacity of 227 mg/g, while that of cross-linked β-CD continued to demonstrate a gradual increase with a higher uptake of 263 mg/g. This shows that the cross-linked β-CD has a better sorption performance than the post-treated β-CD, even though the latter displays a faster adsorption rate. It signifies the contributing roles of hydroxyl groups at the exterior of β-CD in enhancing the affinity and maximum capacity of MB adsorption at equilibrium. The relationship is in accordance with findings reported elsewhere, even though the reported capacities from this work are much greater (Mohamad-Ariff and Ahmad-Zaini 2020; Sulaiman, Zaini, and Arsad 2021).

Figure 6 shows the performance of β-CD polymers. Clearly, the cross-linked β-CD has a greater sorption capacity than the post-treated β-CD at C_o > 100 mg/L. Both β-CD polymers illustrate a similar pattern of removal performance of MB which maintained at >98% for 5 mg/L < C_o < 50 mg/L, then decreased gradually with increasing concentration. At

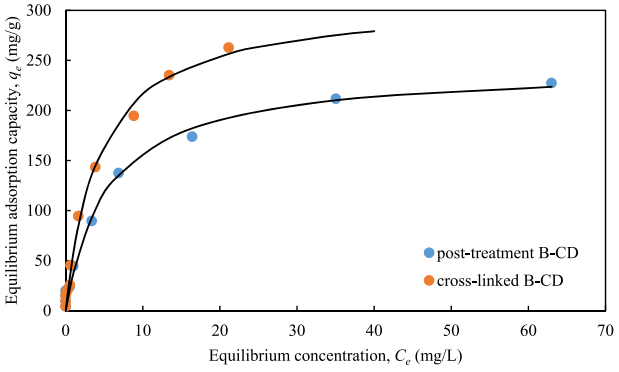

Figure 5: Adsorption isotherm of MB adsorption onto β-CD polymers.

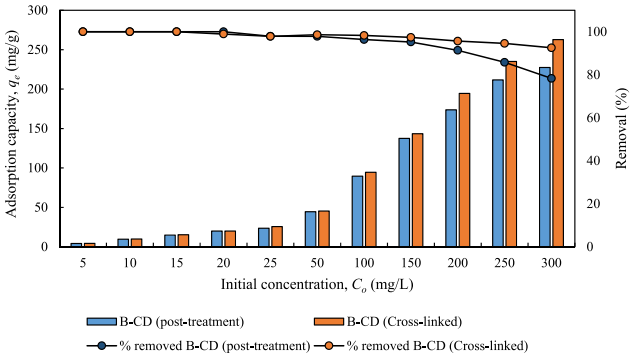

Figure 6: Removal performance of β-CD polymers.

C_o = 300 mg/L, the performance were recorded at 92.5% and 78.3% for cross-linked and post-treated β-CD polymers, respectively. Despite the increase in adsorption capacity, the ability of β-CD polymers to remove dye at higher concentration is quite constricted because of small residual concentration upon adsorption as compared to the initial concentration. The performance of β-CD polymers was compared with some MB adsorbents, as listed in Table 4. The maximum removal capacities of MB by cross-linked and post-treated β-CD polymers from this work are better than some similarly reported adsorbents derived from cyclodextrin in the literature.

The equilibrium data were fitted into isotherm models, and the constants are shown in Table 5. The adsorption of MB by β-CD polymers satisfied the Langmuir model with R^2 of 0.994–0.995, suggesting the monolayer coverage of molecules onto homogeneous adsorbent surface (Hock and Zaini 2022; Sulaiman, Zaini, and Arsad 2021). The Langmuir constant, b is a measure of affinity between adsorbent and adsorbate, whose magnitude represents favourable

Table 4: Comparison of MB removal by some adsorbents.

Adsorbent	q_m (mg/g)	Reference
Cross-linked β-CD	263	This work
Post-treated β-CD	227	This work
R_4-β-CD	138	Duan et al. (2020)
β-CDP@ Fe-Al hydroxide	60.7	Liu, Wu, and Sha (2018)
β-CD@Gly@TiO_2	82.0	Mousavi and Mohammadi (2018)
γ-CD@TiO_2	134	Mousavi, Shokoofehpoor, and Mohammadi (2019)
β-CD adsorbent	248	Huang et al. (2018)
Mesoporous SiO_2	141	Liu et al. (2019)
β-CD adsorbent	5.76	Sulaiman, Zaini, and Arsad (2021)
Carbon-based β-CD	2.20	Mohamad-Ariff and Ahmad-Zaini (2020)
Al-modified activated carbon	182	Kazeem et al. (2018)

Table 5: Constants of isotherm models for MB adsorption by β-CD polymers.

	Cross-linked β-CD	Post-treated β-CD
$q_{e,exp}$ (mg/g)	263	227
Langmuir		
q_m (mg/g)	310	243
b (L/mg)	0.228	0.182
SSE	812	901
R^2	0.994	0.995
Freundlich		
K_f (mg/g) (L/mg)$^{1/n}$	67.0	60.7
n	2.14	2.95
SSE	1719	2055
R^2	0.975	0.950
Dubinin-Radushkevich		
q_s (mg/g)	128	130
K_{ad} (mol^2/kJ^2)	4.2×10^{-7}	3.11×10^{-7}
E (kJ/mol)	1.09	1.27
SSE	38,700	19,200
R^2	0.901	0.752
Redlich-Peterson		
K_R	88.3	54.5
α_R	0.436	0.304
β	0.865	0.925
SSE	671	812
R^2	0.994	0.995

adsorption at low concentration (García-Calzón and Díaz-García 2007).

The Dubinin-Radushkevich model was used to evaluate the porosity and apparent adsorption capacity (Dubinin and Radushkevich 1947). The maximum capacity, q_s by this model agrees with q_m of Langmuir model. The constant, E is the mean free energy of adsorption, where $E < 8$ kJ/mol is due to physical adsorption, 8 kJ/mol $< E <$ 16 kJ/mol is due to electrostatic adsorption and $E >$ 16 kJ/mol is due to chemical adsorption (Santhi 2015). From Table 5, obviously, physisorption dominates the removal of MB. This tied-up with the proposed mechanisms of hydrophobic-hydrophobic (interior torus-shaped) and weak electrostatic (exterior hydroxyl groups) interactions as already discussed.

The Redlich-Peterson isotherm is a three-parameter hybrid model featuring both Langmuir and Freundlich models (Redlich and Peterson 1959). At $\beta = 1$, the Redlich-Peterson isotherm becomes Langmuir isotherm, while at $\beta = 0$, it simplifies into Henry's Law. The Langmuir model fits well with the equilibrium data for both carbon polymers with $\beta \rightarrow 1$. Often, the adsorption involving large molecules has β lesser than one due to the obstruction of solid particles.

4 Conclusions

Beta-cyclodextrin (β-CD) adsorbents were prepared by cross-linking with citric acid and post-treatment with sodium p-toluensulfinate for methylene blue removal. The cross-linking is to insolubilize the β-CD molecules, whereas the post-treatment results in fewer hydroxyl groups at the edges of β-CD. The adsorbents generally demonstrate a promising performance for dye wastewater treatment, surpassing other cyclodextrin adsorbents as previously reported in the literature. The maximum capacities of 263 mg/g and 227 mg/g were recorded for methylene blue adsorption by the cross-linked and post-treated β-CD, respectively. Nonetheless, the latter exhibits faster adsorption due to high specific surface and less restricted access for dye molecules to enter the torus cavity. Physical adsorption involving hydrophobic-hydrophobic interaction at the interior and weak electrostatic interaction at the edges of β-CD with film diffusion as the controlling mechanism could be used to explain dye removal. The β-CD polymers could be employed as effective dye adsorbents for textile wastewater treatment.

Abbreviations

b	Langmuir affinity constant
B	slope of Boyd's plot
C	intercept of intraparticle diffusion plot
C_e	equilibrium concentration
C_o	initial concentration
C_t	concentration measured at any time
D_f	film diffusion coefficient
D_i	effective diffusion coefficient
E	mean free energy of adsorption
k_1	pseudo-first-order rate constant
k_2	pseudo-second-order rate constant
k_d	intraparticle diffusion rate constant
K_F, n	Freundlich isotherm constants
K_R, α_R, β	Redlich-Peterson constants
m	mass of adsorbent
$q_{e,exp}$	experimental equilibrium capacity
q_e	removal capacity at equilibrium
q_m	maximum removal capacity at surface saturation
q_s, K_{ad}	Dubinin-Radushkevich constants
q_t	adsorption capacity at any time
R^2	regression coefficient
t	contact time
V	volume of solution
β-CD	beta cyclodextrin

Author contribution: ANM Faizal (PhD candidate): Conceptualization, experimental work, analysis, first draft. MAC Yunus (Professor): Supervision, methodology, review. Asmadi Ali (Associate Professor): Review, analysis, validation, proof. MAA Zaini (Associate Professor): Grant recipient, supervision, conceptualization, validation.
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Availability of data and material: Data will be made available upon request.

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