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ACTA CHEMICA IASI, **28_1**, 19 - 30 (2020)

DOI: 10.2478/achi-2020-0002

CARBON-BASED BETA-CYCLODEXTRIN ADSORBENT FOR METHYLENE BLUE AND REACTIVE ORANGE 16 REMOVAL FROM WATER

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Abstract: This aim of this work is to evaluate the adsorptive properties of carbon-based beta-cyclodextrin adsorbent towards Methylene Blue (MB) and Reactive Orange 16 (RO16) removal from water. The specific surface area of adsorbent is small (0.1 m^2/g), with intact structure of pristine beta-cyclodextrin upon treatment. MB reaches relatively fast equilibrium (100 min), while RO16 needs more than 2200 min, despite a lower removal capacity of the former. Also, the adsorbent displays a greater affinity for MB. The kinetics data obeyed pseudo-first-order, suggesting the physical interaction of host-complex inclusion. On molar basis, the adsorption capacity of RO16 is 1.26×10^{-2} mmol/g (32 %), while that of MB is 6.8×10^{-3} mmol/g (20 %) at $C_o = 3.4 \times 10^{-2}$ mM. To conclude, carbon-based beta-cyclodextrin is a promising adsorbent candidate for selective dyes removal from wastewater.

Keywords: Beta-cyclodextrin, adsorbent, adsorption, Methylene Blue, Reactive Orange 16, wastewater treatment

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Introduction

Manufacturing industries such as textile and leather use dyes in different shades and colours in their finishing products. Eventually, these dyes may find their way into the water bodies as a result of poor waste handling, management and disposal. The presence of dyes in water even at a low concentration is undesirable as it decreases the infusion of sunlight for photosynthesis, hence threatening the aquatic creatures due to less available soluble oxygen for respiration. Dyes with complex aromatic structure and stability are to degrade, and could potentially render carcinogenic and toxic properties that can cause detrimental effects to human health.[1] Therefore, dyes removal from water is imperative for future sustainable environment.[2]

Adsorption is a preferable wastewater treatment method because it is efficient, economical, and suitable for organic and inorganic water pollutants even at low concentration. Activated carbon is a commonly used adsorbent in wastewater treatment and water purification industries.[3] However, it is expensive, thus triggers great interest on low-cost, natural and environmental friendly adsorbents. A promising adsorbent candidate is beta-cyclodextrin (β-CD), that is economically affordable as compared to other conventional adsorbents such as activated carbon, zeolites and so on. Other than that, it has a simple design, specific affinity and naturally non-toxic.[4,5]

β-CD is a cyclic oligosaccharide consisting of seven α-D-glucose units connected through α-(1,4) linkages. Over the years, β-CD has been used in pharmaceuticals, foods, cosmetics and chemical products. The material is believed to have truncated cone structure with hydrophilic exteriors rich in hydroxyl (–OH) groups and hydrophobic internal cavity. The unique torus-shaped structure enables it to encapsulate target molecules

of suitable size and polarity via inclusion complex formation, also known as host-guest interactions, while the exterior surface groups could act as active sites for the positively charged pollutants.[4,6] β-CD, a water-soluble compound (18.5 g/L) can be cross-linked with citric acid, a cheap and non-toxic carboxylic acid, to produce an insoluble adsorbent.[5] Consequently, the post-treatment using toluene and sulfuric acid results in a carbon-rich β-CD adsorbent.[7] Toluene and sulfuric acid yields p-toluenesulfonic acid or tosic acid that removes the alcohol groups on the edge of β-CD molecular surface, creating a hydrophobic β-cyclodextrin. Therefore, the objective of the present work is to establish the removal of cationic Methylene Blue and anionic Reactive Orange 16 dyes by carbon-based β-CD adsorbent. The kinetics, removal performance and possible mechanisms of adsorption were discussed.

Materials and methods

Beta-cyclodextrin (β-CD) was obtained from Jiangsy Ogo Biotech Co. Ltd. Methylene Blue (MB) and Reactive Orange 16 (RO16) were supplied by HmBG Chemicals. Citric acid and KH_2PO_4 were purchased from Systerm Chemicals. Toluene and sulphuric acid were supplied by Acros Organics. All materials are of analytical grade reagents. Citric acid cross-linked β-CD was prepared according to the method described elsewhere.[4] Briefly, 6 g of dried β-CD, 3 g of anhydrous citric acid, 1.5 g of KH_2PO_4 and 135 mL of distilled water were mixed in 800 mL beaker. The mixture was dried in an oven at 140 ºC for 3.5 h. After that, the crude product was washed, filtered and dried at 50 °C. The post-treatment of β-CD adsorbent was performed according to the method described elsewhere.[7] Briefly, 10 g of sulfuric acid and 10 g of β-CD adsorbent were added into

toluene, and refluxed at 80°C for 6 h. After that, the solid was separated, washed with distilled water, and dried in an oven prior to use.

The resultant adsorbent was characterized using BET analyser and FTIR. The adsorptive properties of adsorbent were evaluated using MB and RO16 in water. The adsorption was performed at different concentrations and contact times, at a fixed dosage of 1 g/L. The residual concentrations were measured using a UV-Vis spectrophotometer at wavelengths of 640 nm (a.u. = 0.0441 × concentration; R^2 = 0.9974, 2 mg/L ≤ C_o ≤ 25 mg/L) and 502 nm (a.u. = 0.0121 × concentration; R^2 = 0.9791, 2 mg/L ≤ C_o ≤ 25 mg/L) for MB and RO16, respectively. The adsorption capacity at time t, q_t was calculated as:

$$q_t = (C_o - C_t) \times V/m,$$

where C_o and C_t (mg/L) are dye concentrations at t = 0 and time t, respectively, V (L) is the solution volume and m (g) is the adsorbent mass. The equilibrium capacity, q_e was calculated as:

$$q_e = (C_o - C_e) \times V/m,$$

where C_e (mg/L) is the equilibrium concentration.

Results and discussion

The yield of carbon-based beta-cyclodextrin is 56.13 %. From the BET analysis, the specific surface area of adsorbent is quite low, of 0.1 m^2/g. Figure 1 shows the FTIR spectrum of carbon-based β-CD. The absorption band at 1720 cm^{-1} could be assigned to stretching vibrations of C=O carboxyl and C—O—C ester groups, suggesting that the hydroxyl groups of soluble β-CD reacted with the carboxyl groups of citric acid via esterification reaction, forming the insoluble adsorbent. The broad band at 3420 cm^{-1} could be attributed to the physisorbed moisture and O—H

stretching vibrations of hydroxyl and carboxyl groups. A peak at 2930 cm^{-1} is the characteristic of CH_2 asymmetric stretching vibration. The bands at 1150 cm^{-1} and 1080 cm^{-1} may be referred to C—O—C stretches and intense C—O stretch. The sharp peaks at 600 cm^{-1} to 500 cm^{-1} exhibit an intact ring structure, despite the modification procedure. These findings indicate that the matrix and structure of pristine β-CD remains unchanged in the insoluble carbon-based β-CD material.[4]

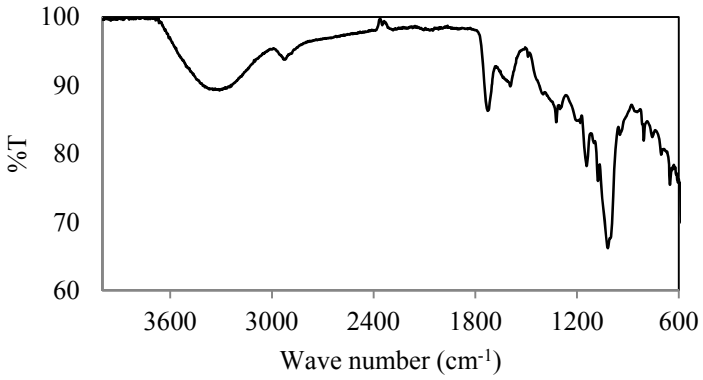

Figure 1. FTIR spectrum of carbon-based beta-cyclodextrin.

The pH of carbon-based adsorbent in water is 6.4, increasing from the value of 4.3 of cross-linked β-CD prior to post-treatment, indicating the hydrophobic character of carbon-based β-CD adsorbent. This could result from the elimination of hydrophilic exteriors that normally endow acidic character in solution. The pH values of Methylene Blue (MB) and Reactive Orange 16 (RO16) solutions are 6.1 and 6.4, respectively. Upon adsorption, the equilibrium pH values were measured as 7.1 and 6.8 for MB and RO16, respectively. A slight increase of the solution pH could result from the hydrophobic behavior of carbon-based β-CD adsorbent and possible interactions between the active sites and the adsorbate molecules.

Figure 2 shows the effect of contact time on the removal of MB by carbon-based β-CD adsorbent. Generally, the adsorption increases with the contact time up to the equilibrium, then levelling-off. At equilibrium, the adsorption rate is equal to the desorption rate. The vacant sites are abundant at $t = 0$, thus promoting the interaction probabilities with dye molecules. At high covering degree, however, the available adsorption sites become the limiting factor, thus restricting the immobilization of molecules. For both cationic and anionic dyes studied, an increase in concentration endows a driving force for molecules to overcome the adsorbent mass transfer resistance, hence enhancing the transport process. However, RO16 requires a longer contact time to attain equilibrium. For the same mass concentration of about 10 mg/L, a duration of more than 2200 min was needed by RO16, while the time was only 210 min for MB. Nevertheless, RO16 demonstrates a slightly better adsorption (by mass value) capacity of 2.64 mg/g as compared to MB (2.16 mg/g).

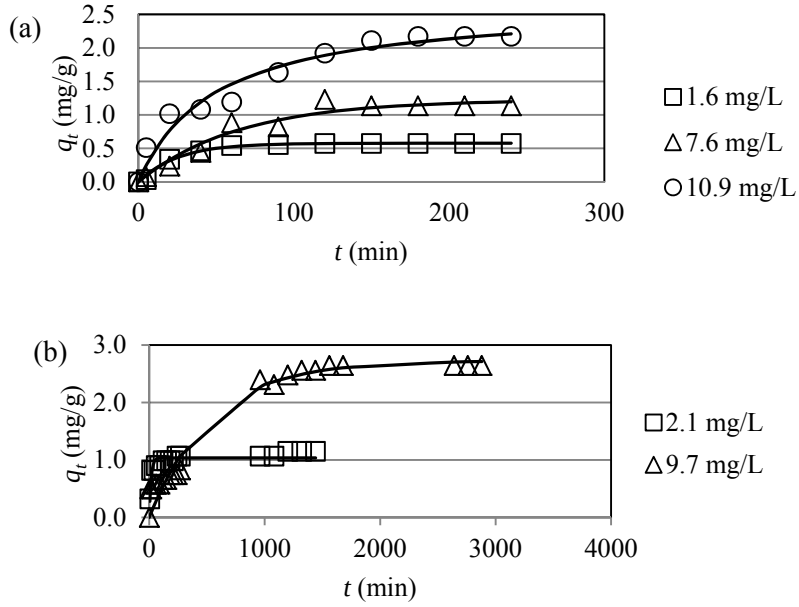

Figure 2. Rate of (a) Methylene Blue, and (b) Reactive Orange 16 adsorption onto carbon-based beta-cyclodextrin adsorbent (lines were predicted by pseudo-first-order model).

An attempt has been made to evaluate the effect of post-treatment against MB adsorption at C_o = 10 mg/L. Prior to the post-treatment, the β-CD adsorbent (yield = 59.4 %, pH = 4.3) bears both hydrophilic and hydrophobic groups. It was found that the adsorption capacity of MB by this adsorbent is higher (5.6 mg/g), although a longer contact time of about 1500 min is needed to achieve equilibrium. A greater adsorption prior to modification is due to the dual active sites with phenolic groups and hydrophobic interior. However, the affinity of MB molecules towards the external oxygen groups is weak, thus prolonging the time taken to reach equilibrium. The hydrophobic adsorbent as a result of post-treatment renders a fast kinetics due to the absence of hydrophilic exteriors, hence facilitating the host-complex inclusion.

The adsorption rate data were analyzed using pseudo-kinetics models, and the constants are summarized in Table 1. Generally, the adsorption data fitted well into pseudo-first-order model with close agreement between the experimental and model values, higher coefficient of determination, R^2 and smaller sum-of-squared errors (SSE). The applicability of this model indicates that the removal of MB and RO16 is mainly governed by the physical adsorption of host-complex inclusion. From the viewpoint of rate constant, k_1 decreased with increasing concentration, and this is true for both dyes studied. It implies that the adsorption of dyes only yields a better performance at lower concentration. Similarly, a higher concentration endows a lower k_1 suggesting a longer moment to reach equilibrium.

Table 1. Pseudo-kinetics constants of Methylene Blue and Reactive Orange 16 adsorption onto carbon-based beta-cyclodextrin adsorbent.

C_o (mg/L)	$q_{e,\ exp}$ (mg/g)	Pseudo-first-order model, $q_t = q_e\ (1 - e^{-k1t})$				Pseudo-second-order model, $q_t = q_e^2 k_2 t\ /\ (1 + q_e k_2 t)$			
		$q_{e,\ model}$ (mg/g)	k_1 (min^{-1})	R^2	SSE	$q_{e,\ model}$ (mg/g)	k_2 (g/mg.min)	R^2	SSE
Methylene Blue									
1.63	0.570	0.578	0.0398	0.9906	0.0057	0.654	0.0774	0.9719	0.0152
7.58	1.14	1.23	0.0156	0.9566	0.100	1.60	0.0087	0.9439	0.128
10.9	2.17	2.21	0.0175	0.9565	0.323	2.67	0.087	0.9615	0.247
Reactive Orange 16									
2.06	1.15	1.03	0.0629	0.8268	0.108	1.10	0.0824	0.9325	0.0410
9.67	2.64	2.73	0.0019	0.9700	0.832	3.38	0.0005	0.9549	1.02
16.6	6.61	7.08	0.0012	0.9731	3.46	9.40	0.0001	0.9632	4.26
20.8	7.77	8.49	0.0010	0.9826	2.75	11.6	0.0001	0.9757	3.71

Figure 3 shows the removal performance of MB and RO16 by carbon-based β-CD adsorbent. Both dyes demonstrate similar pattern of removal efficiency, that decreased with increasing concentration. The carbon-based β-CD adsorbent exhibits a 55.9 % (q_e = 1.15 mg/g) removal performance of RO16 at C_o = 2.1 mg/L, and plummeted to 32.2 % (q_e = 7.93 mg/g) at C_o = 24.6 mg/L. Similarly, the MB adsorption recorded a decrease in efficiency from 35 % (C_o = 1.6 mg/L) to 20 % (C_o = 10.9 mg/L). Despite the increase in adsorption capacity, the ability of hydrophobic β-CD adsorbent to remove dyes at higher concentration is somewhat restricted due to the small residual concentration upon adsorption as compared to the initial concentration. In a related attempt, the cross-linked β-CD adsorbent (prior to post-treatment) displays a 64 % (q_e = 3.6 mg/g) removal efficiency at C_o = 5.5 mg/L, that plunged to 45 % (q_e = 4.64 mg/g) at C_o = 10.3 mg/L.

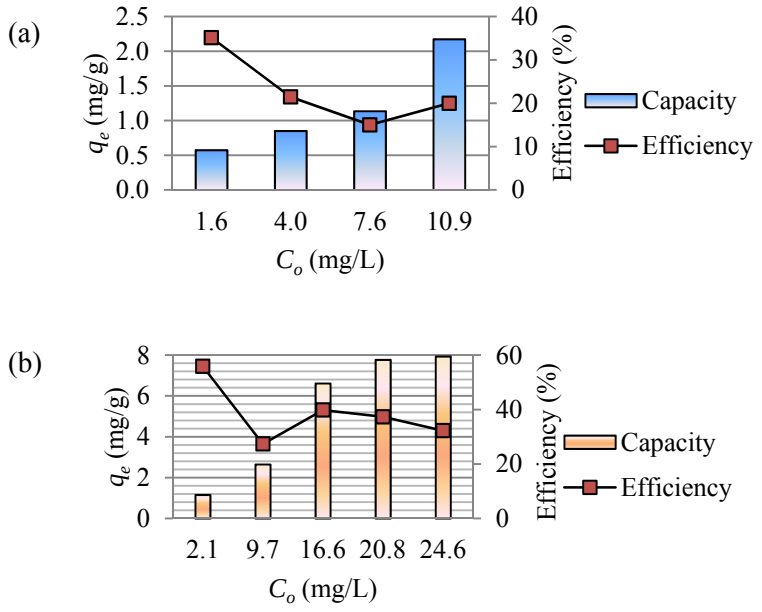

Figure 3. Performance of carbon-based beta-cyclodextrin adsorbent for (a) Methylene Blue and (b) Reactive Orange 16 removal.

Figure 4 shows the adsorption kinetics of MB ($C_{16}H_{18}ClN_3S$, MW = 319.9 g/mol) and RO16 ($C_{20}H_{17}N_3Na_2O_{11}S_3$, MW = 696.7 g/mol) dyes at a molar concentration of 3.4×10^{-2} mM. On molar basis, RO16 endows a 1.26×10^{-2} mmol/g adsorption capacity at equilibrium, that is nearly twice as much as that of MB at 6.8×10^{-3} mmol/g. However, MB exhibits a fast diffusion kinetics leading to equilibrium, by which the time taken to attain the plateau is 9 times faster than that of RO16. This is also in line with the rate constant of MB (0.0175 min^{-1}), that is 17.5 times higher as compared with the slow diffusion of RO16. A dissimilar attribute of adsorption could be associated to the size of dyes molecules under the purview of hydrophobic interior of β-CD adsorbent.

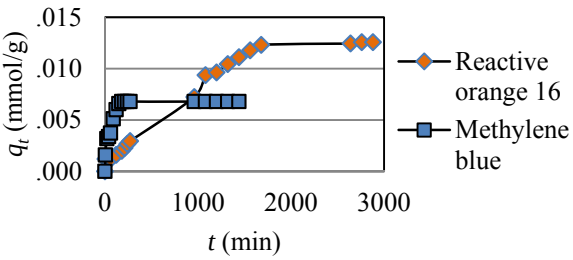

Figure 4. Rate of dyes adsorption at the same molar concentration of 0.034 mM by carbon-based beta-cyclodextrin adsorbent.

Figure 5 illustrates the possible mechanisms of dyes adsorption onto hydrophobic β-CD adsorbent. In the absence of hydrophilic exteriors, the underlying adsorption mechanism for both cationic and anionic dyes is likely host-guest complex formation inside the torus-shaped. The molecular width of both dyes allows them to enter the adsorbent annular (0.72 nm), lodge and finally interact with the hydrophobic skeleton of β-CD. The hydrophobic β-CD cavity tends to host the hydrophobic aromatic rings of dyes molecules. According to the adsorption data, the host-guest complex interactions render a rapid equilibrium for MB due to its smaller molecular size and selective hydrophobic sites in the absence of acidic oxygen functional groups of the adsorbent exteriors. A higher RO16 adsorption could be driven by aromatic stacking and electrostatic interactions between the readily adsorbed molecule with the neighbouring dye molecules in bulk solution. Nevertheless, the interaction is rather weak and longer contact time was required to reach the equilibrium as a result of slow diffusion of dye molecules towards the matrix of β-CD. Generally, the favourable performance of hydrophobic β-CD adsorbent is promising for wastewater treatment. Yet, more future studies would be needed to enhance the adsorptive properties for broader applications towards sustainable environment.[8,9]

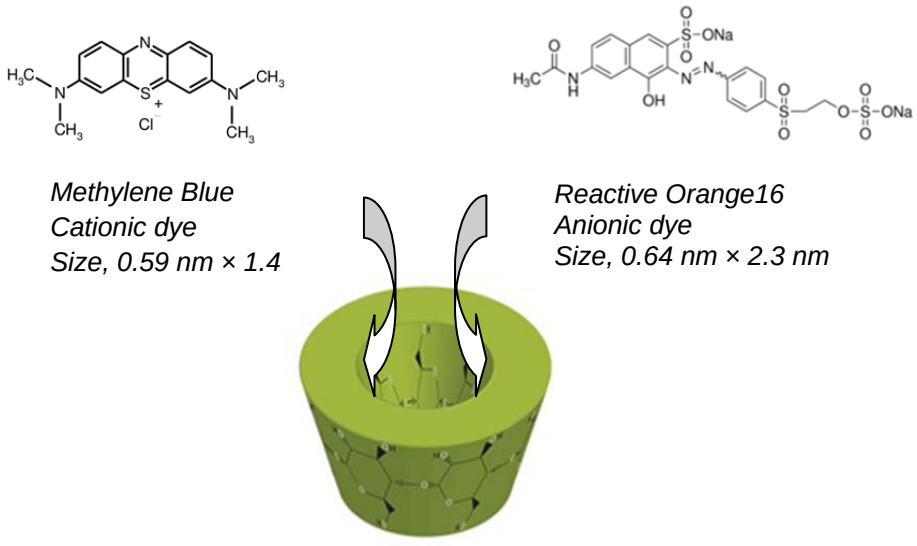

Figure 5. Illustration of dyes adsorption onto carbon-based β-CD.

Conclusion

A beta-cyclodextrin based, carbonaceous adsorbent, was prepared for Methylene Blue (MB) and Reactive Orange 16 (RO16) removal from water. The citric acid cross-linked insoluble solid was treated using toluene and sulphuric acid to yield a hydrophobic adsorbent by carbon deposition and cross-linking on β-CD. The adsorbent exhibits a promising performance for dyes wastewater treatment. The removal yield of RO16 is higher than that of MB, however a longer contact time (more than 2200 min) for a dye concentration higher than 10 mg/L is needed to reach the equilibrium. The adsorption was suggested to be driven by hydrophobic host-guest inclusion for both dyes, with additional aromatic stacking and electrostatic interactions for RO16. The adsorbent is favourable for dyes adsorption, whilst more studies are still needed to boost its adsorptive performance, selectivity and kinetics for wide applications in wastewater treatment.

Acknowledgment

This work was fully funded by Ministry of Education, Malaysia through Fundamental Research Grant Scheme No. 4F995.

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