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Evaluation of dyes removal by beta-cyclodextrin adsorbent

Noor Suhailah Sulaiman [a], Muhammad Abbas Ahmad Zaini [a,b,*], Agus Arsad [b]

[a] Centre of Lipids Engineering & Applied Research (CLEAR), Ibnu-Sina Institute for Scientific & Industrial Research (ISI-SIR), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b] School of Chemical & Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

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ABSTRACT

This work was aimed at evaluating the adsorptive properties of beta-cyclodextrin (β-CD) adsorbent towards methylene blue and congo red dyes removal. The adsorbent was characterized for specific surface area and surface chemistry. The results show that the surface area of β-CD adsorbent is small at 0.1 m^2/g and the surface chemistry is rich in acidic oxygen groups. The dyes adsorption onto β-CD is favourable. Congo red adsorption exhibits a greater rate constant of 0.103 min^{-1} and a relatively shorter time to reach equilibrium at 40 min as opposed to 1500 min for methylene blue. On a molar basis, both dyes display a comparable maximum capacity of 1.80×10^{-2} mmol/g, with β-CD shows a greater affinity for congo red. The congo red adsorption is governed by hydrophobic host-guest complex interactions, while that for methylene blue is thru weak electrostatic interactions at the hydrophilic exterior of β-CD. To conclude, β-CD could be a promising adsorbent candidate for the treatment of dyes wastewater, where future works will be centred in improving the versatility and performance of the material.

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1. Introduction

Water is essential for all living beings on earth. The increase of global population has resulted in increasing demands for clean water resources. Despite the continuous needs, the domestic and industrial activities generate wastewater that inevitably pollutes the water bodies. Water pollutants such as dyes can cause detrimental effects not only to the aquatic ecosystem but also to human health [1]. Among various wastewater treatment strategies, adsorption has become the preferred technique because the process is simple and straightforward, easy to scale-up and efficient to remove trace water pollutants [2]. Activated carbon is a commonly used adsorbent for adsorption process in wastewater treatment and water purification industries [3]. However, commercial activated carbon remains expensive, thus triggers great interest in low-cost, natural and environmental friendly adsorbents [2,3]. A promising adsorbent candidate under this category is β-cyclodextrin (β-CD). β-CD is a cyclic oligosaccharide containing seven α-1,4-linked-D-glucopyranose [4]. Over the years, β-CD has been used in many fields such as 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 by forming inclusion complex, known as host-guest interactions, while the exterior surface groups could act as the active sites for the positively charged pollutants [4]. β–CD is soluble in water (18.5 g/L), hence it requires a modification in order to become insoluble adsorbent. A recent study shows that citric acid cross-linking is a cheap and straight forward modification to form β–CD adsorbent [4]. Therefore, the present work is aimed at evaluating the removal of dyes by β-CD. Two classes of dyes, namely congo red (anionic) and methylene blue (cationic) were employed. The kinetics, removal performance and possible mechanisms of adsorption were discussed.

2. Materials and methods

β-Cyclodextrin (β-CD) was obtained from Jiangsy Ogo Biotech Co. Ltd. Methylene blue and congo red were supplied by HmBG Chemicals. Citric acid and KH_2PO_4 were purchased from Systerm Chemicals. All materials are of analytical grade. Citric acid

* Corresponding author at: Centre of Lipids Engineering & Applied Research (CLEAR), Ibnu-Sina Institute for Scientific & Industrial Research (ISI-SIR), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.
E-mail address: abbas@cheme.utm.my (M.A.A. Zaini).

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cross-linked β-CD was prepared according to [4]. Briefly, 6 g of dried β-CD, 3 g of anhydrous citric acid as cross-linking agent, 1.5 g of KH_2PO_4 as catalyst and 135 mL of distilled water were mixed in a 800 mL beaker. The mixture was dried in an oven at 140 °C for 3.5 h. After that, the crude product was washed, filtered and dried prior to use. The resultant adsorbent was characterized using BET analyzer and FTIR for specific surface area and surface functional final groups, respectively. The adsorbent was used to challenge methylene blue and congo red dyes in water. The adsorption was performed at different concentrations (to attain a point of surface saturation) and contact times (to attain a point of equilibrium), at a fixed dosage of 1 g/L. The residual concentrations were measured using a UV–Vis spectrophotometer at wavelengths of 662 nm and 494 nm for methylene blue and congo red, 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.

3. Main results

The β-CD adsorbent bears a pH of 4.3 and a yield of 59.4%. From the BET analysis, the specific surface area of adsorbent is somewhat negligible at a value of 0.1 m^2/g. Fig. 1 shows the FTIR spectrum of 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 carboxyl groups of citric acid via esterification reaction to form insoluble adsorbent. The broad spectrum at 3420 cm^{-1} could be attributed to 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 surface chemistry signifies that the insoluble adsorbent is rich in acidic oxygen groups. The similar characteristics between the pristine β-CD and the insoluble one indicate that the basic matrix and structure of the material remain unchanged [4].

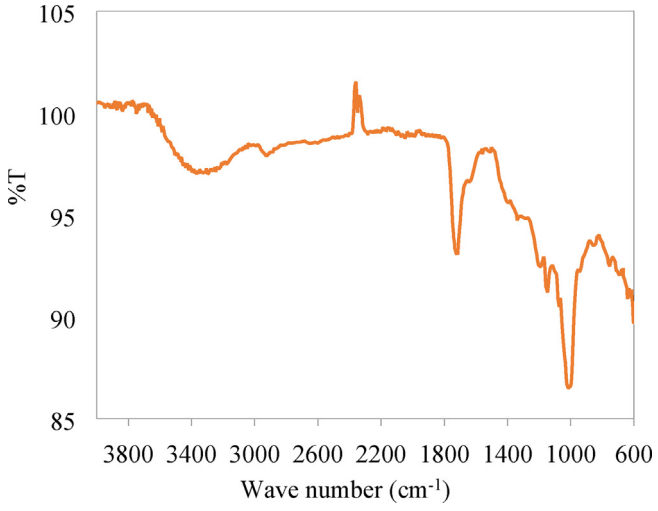

Fig. 1. FTIR spectrum of the β-CD adsorbent.

Fig. 2 illustrates the effect of contact time on the removal of dyes by the β-CD adsorbent. Generally, the dyes adsorption increases with increasing contact time to a point of equilibrium. Likewise, the adsorption rate decreases to a point where the adsorption rate is equal to the desorption rate. The vacant active sites of β-CD adsorbent are plentiful at $t = 0$, thus promoting the interaction probabilities with dyes molecules. At high concentration, however, the adsorption sites become the limiting factor, thus restricting the dyes removal. As the contact time increases, the readily adsorbed species tends to repel the free molecules in the bulk solution, so decreasing the adsorption rate. Notwithstanding that, the rate constant (slope of q_t vs. t) for both dyes increases when the concentration increases. An increase in concentration endows a driving force for dyes molecules to overcome the adsorbent mass transfer resistance, hence enhancing the transport process. From Fig. 2, congo red adsorption shows a greater rate constant of 0.103 min^{-1}, as compared to 1.36×10^{-3} min^{-1} by methylene blue, suggesting the preferably quick adsorption of congo red over methylene blue by β-CD adsorbent. This is also consistent with the shorter duration to attain the equilibrium at about 40 min as opposed to nearly 1500 min for methylene blue.

Fig. 3 shows the removal performance of methylene blue and congo red by the β-CD adsorbent. On mass basis, congo red displays a greater adsorption capacity of 12 mg/g, and this was recorded at a high concentration of more than 90 mg/L. On the other hand, the smaller capacity of 5.1 mg/g for methylene blue adsorption was achieved at C_o = 10 mg/L. Both dyes depict a similar pattern of removal performance which increased from low concentration to a maximum peak, then decreased gradually with increasing concentration. Despite the increase in adsorption capacity, the ability of 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. Both dyes

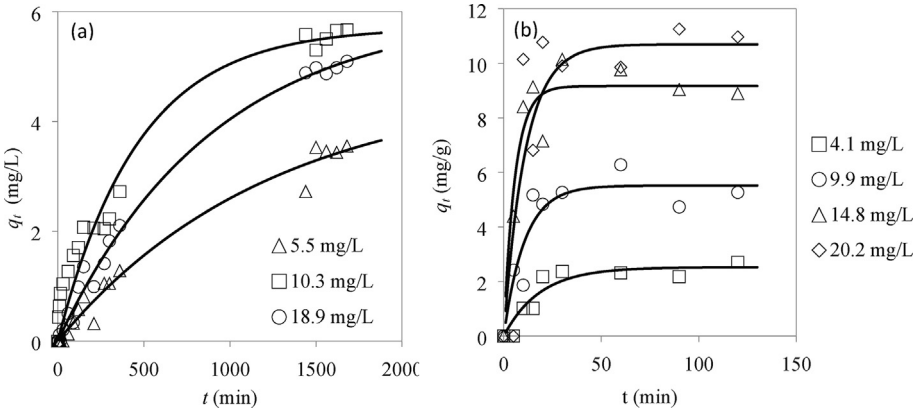

Fig. 2. Adsorption rate of (a) methylene blue and (b) congo red by β-CD adsorbent (Lines were predicted by pseudo-first-order model).

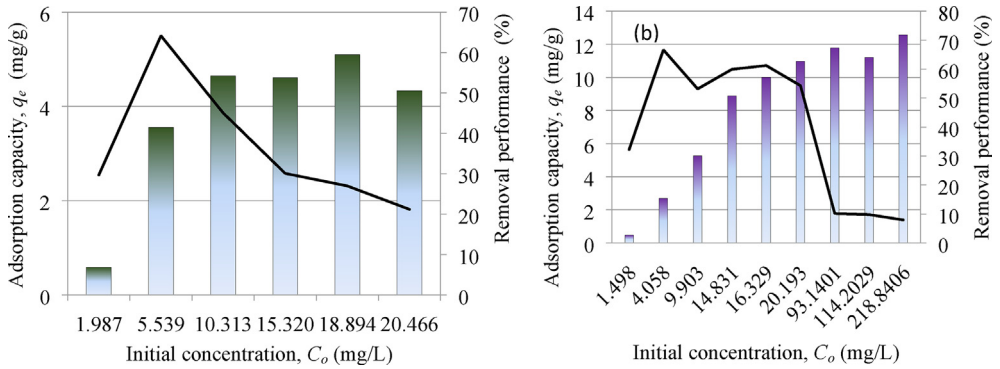

Fig. 3. Removal performance of (a) methylene blue and (b) congo red by the β-CD adsorbent. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

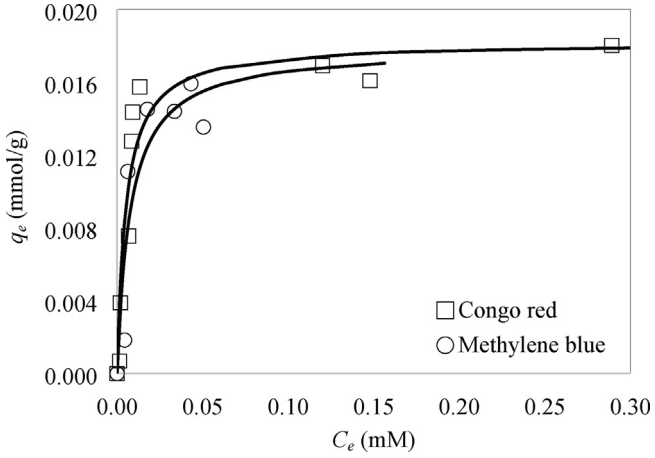

Fig. 4. Equilibrium adsorption of dyes by adsorbent (Lines were predicted by Langmuir model).

show a maximum removal of 65% because of plentiful vacant sites for adsorption at C_o around 5 mg/L.

Fig. 4 shows the equilibrium adsorption of methylene blue (MW = 319.9 g/mol) and congo red (MW = 696.7 g/mol) dyes onto β-CD adsorbent. A similar pattern of increasing adsorption with increasing concentration to a point of surface saturation or leveling-off was observed for both dyes removal [5]. The convex upward profiles imply that the dyes adsorption is favourable at the concentrations studied. On a molar basis, both dyes demonstrate a similar maximum removal capacity of 1.80×10^{-2} mmol/g. However, β-CD adsorbent exhibits a greater affinity towards congo red at a value of 194 L/mmol as compared to 129 L/mmol for methylene blue. The equilibrium data fitted well into Langmuir model with model equations of $q_e = 2.309C_e/(1 + 129C_e)$ and $q_e = 3.53C_e/(1 + 194C_e)$ for methylene blue and congo red, respectively. Generally, the performance of 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 [5,6].

Fig. 5 illustrates the possible mechanisms of dyes adsorption onto β-CD. For congo red adsorption, the underlying mechanism is host–guest complex formation inside the torus-shaped of β-CD. The width of 0.64 nm allows the congo red dye molecules 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 aromatic rings of congo red, which are also hydrophobic [4]. According to the adsorption data, the host-guest complex interactions render a rapid equilibrium with a higher rate constant of 0.103 min^{-1}. On the other hand, methylene blue, which holds an amphiphilic character is reckoned to interact at the exterior via oxygen functional groups and also at the hydrophobic interior of β-CD. At the hydrophilic exterior, the phenolic and carboxylic functional groups could interact with the nitrogen cation of methylene blue through electrostatic interactions. As the rate constant is undeniably small and a longer period was required to acquire equilibrium, it is believed that the methylene blue adsorption is mainly governed by weak electrostatic interactions with acidic oxygen functional groups.

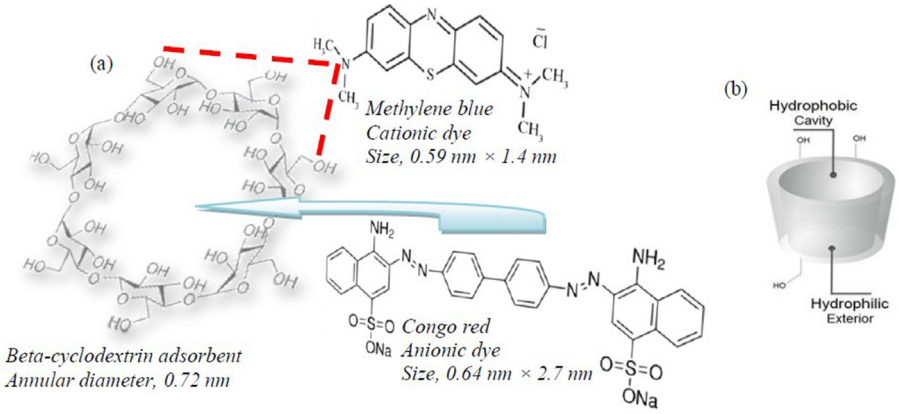

Fig. 5. (a) Mechanisms of dyes adsorption onto β-CD; (b) torus-shaped of β-CD.

4. Conclusion

Beta-cyclodextrin adsorbent was prepared for methylene blue and congo red dyes removal from water. It was cross-linked with citric acid to form insoluble adsorbent. The adsorbent exhibits a promising performance for dyes wastewater treatment. The equilibrium profiles showed a similar maximum capacity of both dyes at 1.80×10^{-2} mmol/g. Although the specific surface area is small at 0.1 m^2/g, the adsorption was found to be driven by hydrophobic host-guest inclusion inside the torus-shaped and electrostatic interactions at the hydrophilic exterior of β-CD, depending on the properties of dyes studied. Nevertheless, future studies may be needed to boost its adsorptive performance, selectivity and kinetics for wide applications in wastewater treatment.

CRediT authorship contribution statement

Noor Suhailah Sulaiman: Conceptualization, Methodology, Data curation, Investigation, Writing - original draft. **Muhammad Abbas Ahmad Zaini:** Supervision, Investigation, Validation, Writing - review & editing. **Agus Arsad:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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