

The Adsorption of Reactive Orange 16 and Basic Blue 3 from Aqueous Solution Using Quaternized Blue Swimmer Crab Carapace

Y. J. Chuah., Y. P. Tan* and A. H. Abdullah

Department of Chemistry, Faculty of Science, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia

ABSTRACT

The crab carapace is a waste which cannot be decomposed. This waste was used to remove the Reactive Orange 16 (RO16) and Basic Blue 3 (BB3) from aqueous solution at different operational parameters such as pH, mass load, the concentrations of dye and the temperature. The crab collected was modified to obtain quaternized crab (QC) using (3-chloro-2-hydroxypropyl) trimethylammonium chloride solution ($C_6H_{15}Cl_2NO$, 65% w/w in water). The pH of the dyes solution was varied from pH 4 to 10. The highest adsorption percentage was achieved at pH 7 for both dyes. Increasing the QC mass for the adsorption process had granted an increase of dyes removal percentage. The highest adsorption percentage was achieved at 91.00% for RO16 and 29.40% for BB3 dyes with 7.5 g/L QC used. However, the adsorption capacity of QC decreased with higher QC mass because the dye molecules occupied on the surface and prevented other molecules to diffuse into the QC. At higher concentration beyond 20 mg/L and 10 mg/L of RO16 and BB3, respectively, the maximum adsorption was achieved at 2.5362 mg/g and 0.6812 mg/g. The adsorption of both dyes by QC was best fitted using Langmuir isotherm model, explaining the adsorption mainly occurred as a single layer on the surface of QC. Comparison to the results obtained

from the kinetic models, the adsorption was chemisorption in nature. According to the thermodynamic studies, the adsorption of RO16 was an exothermic, while BB3 was an endothermic process.

Keywords: Adsorption, BB3, crab, RO16

ARTICLE INFO

Article history:

Received: 13 November 2017

Accepted: 09 April 2018

Published: October 2018

E-mail addresses:

typ@upm.edu.my (Y. P. Tan)

jason_youjian@outlook.com (Y. J. Chuah)

halim@upm.edu.my (A. H. Abdullah)

* Corresponding author

INTRODUCTION

Water as one of the renewable resources becomes an environmental issue when the percentage of usable clean water is decreasing. The contaminants found in the water proved that the wastewater from various industries has not been treated before discharging and the pollutants spread to various water resources. Textile industry uses more than 8000 chemicals for the manufacture processes such as dyeing and printing. A study by Kant (2012) stated that among 72 toxic chemicals used in textile industry, 30 of which could not be removed. This explains why the textile manufacturing is a cause of environmental problems.

Dyes are commonly found in the wastewater especially the untreated wastewater discharged from factories. Dyes are widely used in industries such as textile industry, paper industry, wood or lodging industry, furniture industry, stationery industry and others. Dyes can be grouped into different classes such as cationic dyes, anionic dyes, acid dyes, azo dyes, dispersive dyes, direct dyes and so on. Different classes of dyes are applied onto different products. Sometimes, there are combinations of different classes of dyes which can be applied onto a product. The dyes which are dissolved in water and discharged from the industries will flow into water streams. Some dyes are non-biodegradable and the existing treatments such as precipitation, coagulation and flocculation, ion exchange and membrane separation were not able to remove all dyes from the water. Those dyes are mostly synthetic dyes which are harmful to living things. Hence, it is crucial to remove the dyes from wastewater before releasing to the environment.

Adsorption is one of the efficient methods to remove pollutants from wastewater. It is sometimes being used in the water treatment together with other methods since it has the ability to remove certain contaminants from wastewater. Besides, it is a low-cost method, easy to operate and insensitivity to harmful materials and toxic substances (Chatterjee et al., 2012). Adsorption technology is conducted by adding the adsorbent into the wastewater to remove the contaminants from the water. Adsorption occurs on the surface of the solids (adsorbent) by weak van der Waal's forces (physisorption), covalent bonding (chemisorption) and electrostatic forces. The adsorbent used can be the solid wastes we generate such as fruit peels depending on the adsorption capacity of the materials, hence there is an opportunity to reduce the solid wastes produced since those wastes can be transformed into useful materials. The wastes to be used as adsorbents must fulfil the requirements, where low generation cost, easy to be obtained, and will not introduce any harmful or toxic substances into the water.

Crabs are decapod crustacean, living under the sea, served for the many hence creating a large amount of waste such as carapace. Crab carapace is the upper section of the shell of crab. It contains about 30% of chitin, the rest of the contents are mostly protein (11-29%), calcium carbonate (40-66%), and a small portion of lipids (Kim, 2003; Rae et al., 2009; Lu et al., 2007). Some researchers used chitin extracted from crab shell as adsorbent in their work (Akkaya et al., 2007).

Chitosan is produced by treating the chitin using alkaline substance such as sodium hydroxide. Esquerdo et al. (2014) reported the effectiveness of chitosan obtained from shrimp waste to remove 5 food dyes which were FD&C blue 2, red 40, yellow 5, yellow 6 and Food red 2. Another research was carried out to compare the influence of different chitosan base on azo reactive dye (RR120) from aqueous solution. The chitosan nanoparticle shows higher adsorption capacity and faster adsorption kinetics compared to dissolved chitosan (Momenzadah et al., 2011).

Szygula et al. (2009) reported the anionic dye (Acid Blue 92) removal was achieved at about 99% using coagulation-flocculation method, but a larger amount of chitosan was required in higher pH solution. However, the production of sludge during the process was low.

In the present work, crab carapace was used as the adsorbent for the entire work to test on the effectiveness in the removal of cationic and anionic dyes. The crab carapace is a waste and will be discarded as it cannot be consumed. The generation of this waste without treated caused an environmental issue since it cannot be decomposed. The cationic dye used in the work was Basic Blue 3 (BB3) and the anionic dye was Reactive Orange 16 (RO16). The adsorption of RO16 and BB3 by crab carapace was investigated in batch system to study the influence of operational parameters such as the pH of dyes solutions, the adsorbent mass, the concentrations of the dyes and the temperature.

MATERIALS AND METHODS

Chemicals and Materials

In this study, the chemicals were used without purification. (3-chloro-2-hydroxypropyl) trimethylammonium chloride solution, 65% w/w in water, RO16 and BB3 dyes were purchased from Sigma Aldrich. *Portunus pelagicus* or simply blue swimmer crabs were collected at Pangkor Island, Malaysia.

The carapaces of blue swimmer crab were washed with distilled water and soaked for a day. The sample was then boiled for an hour to soften the skin. Subsequently, it was washed to remove the residue with distilled water and dried in oven at 80°C overnight. The steps were repeated until the soft skin from the inner part of the carapaces was fully removed. The dried carapaces were blended and ground using blender, mortar and pestle to obtain powdered raw crab carapace (RC). The powdered sample was then sieved to pass through 1 mm sieve to ensure the particle size of the sample was less than 1 mm before storing in a desiccator.

The quaternization of the sample was conducted using (3-chloro-2-hydroxypropyl) trimethylammonium chloride solution ($C_6H_{15}Cl_2NO$, 65% w/w in water) which was adjusted to pH 8 using 5 M NaOH solution (Fan et al., 2012). 15 g of the powdered raw crab was soaked in 115 mL of the $C_6H_{15}Cl_2NO$ solution and heated at 50°C for 24 hours in the oven

with intermittent stirring. The mixture was rinsed with distilled water and dried overnight in the oven at 50°C. The sample was labelled as QC.

Characterization of RC and QC

The functional group vibrations were elucidated using Fourier-Transform Infrared (FTIR) spectrometer (Perkin-Elmer FTIR, 1725 X). The RC and QC were dried and mixed with KBr. It was then pressed with the aid of a bench press and the IR spectra were recorded. The surface morphology of the RC and QC were studied using scanning electron microscopy (SEM) method by energy dispersive X-ray spectrometer (SEM-EDX)-JEOL JSM-6400. The RC and QC were dried and put on top of the stubs which was then coated with a thin layer of gold to prevent the charging effect.

Dyes Adsorption (Batch System)

The adsorption of RO16 and BB3 from aqueous solution was conducted in a batch system to study the ability of QC on adsorbing the dye molecules with different operational parameters such as the initial pH, QC mass, initial concentration and temperature. The experiments were done using orbital shaker at 150 revolutions per minute (rpm) at room temperature. The initial pH of the dye solution was controlled at the range of pH 4 to 10 using NaOH and HCl. A preliminary test was carried out to determine the range of QC mass used. The adsorption equilibrium was reached at 7.5 g/L. Hence the QC mass used was varied from 2.5 to 7.5 g/L.

The adsorption isotherm was determined by conducting an experiment agitating 20 mL RO16 and BB3 dye solutions. The concentration of RO16 was varied from 10 to 30 mg/L and for BB3, the concentration was altered in the range of 5 to 15 mg/L. The effect of temperature of dyes adsorption was studied from 30 to 70°C.

The residual dye concentrations were determined using UV-Vis spectrophotometer (Shidmazu UV-1650 PC) at λ_{\max} of 494 nm for RO16 and 654 nm for BB3. The removal percentage of RO16 and BB3 and adsorption capacity of the QC was calculated using the equations below:

$$\begin{aligned} \text{Removal percentage, \%} \\ &= \frac{C_o - C_e}{C_o} \times 100 \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Adsorption capacity, } q_e \\ &= (C_o - C_e) \times \frac{V}{m} \end{aligned} \quad (2)$$

where C_o and C_e are the concentrations (mg/L) of the dye solutions before and after the experiments, V is the volume of the dye solution (L) and m is the mass of QC used (g).

RESULTS AND DISCUSSION

Characterization of RC and QC

Fourier-Transform Infrared Spectroscopy (FTIR). The adsorption ability of the adsorbent is relied on the functional groups. The surface functional groups of RC and QC are illustrated in the FTIR spectra shown in Figure 1. The broad band region of 3200 cm^{-1} observed is due to the stretching of OH and N-H vibration. The infrared spectra of both raw crab (RC) and quaternized crab (QC) show similar spectra, it is believed that there is overlapping between the OH and N-H stretching in the same absorption region. The OH stretching in QC is lower because most OH groups on the RC were replaced. At 1650 cm^{-1} , both infrared spectra of RC and QC show no significant difference because the functional groups of C=O vibration of acetyl groups can be found in RC and QC. However, at region 1000 cm^{-1} to 1500 cm^{-1} , the functional groups for both RC and QC are the same, but broader band for QC in the spectrum. The peak at 1400 cm^{-1} is resulted from the combination of N-H deformation and C-N stretching vibration. The absorbance intensity of infrared spectrum in QC is higher than RC. This shows an increase in C-N bonding in the QC. At 1154 cm^{-1} , it is due to the anti-symmetric stretching of the C-O-C bridge, which can be found in chitosan (Peniche et al., 1999). The similarity in RC and QC spectra might be due to the limitation of the sensitivity of the spectrometer as the quaternization process would alter the functional groups of RC.

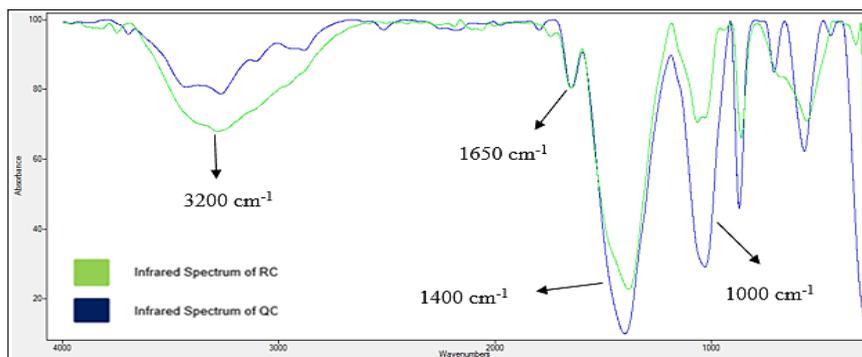


Figure 1. FTIR spectra of RC and QC

Scanning Electron Microscopy (SEM)

The morphological and surface characteristics of QC was examined by scanning electron microscopy (SEM). Figure 2 shows a micrograph of QC captured at magnification of 1000 times. The surface of QC is lumpy and cluster which helps in adsorbing the dye molecules on the surface of QC (Subramani and Thinakaran, 2017). Mohamed et al. (2015) proposed that the surface of QC was covered by methyl groups after quaternization.

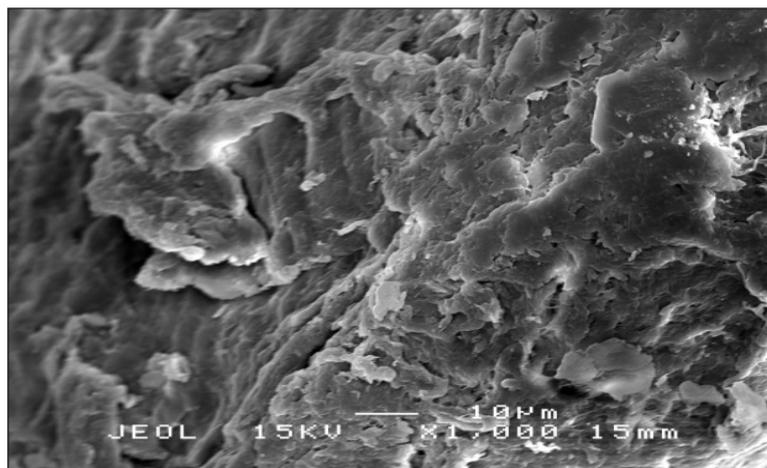
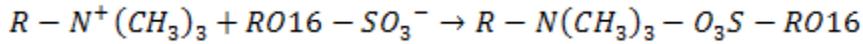
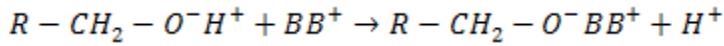


Figure 2. SEM micrograph of QC

Batch Studies of RO16 and BB3

Effect of pH. The pH of dye solutions plays an important role in experiments since it affects the ability of QC to adsorb the dye molecules from aqueous solution. The pH of the solutions takes part in improving the surface charge of the QC or vice versa. At low pH, the adsorption of BB3 must be low but achieves high removal percentage of RO16 theoretically. It is because more protons are generated at low pH and lead to the protonation of the amine groups on QC to form -NH_3^+ (Chiou et al., 2004). The RO16 adsorption by QC at low pH with the existence of -NH_3^+ is high due to the electrostatic attraction between the oppositely charges of RO16 and QC. Increasing the pH of RO16 would decrease the removal percentage because more negatively-charged sites appear after the deprotonation of the QC. An increase in pH of BB3 increases the removal percentage because the negatively-charged sites on the QC are more favor to attract the BB3 dye molecules. The chemical structures of RO16 and BB3 are shown in Figure 3. Figure 4 shows the effect of pH on the adsorption of RO16 and BB3. The removal percentage of BB3 at pH 8 is lower than pH 7. A report by Rosa et al. (2008) had shown that the adsorption of some dyes was independent to the pH of the dye solution. It is believed that the adsorption reaction on QC has insufficient reactive sites at certain pH. The ratio of the reactive sites on the surface of QC to the amount of dye molecules is another factor to consider during the adsorption reaction. For RO16 adsorption, the ability of QC to adsorb the dye molecules is weaker at high pH due to the repulsion between the RO16 dye molecules with the negatively-charged surface group. According to Chiou et al. (2002), decreasing the pH of the anionic dyes would lead to an increase in removal percentage. However, at lower pH than pH 7, excess anions appear to compete for adsorption and limit the uptake of the dye molecules (Guibal, 2004). In addition, not all reactive amine sites are responsible to adsorb the dye molecules.

There is a chance that the reactive sites can form inter and intramolecular hydrogen bonds which further limit the adsorption (Crini et al., 2008). The adsorption mechanism of BB3 and RO16 dye molecules are proposed as below:



where R represents crab carapace, BB^+ and $RO16 - SO_3^-$ represent BB3 and RO16 molecules, respectively.

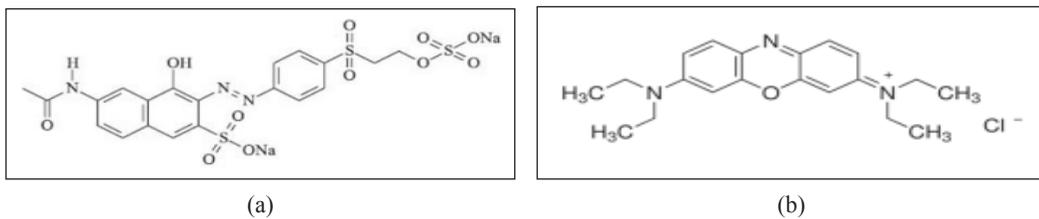


Figure 3. Chemical structures of (a) RO16 and (b) BB3

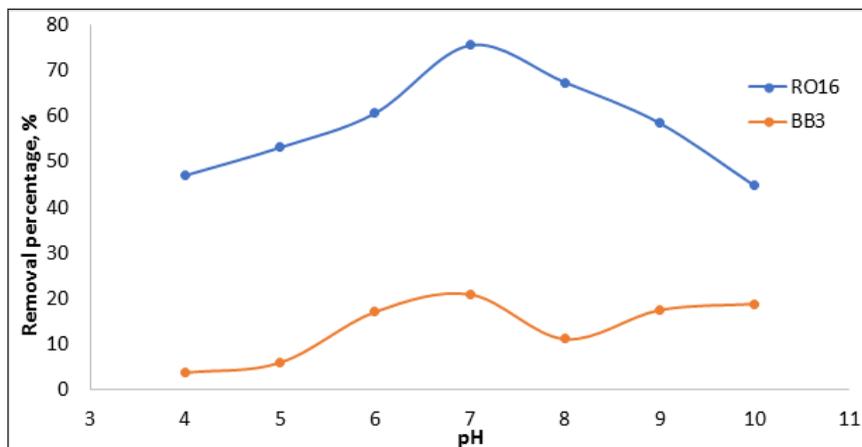


Figure 4. Effect of pH on RO16 and BB3 adsorption

Effect of QC Mass. The effect of increasing QC mass on the dyes removal percentage and adsorption capacity is depicted in Figure 5. An increase in QC mass increases the removal percentage of RO16 and BB3. The increase of QC mass offers more surface area and reactive sites for adsorption (Vijayaraghavan et al., 2006). The adsorption capacity is determined by calculating the amount of dyes adsorbed per unit weight of the QC.

Increasing QC mass in the experiment caused a decrease in adsorption capacity because less dye molecules were adsorbed per unit weight. The overlapping of the adsorption sites could be another reason leading to the decrease of the adsorption capacity with increasing QC mass (Subramani & Thinakaran, 2017). The diffusion of dye molecules onto the reactive sites of QC are harder due to the overlapping of the sites (Crini et al., 2008).

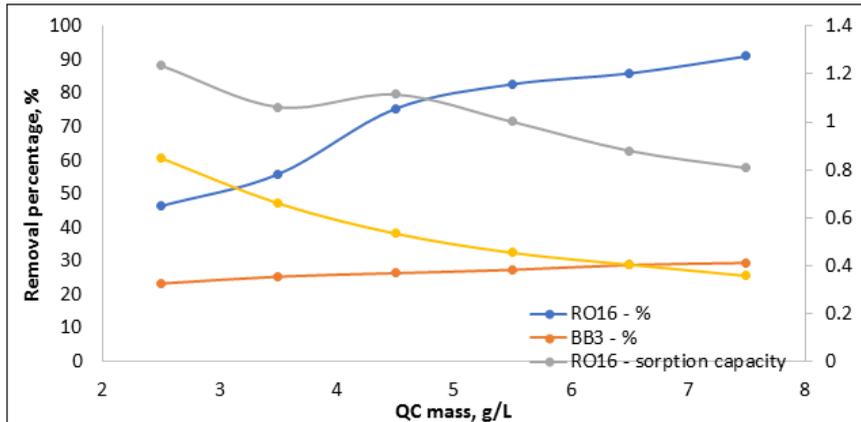


Figure 5. Effect of the QC mass on RO16 and BB3 adsorption

Effect of Dye Concentration. Figure 6 shows the removal percentage of RO16 and BB3 by QC. From Figure 6, at higher concentration, the adsorption capacity of RO16 and BB3 reduced. According to Malik (2003), there are a few steps for the dye molecules to be adsorbed onto the reactive sites of the adsorbent. The dye molecules will first overcome the boundary-layer effect and diffuse into the surface of the adsorbent. The last step is entering the porous sites of the adsorbent. From Figure 6, the adsorption capacity for both dyes increased at lower concentration. However, it is decreased at higher concentration beyond 10 mg/L for BB3 and 20 mg/L for RO16. This is due to the maximum adsorption capacity has been reached at those concentrations.

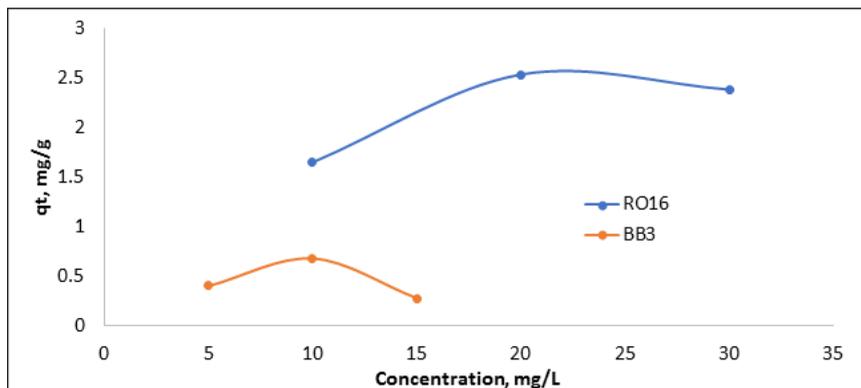


Figure 6. Adsorption capacity of QC on removal of RO16 and BB3 at different concentrations

Effect of Temperature. From Figure 7, the removal percentage of BB3 increased from 30 to 70°C. At high temperature, the diffusion rate of the dye molecules onto the adsorbent is faster. It is believed that the swelling effect of the QC at high temperature enables some larger dye molecules to penetrate further (Mane et al., 2007) which leads to a higher removal percentage. Increasing the temperature of the dye solutions will increase the removal percentage but reduces the adsorption capacity (Crini et al., 2008). When the temperature of the dye solution increases, the solubility of the dye also increases. The interaction forces between solute and solvent become stronger compared to those between solute and adsorbent. Hence, the solute is more difficult to adsorb. However, a report proposed the dye adsorption was not affected by the temperature especially for anionic dyes. Dye adsorption is an exothermic process which will weaken the bonds between the adsorbent and the dye molecules, hence, there is a controversy (Kumar, 2000).

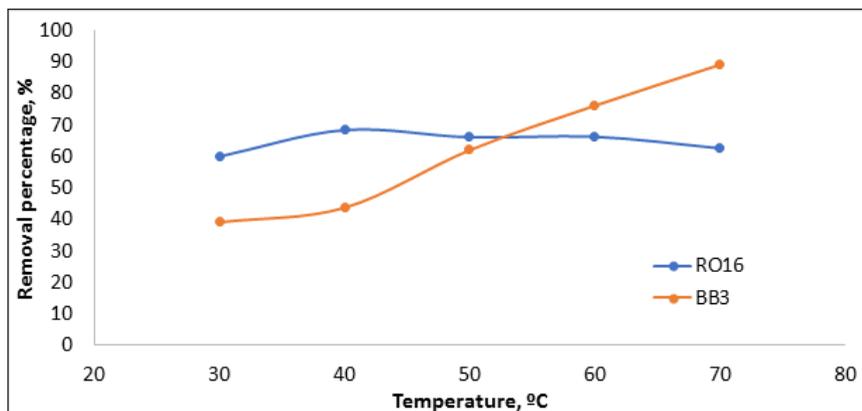


Figure 7. Effect of temperature for the RO16 and BB3 adsorption

The RO16 adsorption did not increase after 40°C using QC. This is because the bonds between the dye molecules and the reactive sites would be weakened with increasing temperature. This leads to a low adsorption ability. At high temperature, the solubility of dye increases, the QC will be difficult to adsorb the dye molecules because the dye molecules keen to bond with the solute rather than QC (Crini et al., 2008).

Isotherm Modelling. The Langmuir isotherm suggests that the adsorption takes place at specific sites of the adsorbent. The reactive sites of the adsorbent are all equivalent where the dye molecules are able to bind at the sites without being affected by nearby sites. Each reactive site is only occupied by a dye molecule and there is no further adsorption process taking place at the same site. The linearized form of Langmuir isotherm equation used in the investigation is as below (Rosa et al., 2008):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (3)$$

where C_e is the equilibrium concentration of the dye (mg/L), q_e is the amount of dye adsorbed per unit weight of adsorbent at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g) and K_L is the adsorption equilibrium constant (L/mg).

The adsorption isotherm can be investigated not only using Langmuir model but Freundlich model which is famous in the adsorption process to determine whether the adsorption of the sorbate on the adsorbent occurs at multilayer. The Freundlich isotherm is used on heterogeneous surfaces during the adsorption between the adsorbent and the dye molecules. The linear form of Freundlich isotherm equation is represented by:

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (4)$$

where q_e is the amount of dye adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of the dye (mg/L), K_F is the Freundlich constant for adsorption capacity and n_F is the Freundlich constant for adsorption intensity.

Figure 8 shows the relationship between the ratio of dye molecules adsorbed on QC and the remaining concentration. The Langmuir constants and the maximum adsorption capacity of QC can be obtained from the graphs. The linear graphs of the plots show that the adsorption of both dyes on QC happened on the homogeneous surface besides forming a monolayer adsorption. The high correlation coefficient of the plot best describes the reaction takes place only at single layer on the adsorbent surface and with constant activation energy (Crini et al., 2008). Figure 9 shows the Freundlich isotherm for the adsorption of RO16 and BB3. The plots show straight lines, however with low correlation coefficient obtained for the adsorption. The Freundlich constants and the correlation coefficients of both dyes were shown in Table 1. The low correlation coefficient shows the adsorption is not a multilayer adsorption process. However, the comparison between both isotherms explaining that the adsorption of both dyes is best fitted using Langmuir isotherm with higher correlation coefficient.

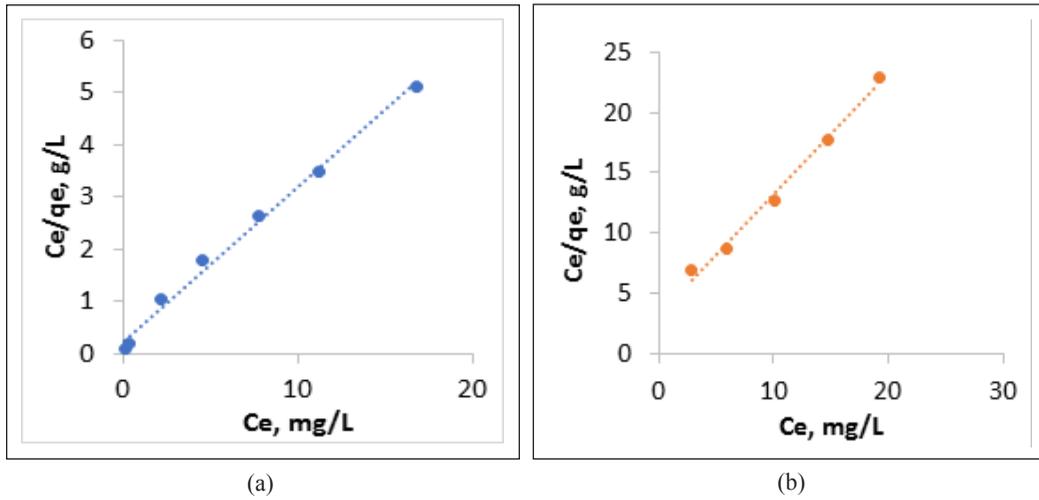


Figure 8. Langmuir linear fit for: (a) RO16; and (b) BB3 adsorption

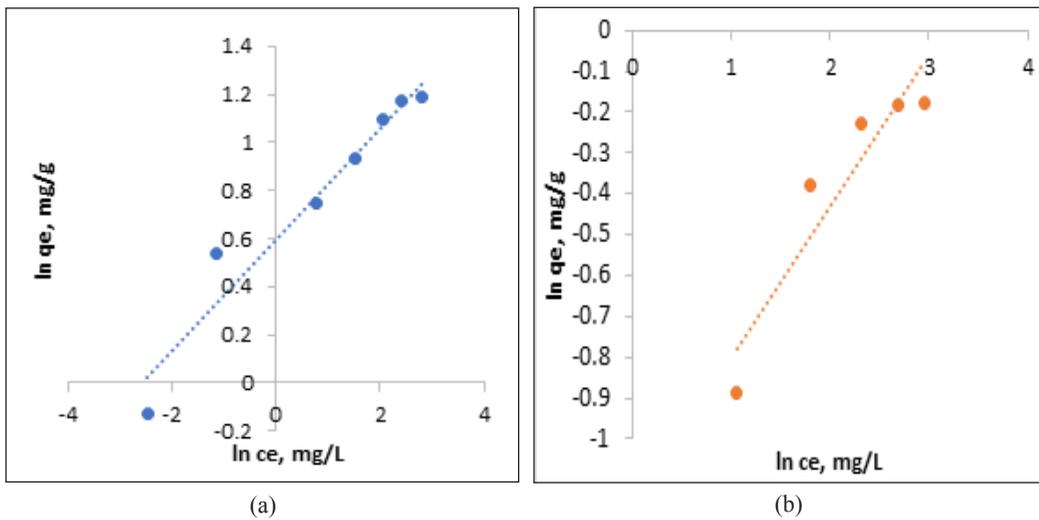


Figure 9. Freundlich fit of isotherm for: (a) RO16; and (b) BB3 adsorption

Table 1
Langmuir and Freundlich Constants for the RO16 and BB3 Adsorption by QC

Dyes	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	K_L (L/mg)	R^2	n_F	K_F	R^2
RO16	3.3887	1.2514	0.9936	1.8090	4.3029	0.9468
BB3	1.0031	0.3047	0.9899	0.3110	2.7122	0.8697

Kinetics Studies

The consideration for the use of an adsorbent to remove unwanted pollutants is not only the adsorption capacity of the adsorbent, the rate of adsorption plays an important role in water treatment. The adsorption kinetics must be determined to find out the rate of the adsorption and the factors involved in the reactions. There are three kinetic models used to explain the rate of the adsorption process and adsorption mechanism (Crini et al., 2008). These three models are (i) Lagergren model, (ii) Ho and McKay model, and (iii) Weber and Morris model. The models are best used to explain the adsorption on surface of the adsorbent, chemical reactions involved in the process and the effect of diffusion through the boundary layer (Annadurai et al., 2008).

Lagergren model with pseudo-first-order equation is used to investigate the adsorption of dyes. The linear form of pseudo-first-order equation is given by:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

Ho and McKay equation with pseudo-second-order equation has been used to explain the adsorption kinetic of an adsorbent in removing the pollutants. According to Cochrane et al. (2006), this equation can be used to explain the rate-limiting process which is due to the chemisorption reaction. There is a sharing or exchanging of electrons during the adsorption process. The linearized equation is given by:

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

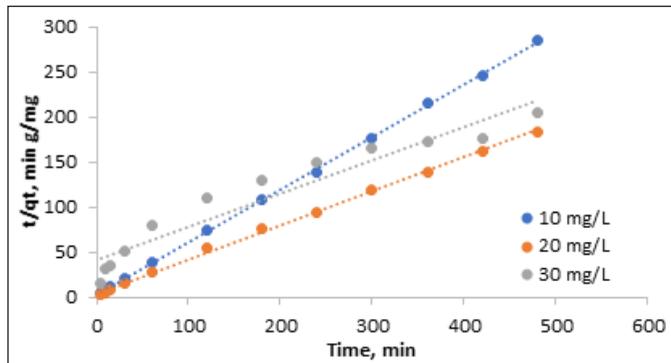
The intraparticle diffusion of the adsorption can be studied using Weber-Morris plot. The equation is represented by:

$$q_t = k_d t^{\frac{1}{2}} \quad (7)$$

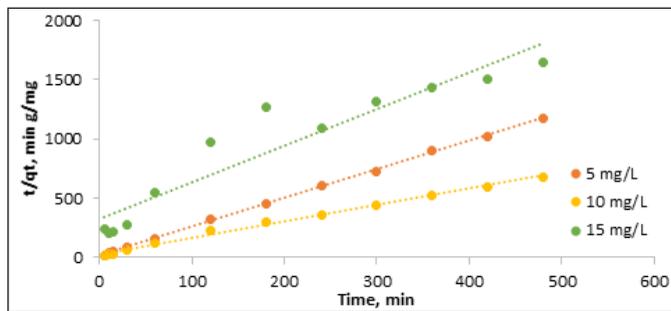
where q_e and q_t = amount of dye adsorbed per unit weight of adsorbent at equilibrium and at a certain time (mg/g), k_1 = the first-order-rate constant (min^{-1}), k_2 is the rate constant of pseudo-second-order adsorption (g/mg min) and k_d is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$).

Figure 10 shows the pseudo-second-order kinetic plots of BB3 dye using QC at different initial concentrations. From the graph plotted, the experiment data for 5 mg/L and 10 mg/L of the dye solution is best fitted with the pseudo-second-order kinetics. However, increasing the dye concentration to 15 mg/L, the correlation coefficient (R^2) is not achieved as high as 0.9900. According to Crini et al. (2008), increasing the dye concentration, the adsorption capacity will decrease as the surface reactive sites are fully

occupied, and the diffusion occurs through the boundary layer. The same phenomenon happened on the 30 mg/L of RO16 dye. The correlation coefficient (R^2) recorded at 0.9243 which is not good to explain the chemisorption mechanism of the adsorbent at this high dye concentration. The intraparticle diffusion rate constants for both BB3 and RO16 dyes in different concentrations can be obtained from the plots shown in Figure 11. From the plots, the intraparticle diffusion is not the main factor of kinetic process since the plots do not pass through the origin (Rosa et al., 2008), and the intraparticle diffusion is not the rate-determining step (Cochrane et al., 2006). According to Cochrane et al. (2006), the pseudo-second order model gives higher R^2 compared to intraparticle diffusion. This explains the rate-limiting step is a chemisorption which occurs between the dye molecules and the adsorbent. Moreover, since the plots do not pass through the origin, there might be some other processes controlling the rate of the adsorption (Crini et al., 2008). From the figures, there are three separate regions which can be observed. The first stage is the bulk diffusion with boundary layer effect, the next stage would be the intraparticle diffusion and the last stage is the final equilibrium stage, where the intraparticle diffusion starts to slow down (Mane et al., 2007). Table 2 shows a summary of rate constants and the correlation coefficients for the three models.

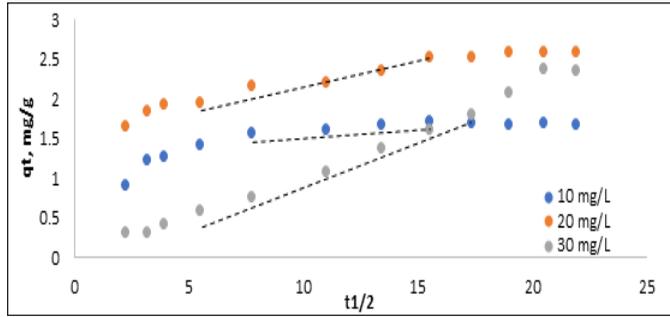


(a)

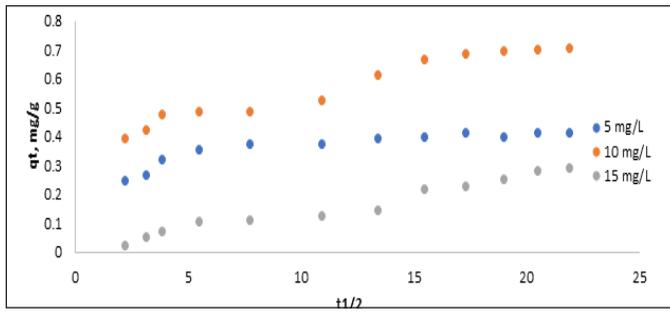


(b)

Figure 10. Pseudo-second-order kinetics of (a) RO16 and (b) BB3



(a)



(b)

Figure 11. Intraparticle diffusion of (a) RO16 and (b) BB3

Table 2
Kinetic parameters for the RO16 and BB3 Adsorption

Model	Parameters	RO16			BB3		
		Initial concentration (mg/L)					
		10	20	30	5	10	15
Pseudo-first-order	q_{∞} exp (mg/g)	1.6732	2.5362	2.3840	0.3928	0.6686	0.2916
	q_{∞} cal (mg/g)	0.5531	0.7386	2.1994	0.1067	0.2584	0.2826
	k_1 (1/min)	0.0210	0.0078	0.0048	0.0182	0.0074	0.0006
	R ²	0.8944	0.9349	0.9688	0.7480	0.8781	0.8970
Pseudo-second-order	q_{∞} cal (mg/g)	1.7112	2.6469	2.7270	0.4145	0.7223	0.3236
	k_2 (g/mg min)	0.1317	0.0355	0.0032	0.3653	0.0769	0.0297
	R ²	0.9997	0.9985	0.9243	0.9995	0.9952	0.8981
Intraparticle diffusion	$k_d \times 10^{-2}$	1.95	5.14	10.53	0.45	2.41	0.43
	R ²	0.9733	0.9435	0.9964	0.9471	0.9517	0.9201

Thermodynamic Studies

The thermodynamic studies are important to determine what processes will occur spontaneously. The thermodynamic equation is shown below:

$$\log K_d = \frac{\Delta S^0}{2.303 R} - \frac{\Delta H^0}{2.303 RT} \quad (8)$$

where K_d = distribution coefficient defined as q_e/C_e (L/g), q_e = amount of dye adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e = equilibrium concentration of dye remaining in solution (mg/L), T = absolute temperature (K). R = gas constant (8.3145 J/mol K), ΔS^0 = entropy change (J/mol K), ΔH^0 = enthalpy change (KJ/mol).

The Van't Hoff plots were shown in Figure 12, the slopes and the intercepts of the graphs were determined to obtain the values of enthalpy (ΔH^0) and entropy (ΔS^0). The sign of ΔH^0 and ΔS^0 can be positive or negative depends on the adsorption condition. A positive value of ΔH^0 indicates that the process is endothermic, while negative is exothermic.

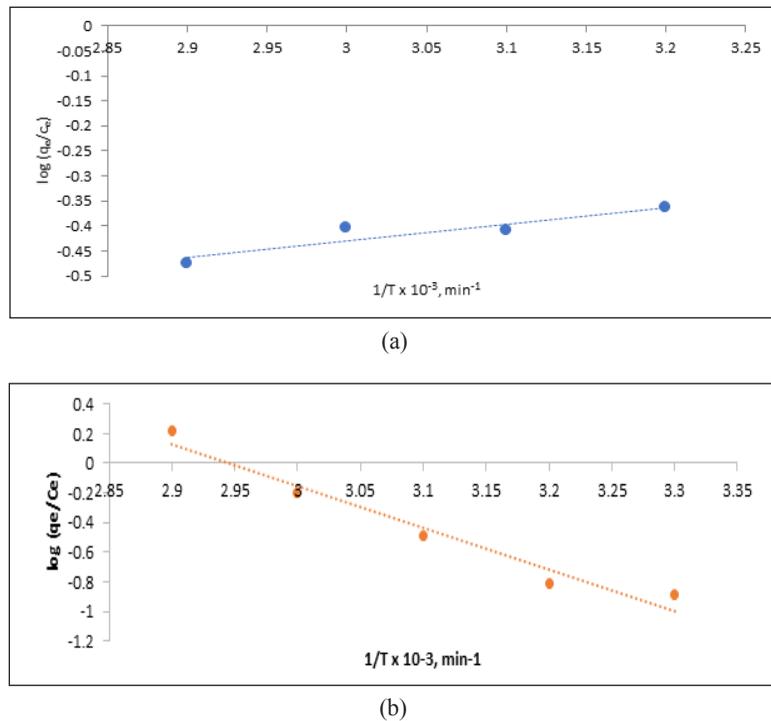


Figure 12. Van't Hoff plots for (a) RO16 and (b) BB3 adsorption

Table 3
 Enthalpy (ΔH°) and entropy (ΔS°) change

Dye	ΔH° (KJ/mol)	ΔS° (J/mol K)
RO16	-6.332	-27.219
BB3	54.222	159.810

From Table 3, the ΔH° for BB3 adsorbed by QC were positive, showing the adsorption process was endothermic while the adsorption of RO16 was an exothermic process. The positive value of ΔS° for BB3 dye indicates that the adsorption increased the randomness at the solid/solution interface. The negative value of ΔS° for RO16 was preferable desorption rather than adsorption (Crini et al., 2008).

CONCLUSION

The quaternized crab (QC) was used for the adsorption of RO16 and BB3. QC showed a stronger adsorption of RO16 compared to BB3. The maximum adsorption of RO16 and BB3 was achieved at pH 7. This can be concluded as the adsorption process on removal of RO16 and BB3 was insignificant over the pH range of the dye solutions. Increasing the QC mass increased the removal percentage of RO16 and BB3 but decreased the adsorption capacity. This is due to the overlapping of the dye molecules on the surface of QC leads to a harder diffusion during the adsorption process. An increase on the concentration of dyes leads to a lower adsorption capacity as the maximum adsorption capacity has been reached. At high temperature, QC has lower adsorption ability to remove RO16, where the solubility of RO16 increases at high temperature, and the dye molecules keen to bond with the solute rather than QC.

The adsorption of RO16 and BB3 occurred mostly on the surface of QC. The dyes did not form multilayers phase on QC. The adsorption process followed pseudo-second-order kinetics with higher correlation coefficient (R^2) compared to pseudo-first-order kinetics. The evaluation of thermodynamic parameters for RO16 ($\Delta H^\circ = -6.332$) KJ/mol and $\Delta S^\circ = -27.21$ J/mol K) shows the exothermic process. For BB3 ($\Delta H^\circ = 54.222$ KJ/mol and $\Delta S^\circ = 159.810$ J/mol K), the adsorption was an endothermic process and a spontaneous reaction. The crab carapace as a waste is a potential adsorbent for water treatment and deserves future research for its uses in removing other pollutants.

ACKNOWLEDGEMENT

The authors wish to thank Graduate Research Fellowship (GRF) and Department of Chemistry, Faculty of Science of Universiti Putra Malaysia.

REFERENCES

- Akkaya, G., Uzun I., & Güzel, F. (2007). Kinetics of the adsorption of reactive dyes by chitin. *Dyes and Pigments*, 73(2), 168-177.
- Annadurai, G. (2002). Adsorption of basic dye on strongly chelating polymer: Batch kinetics Studies. *Iranian Polymer Journal*, 11(4), 237-244.
- Chatterjee, S., Kumar, A., Basu, S., & Dutta, S. (2012). Application of response surface methodology for methylene blue dye removal from aqueous solution using low cost adsorbent. *Chemical Engineering Journal*, 181, 289-299.
- Chiou, M. S., & Li, H. Y. (2002). Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. *Journal of Hazardous Materials*, 93(2), 233-248.
- Chiou, M. S., Ho, P. Y., & Li, H. Y. (2004). Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. *Dyes and Pigments*, 60(1), 60-84.
- Cochrane, E. L., Lu, S., Gibb, S. W., & Villaescusa, I. (2006). A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media. *Journal of Hazardous Materials*, 137(1), 198-206.
- Crini, G., & Badot, P. M. (2008). Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. *Progress in Polymer Science*, 33(4), 399-447.
- Esquerdo, V. M., Cadaval, T. R. S., Dotto, G. L., & Pinto, L. A. A. (2014). Chitosan scaffold as an alternative adsorbent for the removal of hazardous food dyes from aqueous solutions. *Journal of Colloid and Interface Science*, 424, 7-15.
- Fan, L., Wu, P., Zhang, J., Gao, S., Wang, L., Li, M., ... & Nie, M. (2012). Synthesis and anticoagulant activity of the quaternary ammonium chitosan sulfates. *International Journal of Biological Macromolecules*, 50(1), 31-37.
- Guibal, E. (2004). Interactions of metal ions with chitosan-based sorbents: A review. *Separation and Purification Technology*, 38(1), 43-74.
- Kant, R. (2012). Textile dyeing industry an environmental hazard. *Natural Science*, 4(1), 22-26.
- Kim, D. S. (2003). The removal by crab shell of mixed heavy metal ions in aqueous solution. *Bioresource Technology*, 87(3), 355-57.
- Kumar, M. N. V. R. (2000). A review of chitin and chitosan applications. *Reactive and Functional Polymers*, 46(1), 1-27.
- Lu, S., Gibb, S. W., & Cochrane, E. (2007). Effective removal of zinc ions from aqueous solutions using crab carapace biosorbent. *Journal of Hazardous Materials*, 149(1), 208-217.

- Malik, P. K. (2003). Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of acid yellow 36. *Dyes and Pigments*, 56(3), 239-249.
- Mane, V. S., Mall, I. D., & Srivastava, V. C. (2007). Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution. *Dyes and Pigments*, 73(3), 269-278.
- Mohamed, R. R., Elella, M. H., & Sabaa, M. W. (2015). Synthesis, characterization and applications of N-quaternized chitosan/poly(vinyl alcohol) hydrogels. *International Journal of Biological Macromolecules*, 80, 149-161.
- Momenzadeh, H., Tehrani-Bagha, A. R., Khosravi, A., Gharanjig, K., & Holmberg, K. (2011). Reactive dye removal from wastewater using a chitosan nanodispersion. *Desalination*, 271(1-3), 225-230.
- Peniche, C., Argüelles-Monal, Davidenko, N., Sastre, R., Gallardo, A., & Román, J. S. (1999). Self-curing membranes of chitosan/PAA IPNs obtained by radical polymerization: Preparation, characterization and interpolymer complexation. *Biomaterials*, 20(20), 1869-1878.
- Rae, I. B., Gibb, S. W., & Lu, S. (2009). Biosorption of Hg from aqueous solutions by crab carapace. *Journal of Hazardous Materials*, 164(2-3), 1601-1604.
- Rosa, S., Laranjeira, M. C. M., Riela, H. G., & Fávere, V. T. (2008). Cross-linked quaternary chitosan as an adsorbent for the removal of the reactive dye from aqueous solutions. *Journal of Hazardous Materials*, 155(1-2), 253-260.
- Subramani, S. E., & Thinakaran, N. (2017). Isotherm, kinetic and thermodynamic studies on the adsorption behavior of textile dyes onto chitosan. *Process Safety and Environmental Protection*, 106, 1-10.
- Szyguła, A., Guibal, E., Palacín, M. A., Ruiz, M., & Sastre, A. M. (2009). Removal of an anionic dye (acid blue 92) by coagulation–flocculation using chitosan. *Journal of Environmental Management*, 90(10), 2979-2986.
- Vijayaraghavan, K., Palanivelu, K., & Velan, M. (2006). Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles. *Bioresource Technology*, 97(12), 1411-1419.