

Removal of Acid blue 25 using Cempedak Durian peel from aqueous medium: Isotherm, kinetics and thermodynamics studies

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Abstract

The adsorption of Acid blue 25 (AB25) onto Cempedak durian peel (CDP) was investigated. The effects of contact time, pH, ionic strength, initial concentration and temperature were studied. CDP's functional groups were characterized using Fourier Transform Infrared spectroscopy. Langmuir and Freundlich isotherm models were used to investigate the adsorption process. It was found that the Langmuir model best described the experimental data with maximum adsorption capacity of 0.064 mmol g⁻¹ (26.62 mg g⁻¹) at 60 °C. Kinetics data were fitted using Lagergren 1st order, pseudo 2nd order, Weber-Morris intraparticle diffusion and Boyd models and kinetics was found to follow the pseudo 2nd order, and the mechanism may be controlled by film diffusion according to the Boyd model. Thermodynamics properties of the process were also investigated and adsorption of AB25 onto CDP was found to be endothermic in nature. Regeneration study showed that CDP was able to maintain satisfactory adsorption of AB25 even after five cycles of treatments using 0.1 M NaOH.

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Introduction

Since the dye mauveine was synthesized by William Henry Perkin, other scientists soon synthesized many other dyes which eventually replaced the use of natural dyes extracted from roots, leaves, flowers and shells. The synthetic dyes are favoured over natural dyes due to their ease of production as well as low cost. Although the use of synthetic dyestuff is important, it has great negative impact on flora and fauna as well as humans if they are not disposed properly. The normal means of disposing dyestuffs is by dumping them into river or the sea, which is not only toxic to the living organisms but also create repulsive sight of colored water bodies. Water bodies polluted with dyestuff would exhibit low biological oxygen demand (BOD), high chemical oxygen demand (COD) and high amount of dissolved solid (Rajeshwarisivaraj *et al.*, 2001).

Water treatment methods such as reverse osmosis, filtration, electroplating, precipitation, coagulation and electrolysis have been used in order to remove the pollutants from the water bodies (Bhatnagar and Sillanpää, 2010). However, the disadvantages of these methods are: expensive, ineffective at low concentration, high reagent use, high energy and often form toxic secondary sludge (Abdolali *et al.*,

2014). Adsorption is also one of the methods being used for water treatment which utilizes activated carbon to remove pollutants. The use of activated carbon can be effective but is usually high-cost to produce (Deniz *et al.*, 2011). In response to this, many researches are now focusing on finding alternative materials that are cheap, eco-friendly and abundant. Amongst the materials used are fruit peels (Priyantha *et al.*, 2013a, 2015), agricultural wastes (Chowdhury *et al.*, 2009, Lim *et al.*, 2014a), plant materials (Kooch *et al.*, 2015, Dahri *et al.*, 2015a), peat (Chieng *et al.*, 2013, Lim *et al.*, 2013, Zehra *et al.*, 2013, Chieng *et al.*, 2014), fungi (Rodríguez *et al.*, 2013), nut shells (Dahri *et al.*, 2014, Taşar *et al.*, 2014) and bacteria (Rajaram *et al.*, 2013).

Acid blue 25 (AB25) belongs to the anthraquinone dye class which is the second most important dye after azo dyes. It is a dark blue solid that dissolves in water to form a blue solution. AB25 is used mainly for dyeing wool, polyamide, leather, detergent, wood, fur, cosmetic, ink and biological stain (Ghodbane and Hamdaoui, 2010). In this study, Cempedak durian peel (CDP) was used as the adsorbent for the evaluation of its ability to remove AB25. Cempedak durian, an *Artocarpus* spp., is a fruit that belongs to the Moraceae family and can be found in tropical areas such as the Borneo Island. Unlike the other *Artocarpus* fruits e.g.

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jackfruit, breadnut and breadfruit, Cempedak durian is less common. Generally fruits of *Artocarpus* consist of > 50% inedible parts such as the skin and core which are thrown away as wastes (Tang *et al.*, 2013; Lim *et al.*, 2011). Our studies have shown that wastes of *Artocarpus* fruits have been successfully used for the removal of toxic heavy metals (Lim *et al.*, 2012, Lim *et al.*, 2015a, Priyantha *et al.*, 2013b) and cationic dyes (Lim *et al.*, 2014b, 2015b-2016, Chieng *et al.*, 2015). To date, there have only been two reports on the use of CDP as a low-cost adsorbent for the removal of brilliant green and methyl violet 2B cationic dyes (Dahri *et al.*, 2015b-c). However, to the best of our knowledge, the use of *Artocarpus* wastes for the removal of anionic dye has never been reported.

Materials and Methods

Materials

Cempedak durian fruit was purchased from the local open market and the peel was separated and dried in an oven at 85°C until a constant mass was obtained. The dried CDP was then blended and sieved to obtain particles of diameter ranging from 355 µm to 850 µm which was used throughout the experiment.

Chemicals and instrumentations

Acid blue 25 (AB25) of 45% purity, molecular weight 416.38 g mol⁻¹ and molecular formula, C₂₀H₁₃N₂NaO₅S and potassium nitrate were purchased from Sigma-Aldrich. pH was adjusted using sodium hydroxide (Univar) and nitric acid (AnalaR). Spectroscopy grade potassium bromide was used for Fourier transform infrared spectroscopy (FTIR) analysis. Double distilled water was used throughout this study. Stock solution was prepared by dissolving appropriate amount of AB25 in double distilled water. Other concentrations of the dye used in the experiment were done by diluting the stock solution. All reagents were used without further purification.

CDP was dried in Gallenkamp Hotbox oven and was blended using Panasonic MX-J210GN. Stuart orbital shaker was used for agitation of the solution and set at 250 rpm. EDT instruments GP 353 ATC pH meter was used to measure the pH. Shimadzu UV-1601PC UV-Visible spectrophotometer (UV-Vis) was run in wavelength range between 400 to 700 nm; maximum wavelength for AB25 was 597 nm. Functional group characterization of CDP was carried out using Shimadzu IR Prestige-21 spectrophotometer where the FTIR spectra were recorded at spectral range from 4000 to 400 cm⁻¹.

Batch experimental procedure

Batch experiments were carried out by mixing 0.04 g of CDP with 20.0 mL of known concentration of AB25 dye solution in a 125 mL conical flask. The mixtures were then agitated on an orbital shaker set at 250 rpm at room temperature. Effects of contact time (5-240 minutes), medium pH (2-10), initial concentration (20-500 mg L⁻¹), ionic strength (0.01-0.20 M KNO₃) and temperature (25-60°C) were done for optimizing the experimental conditions. After agitation, the mixtures were filtered and the filtrates were analyzed for dye content using UV-Vis spectrophotometer.

The point of zero charge (pHpzc) was determined by mixing 0.040 g of CDP with 20.0 mL of 0.10 M KNO₃, and the pH of the mixture was adjusted from 2 to 10. After 24 h agitation, the mixtures were filtered and the final pH was measured. The value of pHpzc was calculated from the curve that intersects the X-axis of the plot of ΔpH versus pH_i (initial pH) (Shawabkeh *et al.*, 2007).

The amount of dye adsorbed per gram of CDP, q_e (mmol g⁻¹), was calculated using equation (1):

$$q_e = \frac{(C_0 - C_e)V}{Mm} \quad (1)$$

where C_0 is the initial dye concentration (mg L⁻¹), C_e is the equilibrium dye concentration (mg L⁻¹), M is AB25 molecular mass (mol g⁻¹), V is the volume of AB25 solution used (L), and m is the mass of CDP used (g). The percentage removal of the dye is represented by equation (2) below:

$$\text{Percentage removal} = \frac{(C_0 - C_e) \times 100\%}{C_0} \quad (2)$$

Regeneration studies

CDP loaded with AB25 was treated with three different washing solutions: double distilled water, 0.1 M HNO₃ and 0.1 M NaOH in order to evaluate the regenerability of the biosorbent. 0.5 g of CDP was treated with 100 mg L⁻¹ AB25 using the same conditions as described above. After treatment, the AB25-loaded CDP was thoroughly washed with double distilled water and dried in oven for 24 h at 85°C as preparation for the regeneration study. The dried sample was then separated into 3 parts and treated with the different washing solutions mentioned. After agitating AB25-loaded CDP with the washing solutions, double distilled water was used to thoroughly wash the sample to remove any remaining dye, acid or base before drying in the oven for 24 h at 85°C. This is considered as one cycle and the experiment was repeated for four more cycles.

Error analyses

The isotherm model that best describes the experimental data was chosen based on the correlation coefficient (R^2) value, simulation of non-linear isotherm models and error function analyses using Marquart's percent standard deviation (MPSD) and the chi-square test (χ^2) as shown in equations (3) and (4), respectively. Smaller values of these error analyses indicate the better curve fitting (Tsai and Juang, 2000).

$$\text{MPSD: } 100 \sqrt{\frac{1}{n-2} \sum_{i=1}^n (q_{e,\text{meas}} - q_{e,\text{calc}})^2} \quad (3)$$

$$\chi^2 : \sum_{i=1}^p \frac{(q_{e,\text{meas}} - q_{e,\text{calc}})^2}{q_{e,\text{meas}}} \quad (4)$$

where $q_{e,\text{meas}}$ is the experimental value while $q_{e,\text{calc}}$ is the calculated value, n is the number of parameter and p is the number of data in the experiment.

Results and Discussion

Effect of medium pH

The point of zero charge (pHpzc) is a useful information to predict the changes in the surface charge of an adsorbent. It indicates the pH at which the adsorbent's surface has a zero net charge; predominately positively charged if the pH falls below this value and predominately negatively charged above the value. Adsorption process that depends on electrostatic interaction will be heavily affected by these changes. Thus, pHpzc and pH experiments are important tools in determining one of the optimal conditions for the adsorption to occur. The pHpzc of CDP in this study was found to be at pH 4.01.

Control experiment was done whereby pH-adjusted AB25 (pH 2-10) solutions without addition of CDP were left for 2 h before their dye contents were analysed using UV-Vis. The purpose of this experiment was to observe the changes in the dye intensity caused by the alteration of solution pH. It was observed that only slight decrease in absorbance for pH 2 and pH 3 when compared to AB25 solution without pH alteration. From this observation, it can be concluded that pH alteration does not significantly affect the intensity of AB25 and therefore, the pH experiment was conducted within the range of pH 2-10.

Figure 1 shows the removal of AB25 by CDP at different pHs. Highest removal was achieved at pH 2 and the uptake of the dye was drastically decreased beyond pH 3. This trend was similarly obtained in adsorption study on AB25 (Yang *et al.*, 2011, Hanafiah *et al.*, 2012) and many other anionic dyes (Arami *et al.*, 2006, Safa and Bhatti, 2011). As pH

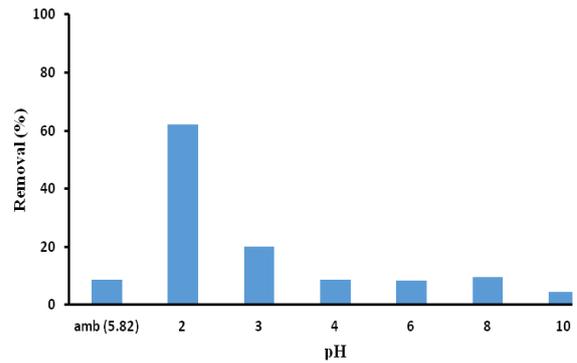


Figure 1. Effect of medium pH on the adsorption of AB25 onto CDP (AB 25 concentration = 10 mg L⁻¹; volume = 20.0 mL; CDP's mass = 0.04 g; agitation time = 2 h; agitation speed = 250 rpm; temperature = 293 K)

2 is below CDP's pHpzc, the charge on the surface is predominately positive due to the neutralization of negative charge and protonation occurring on the surface which is not only electrostatically favourable as AB25 forms negative charge in solution, but also facilitates diffusion and provides more active sites for adsorption to occur. The decrease in uptake of dye as pH increases may be due to an increase of negative charge on the surface which repels the anionic dye (Mittal *et al.*, 2006). This trend suggests that the adsorption of AB25 onto CDP may heavily rely on electrostatic interaction. Since pH 2 gave the highest removal of AB25, all subsequent experiments in this study were carried out at this pH.

Contact time and kinetics study

The effect of contact time on the adsorption of 100 mg L⁻¹ AB25 by CDP at pH 2 showed a rapid uptake of AB25 in the first 100 min which then slowed down beyond 120 min with gradual increase in q_e , from 0.043 mmol g⁻¹ (120 min) to 0.049 mmol g⁻¹ (240 min). The rapid uptake was due to the availability of active sites on CDP's surface which eventually became saturated with AB25 causing the adsorption rate to slow down and eventually reached equilibrium.

Kinetics study is an important tool in understanding the adsorption mechanism as well as the performance of the adsorbent which is essential for effective designing and modeling of the process (Gupta *et al.*, 2006, Senturk *et al.*, 2009). For this purpose, the Lagergren 1st order model (Lagergren, 1898) and pseudo 2nd order model (Ho and McKay, 1998) presented by equation (5) and equation (6) respectively, were used to describe the adsorption mechanism while the Weber-Morris intraparticle diffusion (Weber and Morris, 1963) and the Boyd model (Boyd *et al.*, 1947) presented by equation (7)

and equation (8) respectively, were used to identify the diffusion mechanism.

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

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

$$q_t = k_3 t^{1/2} + C \quad (7)$$

$$B_t = -0.4977 - \ln(1 - F) \quad (8)$$

$$F = \frac{q_t}{q_e} \quad (9)$$

where q_t is the amount of adsorbate adsorbed per gram of adsorbent (mmol g^{-1}) at time t , q_e is the amount of adsorbate adsorbed per gram of adsorbent (mmol g^{-1}) at equilibrium, k_1 is the Lagergren 1st order rate constant (min^{-1}) and t is the contact time (min). k_2 is pseudo second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) while k_3 is the intraparticle diffusion rate constant ($\text{mmol g}^{-1} \text{min}^{-1/2}$) and C is the intercept that represents the thickness of the boundary layer where the larger the C value, the greater the boundary layer effect. F is the fraction of dye adsorbed at different time and B_t is a mathematical function of F .

Lagergren 1st order and pseudo 2nd order models were compared based on two factors: R^2 values and q_e values calculated from respective equations. Lagergren 1st order's $q_e(\text{cal})$ and k_1 were obtained from the intercept and slope of the plot $\ln(q_e - q_t)$ vs t respectively. Similarly, $q_{e,\text{calc}}$ and k_2 of pseudo 2nd order were obtained from slope and intercept of the linear plot $\frac{t}{q_t}$ vs t , respectively. Kinetics study showed that the pseudo 2nd order model has a slightly higher R^2 (0.990) compared to that of the Lagergren 1st order model ($R^2 = 0.984$), indicating the former is better fitted to experimental data. Experimental $q_{e,\text{meas}}$ ($0.050 \text{ mmol g}^{-1}$) was closer to $q_{e,\text{calc}}$ calculated for pseudo 2nd order ($0.053 \text{ mmol g}^{-1}$) than for pseudo 1st order ($0.033 \text{ mmol g}^{-1}$) thereby further confirming that the adsorption kinetics followed the pseudo 2nd order with rate $k_2 = 0.769 \text{ g mg}^{-1} \text{min}^{-1}$. This model is based on the assumption that chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate may be the rate – limiting step (Ho and McKay, 1999). The deviation of $q_{e,\text{calc}}$ of Lagergren 1st order model from experimental value could be due to the inability of this model to describe entire range of adsorption time and limited only to the initial time range (Li et al., 2007).

Weber-Morris and Boyd models were used to identify the diffusion mechanism as the previous two kinetics models are not able to provide such information. According to the Weber-Morris model,

intraparticle diffusion also known as pore diffusion is the rate-limiting step when the plot of q_t vs $t^{1/2}$ gives a linear line that passes through the origin. However, the linear plot does not pass through origin and gave an intercept $C = 0.013$. Hence, it can be said that pore diffusion is present but it is not the rate-limiting step.

In the Boyd model, the plot Bt vs t should yield a straight line passing through origin if particle diffusion is involved whereby the adsorbate transport occurs within the pores controls the adsorption mechanism. Deviation of the straight line from the origin would suggest the adsorption mechanism is controlled by film diffusion whereby the transport occurs at the external surface (Tavlieva et al., 2013). Boyd plot showed that the straight line does not pass through the origin. This suggests that film diffusion controls the adsorption mechanism.

Effect of ionic strength

Typical textile wastewater contains various types of electrolytes and suspended compounds that may hinder the adsorption process. In this study, KNO_3 was used to evaluate CDP's ability to remove AB25 in high ionic strength solution. KNO_3 concentrations beyond 0.2 mol L^{-1} were observed to cause AB25 to precipitate out the solution making the analysis inaccurate. This occurrence is due to the dimerization of the dye and was also observed by Yang et al. (2011). From this study, it can be said that no significant effect was observed on the q_e from 0.01 mol L^{-1} to 0.10 mol L^{-1} KNO_3 and a decrease of 11% was observed at 0.20 mol L^{-1} . This slight decrease may due to the electrostatic repulsion caused by the salt. In theory, increase in ionic strength will decrease the adsorption capacity when the electrostatic forces between the adsorbent and adsorbate were attractive. On the other hand, adsorption capacity is increased when the electrostatic forces between them were repulsive in solution with increasing ionic strength (Newcombe and Drikas, 1997).

Adsorption isotherm and thermodynamics studies

Adsorption isotherm study is mandatory for the analysis and design of adsorption systems as it can provide information on adsorption mechanism, surface properties and capacity or affinity of the adsorbent based on several assumptions (Aksu and Karabayir, 2008). In this study, adsorption of AB25 by CDP were carried out at different temperatures ranging from 25°C to 60°C and the results are presented in Figure 2(A). It can be seen that for all temperatures, the q_e values increased from 10 to 500 mg L^{-1} of AB25. The driving force to overcome all mass transfer resistances the dye between the liquid

Table 1. Langmuir and Freundlich isotherm parameters and error analysis at different temperatures

Temperature (°C)	Langmuir						Freundlich					
	q_{max}	K_L	R_L	R^2	$MPSD$	χ^2	K_F	n_F	R^2	$MPSD$	χ^2	
25	0.047	0.019	0.096	0.989	13.61	0.004	0.004	2.349	0.959	14.91	0.008	
40	0.051	0.031	0.060	0.994	16.22	0.005	0.008	3.303	0.974	7.75	0.002	
50	0.054	0.031	0.060	0.989	21.02	0.009	0.010	3.578	0.974	5.29	0.001	
60	0.064	0.037	0.052	0.995	19.32	0.009	0.011	3.341	0.972	8.37	0.003	

and solid phases became stronger as the initial dye concentration increased; also, the number of collisions between the dye and CDP increased as the initial dye concentration increased. These two factors helped to increase the adsorption process (Aksu and Karabayır, 2008). The percentage dye removal, however, decreased as the initial dye increased for all temperatures. This is due to decrease in availability of vacant sites on CDP which became saturated with AB25 as its concentration increased.

In this work, the experimental data were fitted into two well-known isotherm models namely the Langmuir and Freundlich models. The Langmuir isotherm (Langmuir, 1916) assumes that the adsorption is monolayer and takes place at specific homogeneous sites on the adsorbent, where no further adsorption can occur when a site is occupied with adsorbate. The linear equation is presented by equation (10):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (10)$$

where q_{max} is the maximum monolayer adsorption capacity of the adsorbent (mmol g^{-1}), K_L is the Langmuir adsorption constant (L mg^{-1}) which is related to the free energy of adsorption and C_e (mg L^{-1}) is the equilibrium dye concentration.

The separation factor (R_L) is a dimensionless constant which is an essential indication of the Langmuir model (Weber and Chakravorti, 1974). It is given by the following equation,

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (11)$$

where C_0 (mg L^{-1}) is the highest initial dye concentration, and R_L indicates whether the Langmuir isotherm is either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (McKay et al., 1982).

The Freundlich isotherm (Freundlich, 1906) model, unlike the Langmuir isotherm, takes account of multilayer coverage where adsorption is still possible

on the adsorbate-saturated adsorbent's surface. It is applicable for adsorption on heterogeneous with surfaces reversible adsorption and uniform energy distribution. The linear equation is presented as follows:

$$\ln q_e = \frac{1}{n_F} \ln C_e + \ln K_F \quad (12)$$

where K_F [$\text{mmol g}^{-1} (\text{L mmol}^{-1})^{1/n}$] is the adsorption capacity of the adsorbent while n_F indicates favourability of the adsorption process (adsorption intensity) or surface heterogeneity where n_F value between 1 and 10 represents favourable adsorption.

In order to choose which of these isotherm models fit the experimental data the best, three factors were considered: R^2 value, error analysis and simulated non-linear adsorption isotherm. Comparing the R^2 values between Langmuir and Freundlich at different temperatures, the former has better R^2 values (> 0.98) while error analyses showed that generally the Freundlich model has smaller error values for all temperatures except for adsorption at 20°C (Table 1). Comparison of non-linear regression between the experimental data and the simulated isotherm models at different temperatures, shown in Figure 2 (B to E), indicate that generally the Langmuir model can be seen to have closer plots with that of the experimental data when compared to the Freundlich model. Based on these three comparisons, it can be said that overall the Langmuir isotherm model describes the experimental data better than Freundlich isotherm model. Both R_L and n_F values obtained from both isotherm models indicate that the removal of AB25 by CDP is a favourable process.

Thermodynamics study can be used to evaluate the feasibility of an adsorption process. The parameters i.e. Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K \quad (13)$$

$$K = \frac{C_e}{C_0} \quad (14)$$

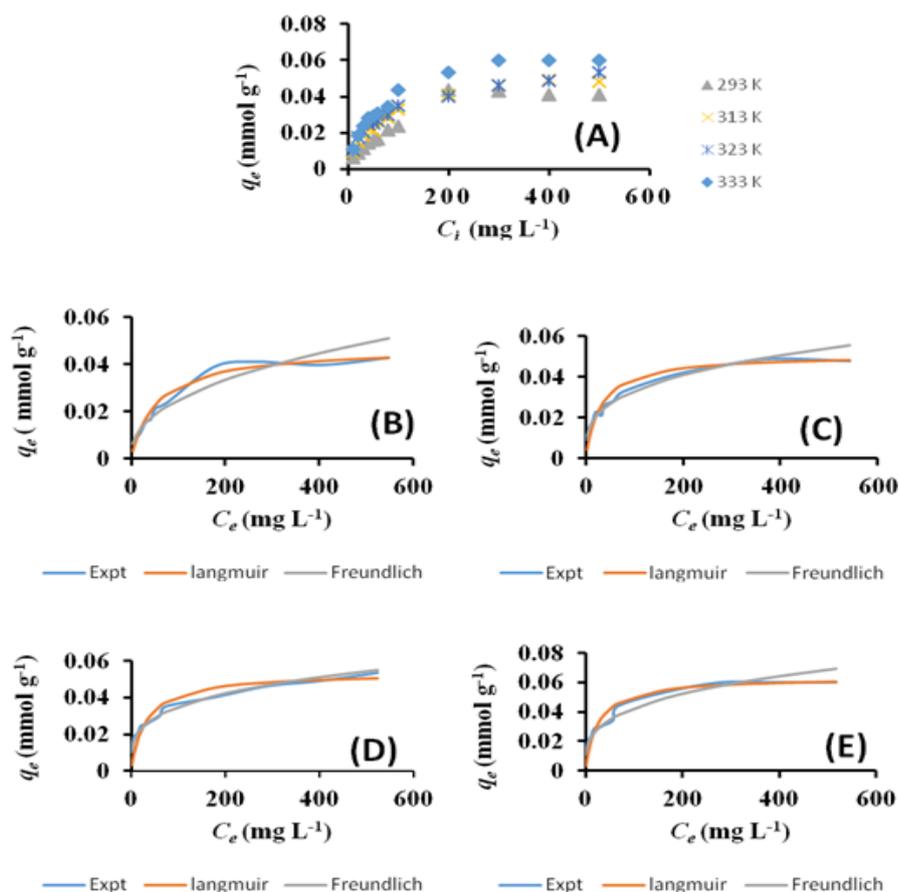


Figure 2. (A) Adsorption of different initial concentrations of AB25 at different temperatures by CDP (AB25 concentration = 10 – 500 mg L⁻¹; volume = 20.0 mL; CDP's mass = 0.04 g; agitation time = 2 h; agitation speed = 250 rpm; temperature = 298 – 333 K) and comparison of the non-linear regression of experimental data with Langmuir and Freundlich isotherm models at (B) 298 K (C) 313 K (D) 323 K and (E) 333K

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (15)$$

By inserting Equation (13) into Equation (15), the following equation is obtained:

$$\ln K = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (16)$$

where K is the distribution coefficient for adsorption, C_s is the equilibrium dye concentration adsorbed (mg L⁻¹), C_e is the equilibrium dye concentration remaining in solution (mg L⁻¹), R is the gas constant (J mol⁻¹ K⁻¹) and T is the temperature (K).

Thermodynamics studies, carried out at temperatures of 298 K, 313 K, 323 K and 333K, showed that the adsorption capacities increased as temperature increased (Figure 2A) indicating the adsorption process in this study was endothermic in nature. A plot of $\ln K$ versus T^{-1} (figure not shown) revealed that the ΔG° values became more negative as temperature raised which indicated that the reaction was more spontaneous and feasible at higher temperature. The positive ΔH° (4.01 kJ

mol⁻¹) confirmed that the adsorption process was endothermic in nature while positive ΔS° (73.86 J mol⁻¹ K⁻¹) reflected good affinity of the AB25 toward CDP.

Being endothermic in nature, the maximum adsorption capacity, q_{max} , increased with increasing temperature with $q_{max} = 0.065$ mmol g⁻¹ (26.62 mg g⁻¹) at 60°C (333K). This value is comparable with q_{max} values obtained from other studies on the removal of AB25 using *Shorea dasphylla* sawdust and diatomite but lower than *Aspergillus oryzae*, *Penicillium* YW 01 and waste tea activated carbon (Table 2).

Regeneration study

Regeneration study is a useful tool in order to evaluate an adsorbent's reusability in removing pollutants. Adsorbents that can be regenerated and reused to remove pollutant is of great advantage as it will reduce material cost as well as less wastage of the material. Recovered pollutant especially heavy metals can be purified and reused while other non-reusable pollutant can be stored safely. Three

Table 2. The q_{max} values of the removal of AB25 by various adsorbents in literature

Adsorbent	q_{max} (mg g ⁻¹)	Reference
<i>Aspergillus oryzae</i>	105.30	(Yang et al., 2011a)
CDAB modified <i>Aspergillus oryzae</i>	160.39	(Yang et al., 2011a)
Waste tea activated carbon	203.34	(Auta and Hameed, 2011)
<i>Shorea dasyphylla</i> sawdust	24.39	(Hanafiah et al., 2012)
Diatomite	21.41	(Badii et al., 2010)
Unmodified <i>Penicillium</i> YW 01	88.33	(Yang et al., 2011b)
Cempedak durian (<i>Artocarpus spp.</i>) at 25°C	19.57	This work
40°C	21.24	This work
50°C	22.48	This work
60°C	26.62	This work

washing solutions: distilled water, 0.1 M HNO₃ and 0.1 M NaOH were used and their capabilities to regenerate CDP. Originally, CDP was able to remove around 24% of 100 mg L⁻¹ AB25 and it was observed that only 0.1 M NaOH gave satisfactory results in regenerating CDP as the removing capability of CDP was still close to the original even after five cycles. 0.1 M HNO₃ treatment was the worst of all three solutions, this might be due to the re-adsorption of AB25 onto CDP instead of leaching it out. The re-adsorption was to be expected as the adsorption of AB25 onto CDP was highly favoured in acidic medium.

Fourier Transform Infrared (FTIR) spectroscopy

The infrared spectra of CDP before and after treatment with AB25 dye were analyzed and shown in Figure 3. The broad absorption peaks around 3385 cm⁻¹ were due to vibration of the O-H and N-H groups. The peak observed at 2924 cm⁻¹ was assigned as the stretching vibration of C-H group. The peak located at 1732 cm⁻¹ was characteristic of C=O group. The C-O stretching band at 1242 cm⁻¹ confirmed the lignin structure of the adsorbent (Gupta et al., 2011). The peak around 1060 cm⁻¹ was due to C-O-C stretching and O-H bending of the lignin (Han et al., 2011). After treatment with the dye, the bands at 3385 and 1732 cm⁻¹ were shifted to 3336 and 1728 cm⁻¹, respectively. This result suggests that these functional groups may be involved in the adsorption process.

Conclusion

Adsorption of AB25 onto DFP was investigated based on batch experimental data. The adsorption was highly effective in acid medium (pH 2) and the equilibrium contact time was determined at 120 minutes. Adsorption isotherm study showed that the

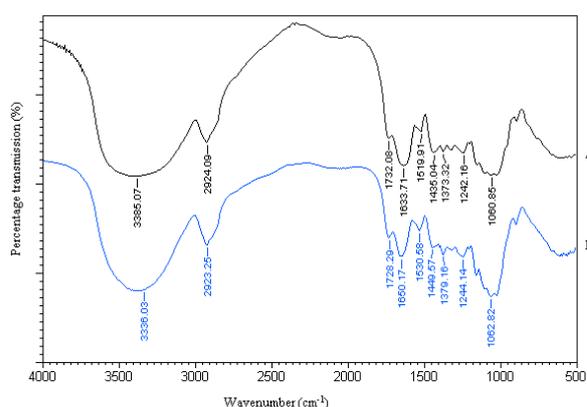


Figure 3. FTIR spectra for (A) untreated CDP and (B) after adsorption with AB25

Langmuir isotherm model best fitted the experimental data with maximum adsorption capacity, q_{max} , of 0.064 mmol g⁻¹ at 60°C. Pseudo 2nd order model was the best fit of the experimental data indicating the adsorption process is chemical in nature. Results from Weber-Morris intraparticle diffusion and Boyd models suggested that intraparticle diffusion was not the rate-limiting step and film diffusion might be majorly involved in the diffusion mechanism. The adsorption process was feasible at high temperature and endothermic in nature. Regeneration study showed that washing with 0.1 M NaOH not only was able to regenerate CDP ability to remove AB25 but maintained its performance up to five cycles. This study shows that CDP has the potential to be used as a low-cost biosorbent as it does not require a long contact time and adsorption of AB25 can be done at acidic conditions which is advantageous since acid dye wastewater is usually low pH.

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