

Dragon fruit skin as a potential biosorbent for the removal of methylene blue dye from aqueous solution

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Abstract

Dragon fruit skin (DFS) was investigated for its potential in the removal of methylene blue (MB) from aqueous solution. Effects of contact time, initial concentration and pH medium were investigated. Adsorption isotherm studies were also carried out. Three isotherm models, namely the Langmuir, Freundlich and Tempkin models, were used to predict the behaviour of the adsorption process. Adsorption equilibrium for the removal of MB was achieved in a relatively short time and the batch experiments were done without any pH adjustment. The experimental data fitted the Langmuir Type II adsorption isotherm with a high maximum adsorption capacity (q_{max}) of 640 mg g⁻¹, which is superior for the removal of MB compared to most reported biosorbents. Kinetics studies were found to follow the pseudo-second order model and intraparticle diffusion is involved but not as the rate-determining step.

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Introduction

Industrial development has been taking place at a significant rate in order to expand production to meet the demand of ever increasing population. Volumes of industrial effluents and types of pollutants present in effluents have increased significantly. Among many industries, textile and garment industries use a large number of dyes and other additives during the colouring process (Wang *et al.*, 2002), some of which are added to the effluents without proper treatment. Since the introduction of the first two synthetic dyes to the market in 1856, synthetic dyes have received wide applicability due to their easy usage, reproducibility and irreversible colouring process. The applicability was challenged about a decade ago when toxicological effects of synthetic dyes became known. Another alarming aspect is that some industrial dyes undergo degradation producing more toxic substances, including carcinogens (Ratna and Padhi, 2012). As it is not practicable to reverse to the use of synthetic dyes, it is therefore important to employ effective and environmentally friendly methods for treatment of effluents containing dyes.

Methylene Blue (MB) is a cationic dye which forms face-to-face dimers in dilute solutions, and aggregates at high concentrations (Cenens and Schoonheydt, 1988). This dye is sensitive to changes

in polarity in the surrounding environment. It is used in textile industry as well as in medicinal purposes. MB is a component of a frequently prescribed urinary analgesic/anti-infective/anti-spasmodic drug as well as able to donate or accept protons demonstrating its redox properties (Galagan and Su, 2008). Some of these properties/reactivities are important to design treatment methodologies for MB.

Amongst available and accepted methods to remove MB, chemical treatment (Gong *et al.*, 2008), Fenton process (Liu *et al.*, 2013), ozonation (Valdés *et al.*, 2012), photocatalytic degradation using UV/TiO₂ (Ehrampoush *et al.*, 2010), biodegradation (Ong *et al.*, 2005) and electrochemical degradation (Panizza *et al.*, 2007) have been commonly used. Recently, biosorption has shown potential as an alternative to remove dyes from aqueous bodies. It is also attractive in terms of availability, low-cost and environmental friendliness. Biosorbents including fruit wastes (Lim *et al.*, 2015a, Chieng *et al.*, 2015a), peat (Chieng *et al.*, 2015b, Zehra *et al.*, 2015), walnut shell (Dahri *et al.*, 2014), plant materials (Dahri *et al.*, 2013, Kooh *et al.*, 2015) have been successfully used for the removal of dyes.

As biosorption is carried out by biological materials of different origins, equilibrium and kinetics aspects of removal vary depending on the type of adsorbent and also on experimental conditions employed. For

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instance, it has been reported that the capacity of removal of MB by modified polysaccharide, mango seed kernel powder and rice husk from solutions of pH = 8 at temperatures in the range from 25 to 32°C are 48, 143 and 41 mg g⁻¹, respectively (Kumar and Kumaran, 2005, Vadivelan and Kumar, 2005, Paulino *et al.*, 2006). Further, adsorption of MB follows the Langmuir adsorption isotherm on many adsorbents, indicating that multilayer coverage is unlikely (Mohammed *et al.*, 2014).

This study focuses on the use of dragon fruit skin (DFS) as a potential low-cost biosorbent for the removal of MB. Reports have shown that the average yield of dragon fruits from commercial plantations in Israel, Malaysia and Taiwan is between 16,000 – 27,000 kg/ha annually while between 18,000 – 22,000 kg/ha of fruits per year have been produced from Sri Lanka (Mizrahi and Nerd, 1996, Mizrahi and Nerd, 1999, Pushpakumara *et al.*, 2005). In Brunei Darussalam, the red-flesh dragon fruits (*Hylocereus costaricensis* also known as *Hylocereus polyrhizus*) are more popular than the white-flesh fruit. The skin is usually discarded as waste, and as such is of no economic value. It has been reported that the skin has the ability to remove Mn²⁺ from aqueous solution (Priyantha *et al.*, 2013) while the fruit (*Hylocereus undatus*) foliage has been used for methyl orange dye removal (Haddadian *et al.*, 2013). To date, to the best of our knowledge, no study on the use of DFS for the removal of MB has been reported. This study would therefore provide an environmentally friendly method to remove MB from wastewater, which can be extended to remove other industrial dyes as well.

Materials and Methods

Materials

Dragon fruit was randomly purchased from a bulk from local supermarkets. The skin of the fruit was removed and dried in an oven at 85°C until a constant mass was obtained. The dried sample was then blended and sieved to obtain particles of diameter ranging from 355 µm to 850 µm.

Chemicals and reagents

Methylene blue (C₁₆H₁₈N₃SCl; Mr = 319.85 g mol⁻¹) was purchased from Sigma Aldrich. 1.0 M NaOH (Univar) and 1.0 M HNO₃ (AnalaR) were used to adjust the pH of the solutions. Spectroscopic grade KBr was used for Fourier transform infrared (FTIR) spectroscopy analysis. All reagents were used without further purification. Double distilled water was used throughout the study.

Instrumentation

Determination of the concentration of MB in solution was performed through absorbance measurements using Shimadzu UV-1601PC UV-Visible (UV-Vis) spectrophotometer at the λ_{max} of 664 nm. Shimadzu IR Prestige-21 spectrophotometer was used for DFS's functional groups analyses, while surface images were recorded using Tescan Vega XMU Scanning Electron Microscope (SEM). The experimental temperature was maintained at the ambient value of (24 ± 1)°C throughout.

Preparation of stock solutions

A stock solution of MB of 1000 mg L⁻¹ was prepared, and appropriately diluted to required concentrations to prepare calibration standards.

Effect of contact time

A mixture of 50.0 mL of 10 mg L⁻¹ dye solution and 0.10 g of DFS was agitated at 250 rpm at ambient temperature. Samples of solutions were taken at fixed time intervals from 0 - 240 min, and the concentration of MB in the filtrate of each solution was determined to obtain the optimum contact time. The amount of MB being absorbed by DFS, q_e (mmol g⁻¹), was calculated as follows:

$$q_e (\text{mmol g}^{-1}) = (C_i - C_f) \frac{V}{mM} \quad (1)$$

where C_i and C_f are the initial and final dye concentrations (mg L⁻¹) respectively, m is the mass of biosorbent used (g), M is the molar mass of MB (g mol⁻¹) and V is the volume of adsorbent used (L).

Percentage removal of MB was calculated as follows:

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

Effect of pH

The pH of 10 mg L⁻¹ MB solution was adjusted using 1.0 M HNO₃ and 1.0 M NaOH to the pH range of 2.0 - 8.0. An aliquot of 50.0 mL of the pH adjusted solution was then mixed with 0.10 g DFS, and agitated at 250 rpm. The MB content of the filtrate was thus determined. Higher concentrations of MB were not attempted as typical concentration levels of MB used in industries are probably below this level.

Effect of initial concentration on adsorption

A sample of 0.10 g of biosorbent was added to 50.0 mL of MB solutions of different concentrations ranging from 10 mg L⁻¹ to 1000 mg L⁻¹. The mixtures were agitated at 250 rpm at ambient temperature and allowed to settle until the equilibrium was reached.

Each mixture was then gravity filtered, and the filtrate was analysed for the MB content. The variation of the extent of removal of MB with the initial concentration was studied in order to understand the adsorption patterns, while the relationship with the equilibrium concentration was used to fit experimental data to adsorption isotherms.

Results and Discussion

Effect of contact time on adsorption of MB by DFS

Contact time is an important parameter in order to determine the time for the adsorption to reach equilibrium. The effect of shaking time on adsorption of 10 mg L⁻¹ MB by DFS showed the uptake of MB by the biosorbent was very rapid initially and becomes constant within 1 h indicating that equilibrium has been reached. Although the equilibrium was reached fast, the contact time used for the rest of the study was set at 2 h to ensure complete equilibrium. Compared to other biosorbents such as yellow passion fruit peel (Pavan *et al.*, 2008), jackfruit peel (Hameed, 2009) and its activated form (Prahas *et al.*, 2008) which required more than 3 h, it is observed that the optimum contact time for DFS is relatively short. This is especially important in real application of wastewater treatment where fast equilibrium would be favourable for cost-effective and economical approaches.

Kinetics studies

Kinetics studies are useful not only for determination of the equilibrium time of an adsorption process but also for designing treatment systems that depend on reaction rate. Three kinetics models namely Lagergren first order, pseudo-second order and Weber-Morris intraparticle diffusion order models were used to describe the adsorption process (Chmielewska *et al.*, 2013). The kinetics models are given by:

Lagergren first order model,

$$\log(q_e - q_t) = \log q_e - \frac{t}{2.303} k_1 \quad (3)$$

Pseudo-second order model,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Weber-Morris intraparticle diffusion model,

$$q_t = k_3 t^{1/2} + C \quad (5)$$

where q_t is the amount of dye adsorbed per unit of adsorbent (mmol g⁻¹) at time t , q_e is the adsorption capacity at equilibrium (mmol g⁻¹), k_1 is the pseudo-

Table 1. Parameter values of Lagergren first order, pseudo-second order and intraparticle diffusion models

Kinetics model	Parameter	Value	q_e (expt)
Lagergren 1st order	q_e (mmol g ⁻¹)	0.969	0.012
	k_1 (min ⁻¹)	6.008	
	R^2	0.808	
Pseudo 2nd order	q_e (mmol g ⁻¹)	0.011	0.012
	k_2 (g mmol ⁻¹ min ⁻¹)	84.894	
	R^2	0.996	
Intraparticle diffusion	k_3 (mmol g ⁻¹ min ^{-1/2})	0.0005	
	C	0.008	
	R^2	0.512	

first order rate constant (min⁻¹), and t is the time shaken (min), k_2 is pseudo-second order rate constant (g mmol⁻¹ min⁻¹) and k_3 is the intraparticle diffusion rate constant (mmol g⁻¹ min^{-1/2}) while C represents the thickness of the boundary layer.

Often the value of q_e is unknown and as adsorption tends to become very slow, the amount adsorbed is still significantly smaller than the equilibrium amount. Hence, it is necessary to obtain q_e , by extrapolating the experimental data to $t = \infty$ or by trial and error method (Aksu and Dönmez, 2003).

From Table 1, it shows that the pseudo-second order model has higher R^2 (0.996) than that of first order model (0.808). Furthermore, the value of q_e calculated from pseudo-second order (0.011 mmol g⁻¹) is closer to the value of q_e from experiment (0.012 mmol g⁻¹), while q_e calculated from pseudo-first order was 0.969 mmol g⁻¹. This clearly indicates that the mechanism follows the pseudo-second order model which assumes chemisorption involving in the exchange or sharing of electrons between the dye and functional groups of the biosorbent.

Weber-Morris intraparticle diffusion model is used to determine the diffusion mechanism of the process as the Lagergren first order and pseudo-second order models cannot do so. A plot of q_t vs $t^{1/2}$ that gives straight line indicates that the intraparticle diffusion is involved in the process and furthermore, if the line passes through the origin, intraparticle diffusion is the rate determining step in the reaction (Aly *et al.*, 2014). In this study, the linear plot of Weber-Morris intraparticle diffusion model showed a straight line that does not pass through the origin thereby indicating that intraparticle diffusion is involved in the process but is not the rate determining step.

Effect of pH on adsorption of MB by DFS

The effect of pH on the sorption of MB by DFS

Table 2. Parameters for all isotherm models

Isotherm model	Parameter	Value
Langmuir Type I	q_{max} (mmol g ⁻¹)	1.950
	b (L mg ⁻¹)	0.004
	R^2	0.631
Langmuir Type II	q_{max} (mmol g ⁻¹)	2.000
	b (L mg ⁻¹)	0.004
	R^2	0.972
Langmuir Type III	q_{max} (mmol g ⁻¹)	0.008
	b (L mg ⁻¹)	1.139
	R^2	0.448
Langmuir Type IV	q_{max} (mmol g ⁻¹)	0.004
	b (L mg ⁻¹)	2.110
	R^2	0.448
Freundlich	K_F (mmol g ⁻¹ (L mmol ⁻¹) ^{1/n})	0.009
	n	1.140
	R^2	0.954
Tempkin	K_T (L mmol ⁻¹)	0.180
	b_T	10790
	R^2	0.934

showed that minimal sorption was observed at pH 2. In strong acidic medium, there is an increase in positive charge on the biosorbent's surface, leading to electronic repulsion between the cationic MB dye and the surface of DFS. Further, high concentration of H⁺ would compete with MB for the same sorption sites. At pH 3, the dye uptake improved but declined beyond pH 5, probably due to the competition for cationic species present in the system with MB. Nevertheless, as the highest uptake was observed for ambient conditions which had a pH of 4.7, further experiments were conducted without any pH adjustment.

Effect of concentration on adsorption

The amount of MB adsorbed per gram of DFS increases with increasing initial dye concentration, as shown in Figure 1, with the levelling of the dye removal at higher concentrations. The point at which the extent of removal is saturated corresponds to the monolayer coverage. The shape of the variation of the amount of MB adsorbed with initial MB concentration corresponds to the Langmuir isotherm. For better understanding of the adsorption system, adsorption isotherm modelling was conducted.

Adsorption isotherm is used to describe the interactions of adsorbate with adsorbent at equilibrium. Adsorption equilibrium data in this study were modelled with three isotherm models: Langmuir (four linearized expressions) (Langmuir, 1918), Freundlich (Freundlich, 1906) and Tempkin (Tempkin and Pyzhev, 1940) models. The non-linear and linearized equations for all three isotherm models are shown in equations below.

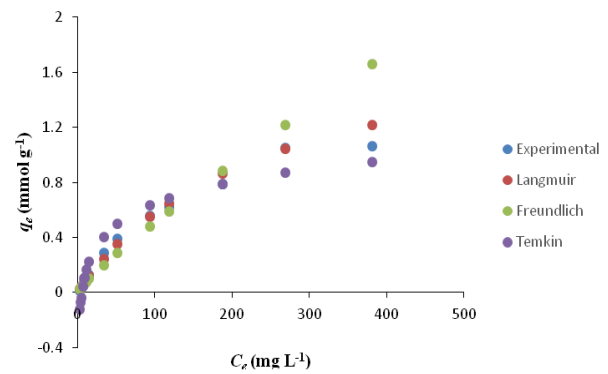


Figure 1. Comparison of experimental adsorption data with simulated Langmuir, Freundlich and Tempkin isotherm models

Langmuir equations:

Non-linear

$$q_e = \frac{q_{max} K_L C_e}{(1 + K_L C_e)} \quad (6)$$

Linear

Type I

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (7)$$

Type II

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}} \quad (8)$$

Type III

$$q_e = q_{max} - \frac{q_e}{K_L C_e} \quad (9)$$

Type IV

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

Freundlich equations:

Non-linear

$$q_e = K_F C_e^{1/n} \quad (11)$$

Linear

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

Tempkin equations:

Non-linear

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad (13)$$

Linear

$$q_e = \frac{RT}{b_T} \ln C_e + \frac{RT}{b_T} \ln K_T \quad (14)$$

where C_e is the equilibrium adsorbate concentration in solution (mg L⁻¹), q_{max} is the monolayer maximum

Table 3. Comparison between q_{max} obtained in this work and that of literature

Biosorbent	q_{max} (mg g ⁻¹)	Reference
Dragon fruit skin	640.0	This work
Activated <i>Ficus carica</i> bast	47.6	(Pathania et al., 2013)
<i>Gelidium sesquipedale</i>	171.0	(Vilar et al., 2008)
Potato leaf	52.6	(Gupta et al., 2011)
<i>Artocarpus odoratissimus</i> skin	185.0	(Lim et al., 2015b)
Peat	111.0	(Lim et al., 2013a)
Peat	143.9	(Chieng et al., 2014)
<i>Haloxylon recurvum</i> stem	22.9	(Hassan et al., 2013)
<i>Amona squamosa</i>	25.9	(Santhi et al., 2010)
Yellow passion fruit peel	2.2	(Pavan et al., 2008)
Ground palm kernel coat	277.0	(Oladoja et al., 2008)
Breadnut peel	409.0	(Lim et al., 2013b)
Breadnut core	369.0	(Lim et al., 2015c)

adsorption capacity (mmol g⁻¹), K_L is the Langmuir adsorption constant (L mg⁻¹) related with the free energy of adsorption, K_F [mmol g⁻¹ (L mmol⁻¹)^{1/n}] is the adsorption capacity, n gives indication of how favourable the adsorption process (adsorption intensity) or surface heterogeneity. K_t is equilibrium binding constant (L mmol⁻¹), b_T is Tempkin constant, R is the gas constant (J K⁻¹ mol⁻¹) and T is the room temperature (K).

The Langmuir isotherm assumed that the process takes place at specific homogeneous sites within the biomass. The Freundlich isotherm assumed that the process takes place at heterogeneous sites within the biomass while the Tempkin isotherm assumes a linear decrease in the fall in the heat of sorption due to adsorbate-adsorbate interaction.

Table 2 shows the parameters for each of the isotherm model. Langmuir Type II equation has the highest coefficient of correlation ($R^2 = 0.9718$) value and therefore provides a better fit for the experimental data of MB on DFS. This is further supported by comparing the simulated isotherm models with the experimental data as shown in Figure 1. It can be seen that the Langmuir model is the closest to the experimental data amongst all the three models used. The Langmuir isotherm model assumes that adsorption occurs as a monolayer which is supported by experimental data plot in Figure 1 which shows the adsorption of MB does not continue for a multilayer.

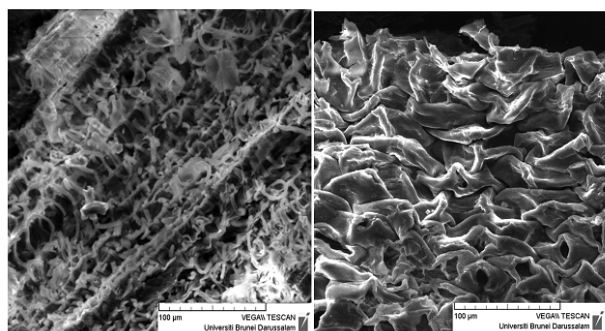


Figure 2. The SEM image of untreated dragon fruit skin (left) and MB-loaded DFS (right) with 1000x magnification

Dimensionless separation factor (R_L) is an essential characteristic of the Langmuir model and given by the following equation,

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

where C_0 (mg L⁻¹) is the highest initial concentration of adsorbate and K_L (L mg⁻¹) is the Langmuir constant. R_L indicates whether the isotherm is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Adsorption of MB by dragon fruit skin yields R_L value of 0.2, indicating that the process is favourable. The parameter n obtained from the Freundlich model also indicates the similar property as R_L value, where in this case any value between $1 < n < 10$ is considered to be a favourable process. In this study, the n value was found to be 1.14, and therefore the adsorption process is favourable.

The maximum adsorption capacity, q_{max} , of DFS for the removal of MB is 2.00 mmol g⁻¹ (639.70 mg g⁻¹). This value is much higher when compared to many other biosorbents reported (Table 3). This therefore shows the superiority of DFS as a potential low-cost biosorbent for adsorption of MB in the treatment of wastewater.

Fourier transformed infrared (FTIR) spectroscopy

The infrared spectra of DFS before and after treatment with MB dye were analyzed. The broad absorption peaks around 3400 cm⁻¹ is due to vibration of the O-H and N-H groups. The peak observed at 2926 cm⁻¹ is assigned to the stretching vibration of C-H group. The peak located at 1637 cm⁻¹ is characteristics of C=O group. The peak around 1373 cm⁻¹ is due to bending vibration of C-H group. The C-O stretching band at 1244 cm⁻¹ confirms the lignin structure of the adsorbent (Gupta et al., 2011). The peak around 1049 cm⁻¹ is due to C-O-C stretching and O-H bending of the lignin (Han et al., 2011). After treatment with MB, the bands at 1637, 1244 and 1049 cm⁻¹ were shifted to 1629, 1246 and 1060 cm⁻¹, respectively. This result suggests that these

functional groups may be involved in the adsorption process.

Scanning Electron Microscope (SEM)

Figure 2 shows SEM images of DFS before and after treatment with MB. The surface of DFS appears rough and consists of many holes and cavities with curly strands of fibrous-like materials arranged in rows. Upon adsorption with MB, holes and cavities are clearly seen to be covered with dye molecules and as a result, the surface became smoother.

Conclusion

The heterogeneous system comprising of dried and powdered dragon fruit skin (DFS) and aqueous MB solution reaches adsorption equilibrium within 60 min. The adsorption is most efficient at ambient pH of 4.7. The MB molecules cover the surface of DFS effectively completing a monolayer fulfilling the requirements of the Langmuir adsorption isotherm, where the plot of reciprocal adsorbed amount vs reciprocal equilibrium leads to the best fit with a high regression coefficient of 0.972. This model results in a maximum adsorption capacity of 640 mg g⁻¹, demonstrating the superior nature of DFS as compared to many other biosorbents. Hence, this study shows that dragon fruit skin has a great potential to be used as a low-cost biosorbent for the removal of toxic dye, methylene blue.

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