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# Utilizing *Artocarpus altilis* (breadfruit) skin for the removal of malachite green: isotherm, kinetics, regeneration, and column studies

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#### ABSTRACT

Tropical fruit waste, breadfruit skin (BS), demonstrates great potential as a low-cost adsorbent for the removal of toxic malachite green (MG) dye. The optimum values of shaking time, settling time, and pH for the interaction of MG on BS are determined to be 3.5 h, 1 h, and pH 4.58, respectively. Further, adsorption of MG by BS is ionic strength dependent. Six isotherm models analyzed using adsorption equilibrium data indicate that the MG–BS adsorbate–adsorbent system can be best described by the Langmuir model with the maximum adsorption capacity ( $q_{max}$ ) of 55.2 mg g<sup>-1</sup>, which is further confirmed by six different error functions. This adsorption system follows the pseudo-second-order kinetics, and the intraparticle diffusion could be the rate-determining step. Regeneration studies using NaOH washing illustrate the ability of BS to retain its high adsorption capacity of >90% even after 5 consecutive cycles. Column study reveals that more than 1,200 mL of 100 mg L<sup>-1</sup> MG solution can be introduced to the column for up to 95% dye removal.

Keywords: Artocarpus altilis (Breadfruit); Adsorption isotherm; Malachite green dye; Kinetics; Regeneration

## 1. Introduction

Rapid development of the industrial sector results in an increase in environmental pollution as many industries discard and discharge different types of waste into air and water systems. In many instances, waste is chemical in nature, which would contain toxic materials, such as dyes and heavy metals. It has been reported that some dyes at concentrations as low as 1 mg L<sup>-1</sup> is highly visible, toxic, and mutagenic [1,2]. A survey conducted by Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) reported that about 4,000 dyes have  $LD_{50}$  values greater than 2,000 mg kg<sup>-1</sup>, showing the necessity of removing dyes from wastewater [3].

Various physical and chemical techniques are in use in the treatment of the dye effluents. Even though techniques, such as chemical precipitation, coagulation, filtration, and electrodialysis, are efficient, these methods not only produce large amounts of sludge but also they are not economical. A more economical method is the use of adsorption which has been gaining popularity in the past decade. Various adsorbents have been investigated for their ability to adsorb

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pollutants and these include peat [4–7], fruit wastes [8–10], plant materials [11,12], industrial waste [13], and many others [14–17].

This study focuses on the use of *Artocarpus altilis* (breadfruit), locally known as Sukun, to evaluate its potential for the removal of malachite green (MG) dye from aqueous solution. Breadfruit is a more edible popular fruit from the *Artocarpus* family. Generally, the skin of *Artocarpus* fruits has no economical use and is discarded as a waste [18,19]. MG, with  $LC_{50}$  of 80 mg kg<sup>-1</sup> when tested against mouse, is classified as a Class II health hazard toxic dye and is found to be a tumor promoter. Although it was traditionally used to dye silk, leather, and paper, its main use at present is in aquaculture as a therapeutic agent. Eating fish contaminated with MG can have adverse health effects [2].

Various studies showed that Artocarpus waste, such as skin and core, has been successfully used to adsorb heavy metals and dyes. For example, A. odaratissimus core and skin have been utilized in the adsorption of Cu(II)/Cd(II) and dyes, respectively [20,21]. It has been reported that A. altilis skin leads to high adsorption capacity toward crystal violet dye [22] as compared to many other adsorbents, including acid/base modified adsorbents. A. altilis skin and core were also shown to have great affinity toward Cd(II) and Cu(II) [23], while A. camansi skin was successfully used as a low-cost biosorbent for the removal of dyes [24]. As an extension to our previous research, this study investigates the potential use of A. altilis skin as a low-cost adsorbent for the removal of toxic MG dye. To the best of our knowledge, such studies have not been previously reported. Effect of contact time, pH, ionic strength, and dosage on the extent of removal was carried out to optimize parameters for the highest efficiency of the process. Kinetics and equilibrium studies of MG removal were also elaborated under optimized conditions. Furthermore, the regeneration ability and column study of BS were also investigated.

## 2. Materials and methods

# 2.1. Sample preparation and chemicals

Stock solutions of MG of  $1,000 \text{ mg L}^{-1}$  were prepared by dissolving MG,  $C_{23}H_{25}N_2 \cdot C_2HO_4 \cdot 0.5C_2H_2O_4$ (Sigma–Aldrich) in double distilled water. Solutions of different pH were prepared using NaOH (Univar) and HNO<sub>3</sub> (AnalaR). Breadfruit samples were randomly purchased from the local market in Brunei Darussalam. The breadfruit skin (BS) was separated from the fruit and oven dried at 80 °C until a constant mass was obtained. This temperature was chosen as lower temperatures resulted in turbid solutions, while charring occurred at higher temperatures. Dried BS was then blended and sieved to obtain the fraction of particle sizes of  $355-850 \,\mu\text{m}$  as previously used [22]. All experiments were carried out in duplicate with adsorbent/solution ratio of 1:500.

## 2.2. Instrumentation

Shimadzu UV-1601PC UV-visible (UV-vis) spectrophotometer used for absorbance was measurements of absorbance of MG solutions at  $\lambda_{max}$ of 618.0 nm for the determination of the concentration of MG. Functional group and elemental analyses were performed using Shimadzu Model IRPrestige-21 FTIR spectrophotometer and X-ray fluorescence spectrophotometer (PANalytical Axios<sup>max</sup>), (XRF) respectively.

#### 2.3. Adsorption experiments

The effect of dosage on the removal of MG was conducted by mixing different dosages (0.050, 0.100, 0.200, 0.400, 0.600, 0.800, and 1.00 g) of BS samples with 100 mg  $L^{-1}$  MG solution of a fixed volume (25.0 mL) and agitated on an orbital shaker at a rate of 250 rpm. This is to determine the suitable dosage for the adsorption of MG.

All experiments were done by agitation of BS sample (0.050 g) in 25.0 mL of MG solution on an electric shaker set at a rate of 250 rpm at ambient temperature, unless otherwise stated. The solution mixture was separated using a metal sieve and the filtrate was analyzed using UV–vis spectrophotometer.

Investigation of shaking time required to reach equilibrium was carried out by analyzing filtrates at fixed time interval between 30 and 240 min. Once the shaking time has been determined, similar procedure was done for settling time where the mixture was allowed to stand after optimum agitation time and taken at fixed time interval.

Effect of pH was conducted by adjusting the pH of 10 mg  $L^{-1}$  MG solution using 0.1 M NaOH or 0.1 M HNO<sub>3</sub> to the pH range of 2–10. Adsorption isotherm was investigated with MG solutions of concentration ranging from 10 to 1,000 mg  $L^{-1}$ . Kinetics was carried out by agitating 0.050 g of BS with 100 mg  $L^{-1}$  MG solution. Dye solutions were withdrawn at every 1 min interval until equilibrium was reached. The effect of ionic strength was conducted by mixing the MG solution with KNO<sub>3</sub> solutions of various concentrations (0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 M).

## 2.4. Regeneration studies

Regeneration studies were conducted by mixing BS (0.050 g) with 100-mg L<sup>-1</sup> MG solution. The BS–MG-treated samples were then desorbed with 25.0 mL of distilled water, 0.1 M NaOH, and 0.1 M HCl. The amount of MG adsorbed at various cycles was analyzed and recorded.

# 2.5. Column studies

Columns of internal diameter (i.d.) 2.0 cm were closely packed manually with dried BS particles of diameter  $850 < d < 355 \ \mu\text{m}$  up to a length of 3 inches (7.6 cm). All 25.0-mL aliquots of 100-mg L<sup>-1</sup> MG solution were passed through at a flow rate of 2.5 mL min<sup>-1</sup>. The concentration of MG in the eluent was analyzed, and the experiment was continued until the concentration of MG fell below 80% of the initial concentration used.

# 3. Results and discussion

## 3.1. Effect of contact time on MG removal

An important parameter in adsorption studies is the contact time as it provides crucial information on the optimum time taken for the system to reach equilibrium. In this study, a rapid uptake of MG within the first 30 min, as shown in Fig. 1, was observed. This can be attributed to the initial availability of many vacant sites on the surface of BS for MG to be adsorbed which would then become saturated when sufficient contact time is allowed. The removal of MG reaches its maximum at 3.5 h, as indicated by observing a plateau in the figure. Therefore, the shaking time was taken as 3.5 h. Having determined the optimum shaking time, the effect of settling time was then investigated. Although the equilibrium was achieved

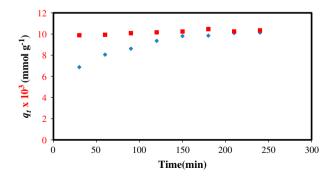


Fig. 1. The effect of contact time for shaking ( $\bullet$ ) and settling ( $\blacksquare$ ) (0.050 g BS, 25.0 mL of 10.0 mg L<sup>-1</sup> MG).

at 30 min, a 1.0-h time period was set for settling time to ensure that the equilibrium was fully established. Subsequent adsorption equilibrium experiments were performed using these optimum shaking and settling time periods.

## 3.2. Dosage of adsorbent

Investigation of the effect of BS dosage on the removal of MG from 100 mg  $L^{-1}$  solution shows that, under the experimental conditions employed, there is an increase in the removal of MG from approximately 36 to 78% as the mass of BS increases from 0.05 to 0.40 g (Fig. 2). Removal of MG reaches its maximum when the mass of BS was 0.40 g followed by a constant rate of removal. Even though an increase in the percentage removal was observed with increasing BS dosage, in terms of adsorption capacity  $(q_e)$ , calculated using the equation below, it was found that 0.050 g of BS gave the highest value of  $q_e$ . Hence, all subsequent reactions were carried out using 0.050 g of BS sample. Decrease in the value of  $q_e$  with the dosage is indicative that BS surface has not achieved the saturation limit with the concentration of the MG employed.

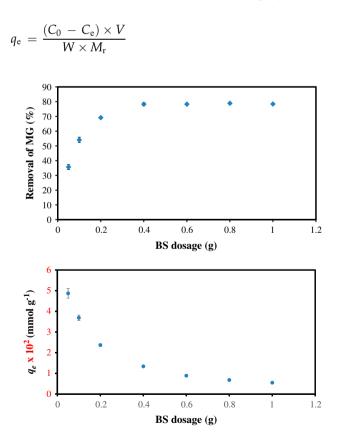


Fig. 2. The effect of BS dosage in terms of rate of removal (top) and  $q_e$  (bottom) of adsorption of 100 mg L<sup>-1</sup> MG dye.

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of the dye (mg L<sup>-1</sup>), respectively. *V* is the volume of the adsorbate solution (L), *W* is the mass of the adsorbent (g), and  $M_r$  is the molar mass of the dye (g mol<sup>-1</sup>).

# 3.3. Effect of pH

Solution pH is also an important factor in controlling sorption process, especially for charged species. The effect of pH on sorption of MG on BS was investigated by monitoring the extent of removal of MG in solutions of different pH for a fixed adsorbent dose of 0.050 g of BS at a concentration of 10 mg L<sup>-1</sup> MG solution shows that the percentage removal of MG falls below 30% at pH 2 (Fig. 3). This could be due to an increase in the concentration of H<sub>3</sub>O<sup>+</sup> ions in the solution, leading to the competition between  $H_3O^+$  and bulky MG cationic dye species for the limited vacant sites on the surface of the adsorbent. At higher pH, the extent of removal of MG gradually increases and the removal of MG remains almost constant over the pH range from 3.0 to 10.0. Similar trend was reported for sorption of MG on cyclodextrin-based adsorbent [25] and walnut shell [8]. Since the ambient pH of MG solutions (pH 4.58) shows the highest removal (83%), no adjustment of the pH of MG solutions was made for subsequent studies.

## 3.4. Effect of ionic strength

Industrial wastewater usually contains various ionic substances in different amounts which would influence the amount of dye being adsorbed. The presence of salts could lead to high ionic strength, indirectly affecting the ability of adsorbents in removing dyes [2]. The percentage removal of MG in 0.01 M KNO<sub>3</sub> solution decreased by 12% as compared to that in water, and a further reduction of 8% was observed in the 0.10 M KNO<sub>3</sub> medium (Fig. 4). However, no further reduction of the extent of removal was observed when the concentration of KNO<sub>3</sub> solution was increased up to 1.0 M, indicating that the inner Helmholtz plane of adsorbent particles gets saturated with 0.10 M KNO<sub>3</sub> medium.

## 3.5. Adsorption equilibrium studies

Application of linear and nonlinear models of adsorption models, and investigation of their validity through error and regression analyses are of great importance in adsorbate-adsorbent systems [26]. Table 1 shows the nonlinear and linear equations of six isotherm models, namely the Langmuir [27], Freundlich [28], Temkin [29], Dubinin-Radushkevich (D-R) [30], Redlich-Peterson (R-P) [31], and Sips [32], used for the investigation of adsorption of MG on the biosorbent. The error functions used to compare experimental adsorption data with expected results for each isotherm, and the uncertainty of experimental results are shown in Table 2. Table 3 shows the values of parameters for the adsorption of MG on BS determined by fitting experimentally obtained data to various isotherm models, while Table 4 shows the values of  $R^2$  and error values of the different isotherm models used in this study.

Among the six adsorption isotherms tested, the Langmuir isotherm gave the best  $R^2$  (close to unity) and the lowest error for adsorption of MG on BS, and hence it was selected as the best-fit isotherm. This is in line with the smallest deviation observed between the experimental data and the Langmuir isotherm with a maximum adsorption capacity ( $q_{max}$ ) of 55.2 mg g<sup>-1</sup> (Fig. 5). It should be noted that BS showed comparable,

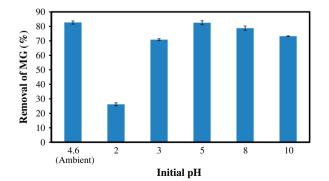


Fig. 3. Effect of pH on the extent of removal of MG by BS (0.050 g BS, 25.0 mL of  $10.0 \text{ mg L}^{-1}$  MG, 3.5 h shaking, 1.0 h settling).

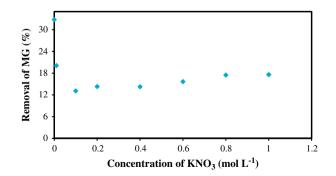


Fig. 4. Effect of ionic strength on the adsorption of MG on BS (0.050 g BS, 25.0 mL of  $100.0 \text{ mg L}^{-1}$  MG, 3.5 h shaking, 1.0 h settling, concentration of KNO<sub>3</sub> 0–1.0 M).

ls, their non-linear and linear forms, and plotting options				
Non-linear	Linear	Plot		
$q_{\rm e} = \frac{K_{\rm L}q_{\rm max}C_{\rm e}}{1+K_{\rm L}C_{\rm e}}$	$rac{C_{\mathrm{e}}}{q_{\mathrm{e}}} = rac{1}{K_{\mathrm{L}}q_{\mathrm{max}}} + rac{C_{\mathrm{e}}}{q_{\mathrm{max}}}$	$\frac{C_{\rm e}}{q_{\rm e}}$ vs. $C_{\rm e}$		
$q_{\rm e} = K_{\rm F} C_{\rm e}^{\frac{1}{n}}$	$\ln q_{\rm e} = \frac{1}{n} \ln C_{\rm e} + \ln K_{\rm F}$	$\ln q_{\rm e}$ vs. $\ln C_{\rm e}$		
$q_{\rm e} = \frac{RT}{b} \ln K_{\rm T} C_{\rm e}$	$q_{\rm e} = B \ln K_{\rm T} + B \ln C_{\rm e}$	$q_{\rm e}$ vs. ln $C_{\rm e}$		
where $B = \frac{RT}{b}$				
$q_{ m e}~=~q_{ m max}\exp(-etaarepsilon^2)$	$\ln q_{\rm e} = \ln q_{\rm max} - \beta \varepsilon^2$	$\ln q_{\rm e}$ vs. $\varepsilon^2$		

 $\ln\left(\frac{q_{\rm e}}{q_{\rm max}-q_{\rm e}}\right) = \frac{1}{n}\ln C_{\rm e} + \ln K_{\rm S}$ 

 $\ln\left(K_{\rm R}\frac{C_{\rm e}}{q_{\rm e}}-1\right) = g\ln C_{\rm e} + \ln a_{\rm R} \qquad \qquad \ln\left(K_{\rm R}\frac{C_{\rm e}}{q_{\rm e}}-1\right) \text{vs.} \ln C_{\rm e}$ 

 Table 1

 Isotherm models, their non-linear and linear forms, and plotting options

 $\varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right]$ 

 $E = \frac{1}{\sqrt{2}\beta}$ 

 $q_{\rm e} = \frac{q_{\rm max}K_{\rm S}C_{\rm e}^{\frac{1}{n}}}{1+K_{\rm S}C_{\rm e}^{\frac{1}{n}}}$ 

 $q_{\rm e} = \frac{K_{\rm R}C_{\rm e}}{1 + a_{\rm P}C_{\rm e}^{\rm g}}$ 

Table 2

Isotherm model Langmuir Freundlich Temkin

D-R

Sips

R-P

List of error functions used to estimate uncertainties of experimental results

Error function	Abbreviation	Expression
Average relative error	ARE	$\frac{100}{n} \sum_{i=-1}^{n} \left  \frac{q_{e,\text{meas}} - q_{e,\text{calc}}}{q_{e,\text{meas}}} \right _{i}$
Sum squares errors	ERRSQ	$\sum_{i=1}^{n} (q_{e,\text{calc}} - q_{e,\text{meas}})_i^2$
Sum of absolute error	EABS	$\sum_{i=1}^{n}  q_{e,\text{meas}} - q_{e,\text{calc}} $
Hybrid fractional error function	HYBRID	$\frac{\sum_{i=1}^{n}  q_{e,\text{meas}} - q_{e,\text{calc}} }{\frac{100}{n-p} \sum_{i=1}^{n} \left[ \frac{(q_{e,\text{meas}} - q_{e,\text{calc}})^2}{q_{e,\text{meas}}} \right]_i$
Marquardt's percent standard deviation	MPSD	$100\sqrt{\frac{1}{n-p}\sum_{i}^{n}\left(\frac{q_{e,meas}-q_{e,calc}}{q_{e,meas}}\right)^2}$
Non-linear chi-square test	χ <sup>2</sup>	$\sum_{i=1}^{n} \frac{\left(q_{\text{e,calc}} - q_{\text{e,meas}}\right)^2}{q_{\text{e,meas}}}$

if not better, adsorption ability to many adsorbents, such as peat, *Annona squmosa* seed, chemically modified peanut shell, and many others (Table 5).

# 3.6. Kinetics of adsorption of MG on BS

Kinetics models, such as the pseudo-first-order, pseudo-second-order kinetics, and intraparticle diffusion models, are important for further investigation on the mechanism of adsorption. The linearized forms of these models are given in Table 6. It is clear from the regression coefficients of the plots in Fig. 6 that the pseudo-second-order model is valid and that the value of  $q_e$  calculated from this model is close to the experimental value, further supporting the validity of the model for biosorption of MG on BS (Table 6). A similar result has been reported by Chowdhury et al., where adsorption of MG on eggshells [43] and Ca(OH)<sub>2</sub>-treated fly ash [44] has followed the pseudo-second-order kinetics. Since both the pseudo-first-order and pseudo-second-order kinetics do not apply to diffusion mechanism, the Weber–Morris intraparticle diffusion model, which indicates that the intraparticle diffusion being the rate-determining step, was applied. The validity of this model suggests that the intraparticle diffusion

 $\ln\left(\frac{q_{\rm e}}{q_{\rm max}-q_{\rm e}}\right)$  vs.  $\ln C_{\rm e}$ 

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Table 3

Parameters determined for adsorption of MG on BS by fitting experimental data to various isotherm models

Model	Parameters	Values
Langmuir	$q_{\rm max} \ ({\rm mg \ g}^{-1})$	55.2
0	$K_{\rm L}$ (L mmol <sup>-1</sup> )	0.01
Freundlich	$K_{\rm F}^{-}$ (mg <sup>1-1/n</sup> L <sup>1/n</sup> g <sup>-1</sup> )	0.01
	n	2.30
Temkin	$K_{\rm T}$ (L mmol <sup>-1</sup> )	0.19
	$b_{\rm T}$ (kJ mol <sup>-1</sup> )	$89.54 \times 10^{3}$
D-R	$q_{\rm max} \ ({\rm mg \ g}^{-1})$	28.68
	$B (J \text{ mol}^{-1})$	$5.50 \times 10^{-7}$
	E (kJ mol <sup>-1</sup> )	$9.53 \times 10^{2}$
R-P	$K_{\rm R}$ (L g <sup>-1</sup> )	0.04
	a	0.59
	$a_{\rm R}$ (L mmol <sup>-1</sup> )	3.78
Sips	$q_{\rm max} \ ({\rm mg g}^{-1})$	72.9
Ŧ	$K_{\rm S}$ (L mmol <sup>-1</sup> )	0.01
	n	2.21

could be the rate-limiting step of the adsorption process under consideration. These findings are similar to adsorption of MG by adsorbents, such as fly ash [45].

# 3.7. Regeneration of adsorbent

Used adsorbents are generally of no use and are disposed of as waste, which would give rise to health hazards requiring and need for incineration. One alternative solution to this problem is to regenerate adsorbents, which would lead to the recovery of valuable adsorbates. In this study, the possibility of regenerating BS adsorbent was investigated in order to evaluate its practicality and feasibility to be used and reused in real-life application of wastewater treatment. Fig. 7 shows the performance of BS in adsorbing 100 mg L<sup>-1</sup> MG after washing with three different solvents (distilled water, 0.1 M HCl, and 0.1 M NaOH) in

Table 4 Values of  $R^2$  and error functions for different isotherm models

Model	$R^2$	ARE	EERSQ	HYBRID	EABS	MPSD	$\chi^2$
Langmuir	0.9857	20.13	0.0002	0.27	0.172	27.79	0.044
Freundlich	0.9417	14.40	0.0006	0.31	0.227	17.61	0.051
Temkin	0.8834	36.50	0.0055	0.98	0.257	65.74	0.157
D-R	0.4705	103.68	0.0436	5.35	0.867	133.70	0.856
R–P	0.9620	14.44	0.0058	0.32	0.217	18.33	0.049
Sips	0.9320	14.29	0.0058	0.32	0.220	18.02	0.049

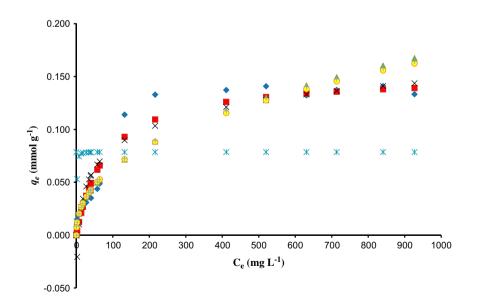


Fig. 5. Comparison of adsorption isotherm of experimental data points vs. various non-linear isotherm models for adsorption of MG on BS: Experimental ( $\bullet$ ), Langmuir ( $\blacksquare$ ), Freundlich ( $\bullet$ ), Temkin (x), D–R ( $\ast$ ), R–P ( $\bullet$ ), and Sips (+).

Table 5 Comparison of  $q_{\text{max}}$  values of various adsorbents toward MG

Adsorbent	$q_{\rm max}~({\rm mg~g}^{-1})$	Refs.
Breadfruit skin	55.2	This work
Breadnut peel	177.4	[33]
Base-modified breadnut peel	227.0	[33]
Walnut shell	90.8	[8]
Peat	15.3	[34]
Mango seed husk	47.9	[35]
Annona squmosa seed	25.9	[36]
Solanum tuberosum leave	33.3	[37]
Solanum tuberosum stem	27.0	[37]
NaOH-activated rice husk	57.1	[38]
Limonia acidissima shell	80.7	[39]
Modified peanut shell	32.7	[40]
Cyclodextrin-based material	91.9	[25]
Sea shell powder	42.3	[41]
Conch shell powder	92.3	[42]

order to investigate its reusability. The initial adsorption of MG by BS gave a removal of 40% with distilled water and HCl washing. Unlike the washing of BS with HCl and distilled water, which showed an overall decrease in the removal rate of MG dye from the first cycle to the fifth cycle, NaOH washing was observed to result in a higher removal rate of 85% for the first cycle. The removal rate increases subsequently until the fifth cycle where the removal rate of MG rises above 95%. One possible reason could be NaOH washing results in deprotonation of the adsorbent's surface, thereby enhancing attraction to the cationic MG dye. From this regeneration experiment, it can thus be deduced that BS has a great potential to be used in real-life application in the wastewater treatment.

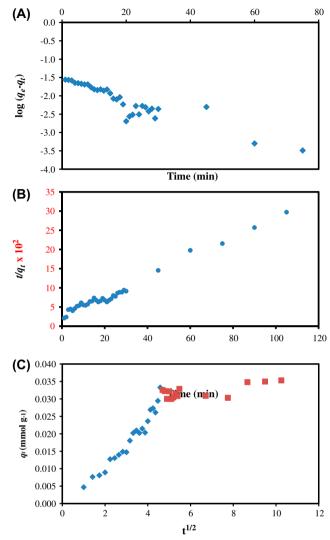


Fig. 6. Fitting of experimental data to (A) Pseudo-firstorder model, (B) Pseudo-second-order model, and (C) Weber–Morris intraparticle diffusion model.

Table 6

Equations and parameters of pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetics models

Kinetics models	Linear equations	Parameters
Pseudo first-order	$\log (q_{\rm e} - q_t) = \log (q_{\rm e}) - \frac{k_{\rm l}}{2.303}t$	$k_1 = -0.048 \text{ min}^{-1}$ $q_{e,calc} = 0.022 \text{ mmol g}^{-1}$ $q_{e,expt} = 0.049 \text{ mmol g}^{-1}$ $R^2 = 0.842$
Pseudo-second-order	$\frac{t}{q_t} = \frac{q}{k_2 q_e^2} + \frac{1}{q_e} t$	$k_{2} = 0.042$ $k_{2} = 1.580 \text{ g mg}^{-1} \text{ min}^{-1}$ $q_{e,calc} = 0.041 \text{ mmol g}^{-1}$ $q_{e,expt} = 0.049 \text{ mmol g}^{-1}$ $R^{2} = 0.983$
Weber-Morris intraparticle diffusion	$q_t = k_{\rm id} t^{1/2} + C$	$k_{id} = 0.007 \text{ mg g}^{-1} \text{ min}^{1/2}$ C = -0.004 y = 0.007x + 0.004 $R^2 = 0.950$

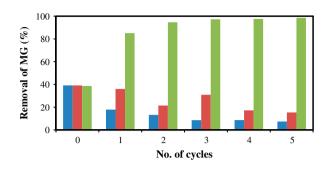


Fig. 7. Removal of MG by BS showing five cycles of regeneration (0.050 g BS, 25.0 mL adsorbent, 2.0 h shaking, and 1.0 h settling) using  $H_2O$  (7), HCl ( $\blacksquare$ ), and NaOH ( $\blacksquare$ ).

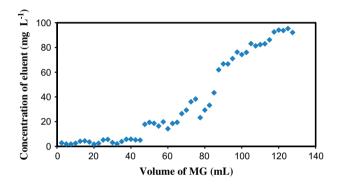


Fig. 8. Concentration of MG eluent vs the number of 25.0 mL aliquots of  $100 \text{ mg L}^{-1} \text{ MG}$ .

# 3.8. Column study

Under dynamic conditions, adsorption experiments of MG indicate that BS sample particles packed in the column exhibit a significant ability to retain MG on the surface of BS. Allowing sufficient time after elution of 25.0 mL aliquot of 100 mg  $L^{-1}$  MG solution leads to

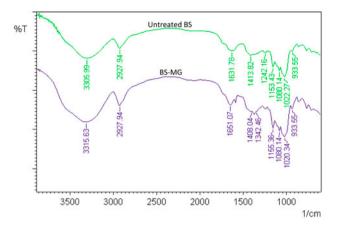


Fig. 10. FTIR spectra of untreated BS and BS treated with  $1,000 \text{ mg L}^{-1} \text{ MG}$ .

no detectable levels of MG present in the eluent until 425 mL of additions were introduced (Fig. 8). Furthermore, it is estimated that a volume of 850 mL of MG can be introduced to the column for up to 50% removal of MG present in the original solution. According to these results, it can be concluded that a layer of MG molecules can be arranged on an underlying layer in which it provided sufficient time for adsorption [46].

# 3.9. Characterization of BS using XRF and FTIR

Elemental characterization of BS by XRF shows that potassium was present in the highest amount (28.9%), followed by zinc (17.2%) and iron (8.2%). Fig. 9 shows that adsorption with MG reduced the amount of potassium present from 28.9 to 1.2%. Similar finding was also observed for adsorption of MG by peat and there is a possibility that the MG cationic dye is able to replace

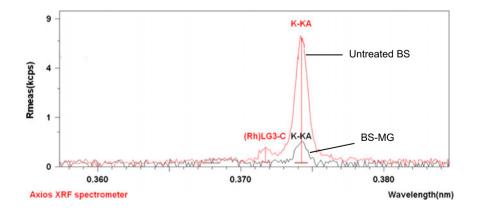


Fig. 9. XRF of BS showing potassium before and after adsorption with  $1,000 \text{ mg L}^{-1} \text{ MG}$ .

metals, such as *K*, which could be present in its cationic form at a higher concentration [30].

The infrared spectrum of BS, presented in Fig. 10, shows bands at 3,400 cm<sup>-1</sup> due to the stretching vibration of bonded OH and amino groups, and the asymmetric stretching vibration of  $-CH_3$  at 2,900 cm<sup>-1</sup>. A band at 1,631 cm<sup>-1</sup> represents the C=C aromatic bonding, while the band at 1,413 cm<sup>-1</sup> is attributed to the symmetric bending of  $-CH_3$ . After treatment of BS with 1,000 mg L<sup>-1</sup> MG dye, major shifts were observed at 3,316 cm<sup>-1</sup> (OH and amino groups) and 1,651 cm<sup>-1</sup> (C=C), indicating that these functional groups could be involved in the adsorption of MG. Similar findings were also reported for adsorption of MG onto breadnut skin [32].

## 4. Conclusion

The skin of A. altilis shows a great potential to be utilized as a low-cost biosorbent for the removal of MG. Time taken to reach equilibrium is 3.5 h, and the presence of salts affects the ability of BS in removing MG dye. Adsorption isotherm can be explained by the Langmuir model with the adsorption capacity of 55.2 mg  $g^{-1}$ , which is higher than those of many reported low-cost biosorbents. Adsorption processes are best described by the pseudo-second-order kinetics with an apparent rate constant of 0.049 mmol  $g^{-1}$  for MG-BS. The biosorbent, BS, is an excellent adsorbent, which can be regenerated and reused, while maintaining its high removal efficiency even after five repetitive adsorption-desorption cycles with 0.1 M NaOH. This is further supported by column studies which show that BS is able to retain a high volume of MG. The adsorption of MG on BS can be partly explained by an ion-exchange mechanism.

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