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Diplazium esculentum (Paku Pakis) adsorption characteristics toward toxic Brilliant green dye

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ABSTRACT

Diplazium esculentum, an edible fern, was investigated for its potential as a low-cost and effective biosorbent for the removal of toxic Brilliant green (BG) dye. Batch experiments were performed to investigate parameters such as contact time, ionic strength, kinetics, isotherm, and pH on the adsorption capacity. The Pakis adsorbent reached equilibrium within 2 h of contact time with BG dye, and of the five adsorption isotherm models tested, the Sips model gave the best fit with a maximum adsorption capacity (q_{max}) of 347.5 mg g^{-1}. Kinetics study revealed that the pseudo-second-order model was best fitted to the experimental data, suggesting that chemisorption could be involved. Analyses of adsorption isotherm and kinetics were carried out using linear and nonlinear regressions and compared. ANOVA tests revealed a significant difference between the two methods of analyses for adsorption kinetics. The experimental data of both kinetics and isotherm fitted better when nonlinear regression was used, as compared to the corresponding linear regression analysis. The adsorbent maintained its effective adsorption of BG with varying pH solutions and salt concentrations. Treatment with 1.0 M NaOH of spent Pakis adsorbent could remove >80% BG dye even after five consecutive cycles. High adsorption capacity, relative stability, ability to be regenerated, and reused all lend support to the possible future application of Pakis as a potential low-cost adsorbent in wastewater treatment.

Keywords: Adsorption isotherm; Brilliant green dye; Kinetics; Pakis adsorbent; Regeneration; Nonlinear regression

1. Introduction

Dyes have a diverse range of industrial applications, but as a mitotic poisoning agent, their discharge in the environment poses a serious health threat to both humans and animals. The careless discard of waste dyes and dye-based effluents would pollute land and water; hence they are regarded as a biohazard [1]. As such, it is essential to remove these dyes from effluents not only to safeguard the health of humans and animals but also to protect water resources. Water contaminated by dyes has both toxicology and aesthetic concerns, and removal of dyes from wastewater is necessary before the water can be safely discarded. Water treatment aims to produce water with quality that conforms to a country's water safety standard to ensure the water is safe for human consumption and is aesthetically appealing.

It is both important and challenging to ensure that a chosen wastewater treatment method is efficient, fast, inexpensive, and does not produce any secondary hazardous

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by-products. The past decade has seen the emergence of various methods for the removal of toxic dye effluents from wastewater. Such methods include ion exchange, membrane filtration, flocculation, reverse osmosis, ozonation, Fenton reaction, ultraviolet irradiation, etc. The advantages and disadvantages of these methods have been widely reviewed [1–4].

The adsorption method has advantages over the other techniques for remediation of pollutants from wastewater due to its simple design, low-cost adsorbents, and no sludge formation. This method has also been found to be efficient in the treated water is of higher quality without the production of secondary hazardous pollutants. Further, the adsorption method shows flexibility and does not require any complicated or special equipment, or highly skilled and trained technicians [5,6]. Various adsorbents have been studied in the treatment of wastewater, such as wastes derived from fruits [7,8], leaves [9–11], vegetable [12], agriculture [13,14], industries [15], minerals [16], and polymers [17,18], and the search for better and more effective adsorbents has been an on-going quest [19]. In recent years, synthesized and modified adsorbents have also been researched on in the hope to enhance the adsorption capacity of the adsorbents [20–22].

Brilliant green (BG), also known as malachite green G or emerald green, is a diamino-triphenylmethane dye with molecular formula $C_{27}H_{34}N_2O_4S$. Due to its inhibitory effect against gram-positive bacteria, BG has found its uses as a local antibacterial and antiseptic agent. Its vibrant color has resulted in BG's vast application as a textile dye, paper dye, histological dye, and others. However, BG is also known to be carcinogenic and genotoxic when ingested, and it can cause blindness when comes in contact with the eye [23,24]. Hence, BG is rendered toxic, and it is of utmost importance that steps are taken to remove it from wastewater contaminated with used BG dye to prevent it from entering water sources, which may have detrimental effects on aquatic animals, land animals, and humans alike. BG dye has been successfully removed using the adsorption method with adsorbents, such as nanoparticles [25,26], modified cellulose [27], mesoporous adsorbents [28], and synthesized biocomposites [29]. Apart from adsorption, studies have shown that BG dye can also be removed via photocatalytic degradation [30] and microwave-induced catalytic treatment [31].

In Brunei Darussalam as well as other parts of South East Asia, Asia, and Oceanian countries, *Diplazium esculentum*, an edible fern, grows in abundance in backyards, along roadsides, streams, and drains [32]. Locally known as Pakis, these ferns are considered as "organic vegetables" as no artificial fertilizers or pesticides are used on them. They have long stipes that are thick at the base and gradually thin at the top with a lot of frond curls and a few leaves. Being cheap and readily abundant, Pakis is a popular local vegetable dish. Typically, the fronds, leaves, and softer part of the stipe are used in preparing a dish, and the harder stipe portion is discarded [33]. Recent study has shown that Pakis exhibits medicinal properties and has been used in traditional medicine [34]. Apart from being used for culinary purpose, Pakis offers the possibility of being utilized as a low-cost, green, and environmentally friendly adsorbent in treatment of wastewater, as it is a perennial fern which is available throughout the year in great abundance. Therefore, it would exhibit the great potential to be an adsorbent although much scientific advancement on its use has not been reported.

This study focuses on the use of the hard portion of the stipes of Pakis as a potential adsorbent in the removal of BG from wastewater. The adsorption characteristics of Pakis toward BG dye with respect to the variation of experimental parameters will be investigated and discussed. Further, a comparison of adsorption isotherm and kinetics using both linear and nonlinear regression analyses will be made. Its ability to be regenerated and reused will also be reported.

2. Materials and methods

2.1. Sample preparation and dye used

Random samples of Pakis were purchased from the local market. The thick, hard stipes at the base of the plant, being the inedible parts of Pakis, were separated from the edible parts and used in this study. They were rinsed with distilled water and oven-dried at 60°C until a constant mass was obtained. The dried Pakis samples were blended and sieved using the laboratory sieve to get particles of less than 355 μm in diameter.

Brilliant Green (BG) dye was purchased from Sigma-Aldrich, Paris, and 1,000 mg L^{-1} BG stock solution was prepared. BG solutions of subsequent concentrations required to carry out experiments were obtained through serial dilution of the stock solution. Shimadzu UV-1601PC UV-visible spectrophotometer (UV-vis), Japan, was used for the measurement of absorbance of BG solutions at the characteristic wavelength of 624 nm.

2.2. Optimization of parameters and batch adsorption experiments

Throughout this study, 0.020 g of Pakis and 10.0 mL of known BG concentration were used, unless stated otherwise. Mixtures were agitated using an orbital shaker at 250 rpm at room temperature. Effects of contact time (30 min interval for up to 4.0 h), ionic strength (0.10–0.80 M NaCl), and pH (4–10) on the extent of removal of BG were investigated. Investigation of adsorption kinetics was performed using 100 mg L^{-1} BG dye solution, and samples were withdrawn at 1 min intervals up to 9 min, followed by 3 min intervals until 30 min; thereafter at 10 min intervals until 60 min and finally at 30 min intervals from 60 to 120 min. Batch adsorption isotherm study was investigated with BG solutions of concentration ranging from 0 to 1,000 mg L^{-1} following the method as outlined by Chieng et al. [35]. Regeneration studies were carried out for five consecutive cycles as described by Zaidi et al. [36].

2.3. Characterization of adsorbent

The KBr pellet method was used to record the infrared (IR) spectra of Pakis, before and after adsorption of BG dye, in the range of 500–4,500 cm^{-1} using the Shimadzu IR Prestige-21 spectrophotometer (Japan). Surface morphology images of Pakis and BG loaded Pakis were taken using scanning electron microscopy (SEM), JSM-7610F JEOL model, Japan.

2.4. Error analyses

To help determine the suitability of isotherm and kinetics models, five error functions, shown in Table 1, were used where smaller error values of the model indicate the better it fits to the experimental data.

3. Results and discussion

3.1. Characterization of Pakis

Infrared spectra of Pakis before and after adsorption, shown in Fig. 1, indicate significant shifts of peaks between 3,000 and 3,700 cm^{-1}. The peak at 3,353 cm^{-1}, which could be due to primary or secondary amines, has shifted positively by 64 cm^{-1} after treatment with BG dye; the peaks at 3,179 and 3,065 cm^{-1}, which could be due to –OH stretching in alcohols or carboxylic acids, have been shifted positively by 104 and 109 cm^{-1}, respectively; the peak at 2,852 cm^{-1}, which could be due to ammonium salt or alcohol –OH stretching, is unaffected; however, a new peak at 2,920 cm^{-1} has appeared which can be attributed to shift in the peak due to some ammonium salt or alcohol –OH stretching. These observations suggest the involvement of O–H and N–H groups in adsorption of BG dye. On the other hand, the C=O and C=C stretching peaks at 1,740 and 1,654 cm^{-1} are slightly shifted negatively by 10 and 1 cm^{-1}, showing their minimal involvement in bonding between BG dye and the adsorbent. Further, the shifts of peaks at 1,276 and 1,188 cm^{-1} attributed to aromatic and aliphatic C–N stretching absorptions of BG dye, respectively, confirm its adsorption onto Pakis.

Table 1
Error functions used in adsorption experiments under equilibrium conditions

Error function (abbreviation)	Equation
Sum square error (SSE)	$\sum_{i=1}^{n}\left(q_{e,\text{calc}} - q_{e,\text{meas}}\right)_i^2$
Sum of absolute error (EABS)	$\sum_{i=1}^{p}\left\lvert q_{e,\text{meas}} - q_{e,\text{calc}}\right\rvert$
Hybrid functional error function (HYBRID)	$\frac{100}{n-p}\sum_{i=1}^{n}\left[\frac{\left(q_{e,\text{meas}} - q_{e,\text{calc}}\right)^2}{q_{e,\text{meas}}}\right]_i$
Chi-square test (χ^2)	$\sum_{i=1}^{p}\frac{\left(q_{e,\text{meas}} - q_{e,\text{calc}}\right)^2}{q_{e,\text{meas}}}$
Average relative error (ARE)	$\frac{100}{p}\sum_{i=1}^{p}\left\lvert\frac{q_{e,\text{meas}} - q_{e,\text{calc}}}{q_{e,\text{calc}}}\right\rvert$

$q_{e,\text{meas}}$ is the value of the experiment while $q_{e,\text{calc}}$ is the value calculated for the isotherm model and p is the number of observations in the experiment.

Surface morphology of Pakis investigated with the aid of SEM images, before and after adsorption of BG (Fig. 2), clearly indicates that the irregular nature of the adsorbent with hollow spaces changed upon adsorption. The surface covered by the BG dye becomes less irregular and more flat with fewer cavities, further supporting the adsorption of the BG dye onto the surface of the Pakis.

3.2. Effect of contact time

The knowledge of contact time of an adsorption process is significant as it determines the time needed for the adsorbate–adsorbent system to reach equilibrium state. From Fig. 3, it can be seen that during the first 30 min, the rate of removal of BG dye sharply increases to 90.9% (100 mg L^{-1}) and 75.5% (500 mg L^{-1}). This is due to the presence of a large number of active vacant sites on the surface of Pakis being available for fast adsorption of BG dye molecules. As more of these vacant sites were being filled, the adsorption rate decreased and eventually equilibrium was achieved within two hours of contact time. Peat was also reported to have the same contact time [37], while leaves of *Dimocarpus longan* ssp. malesianus var. malesianus were able to reach equilibrium within 30 min [38]. Zhang et al. [39] and Rehman et al. [40] reported 600 and 240 min contact time for magnetic composite materials and red clay, respectively.

Further, it can be observed from Fig. 3 that the removal of BG is lower for higher initial dye concentration. Such observation is similar to various reports and

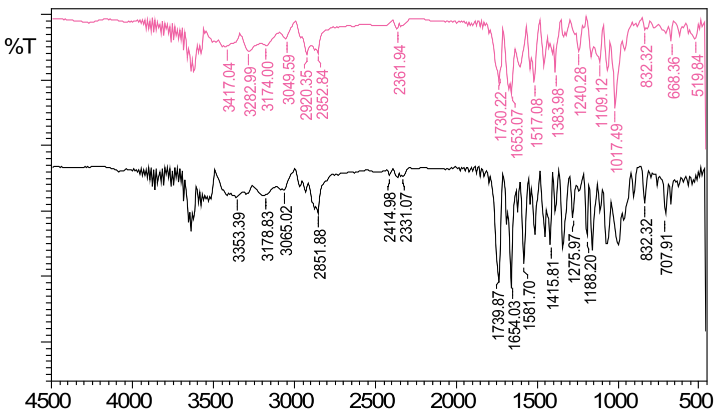

Fig. 1. FTIR spectra of Pakis before (black) and after (pink) adsorption of BG.

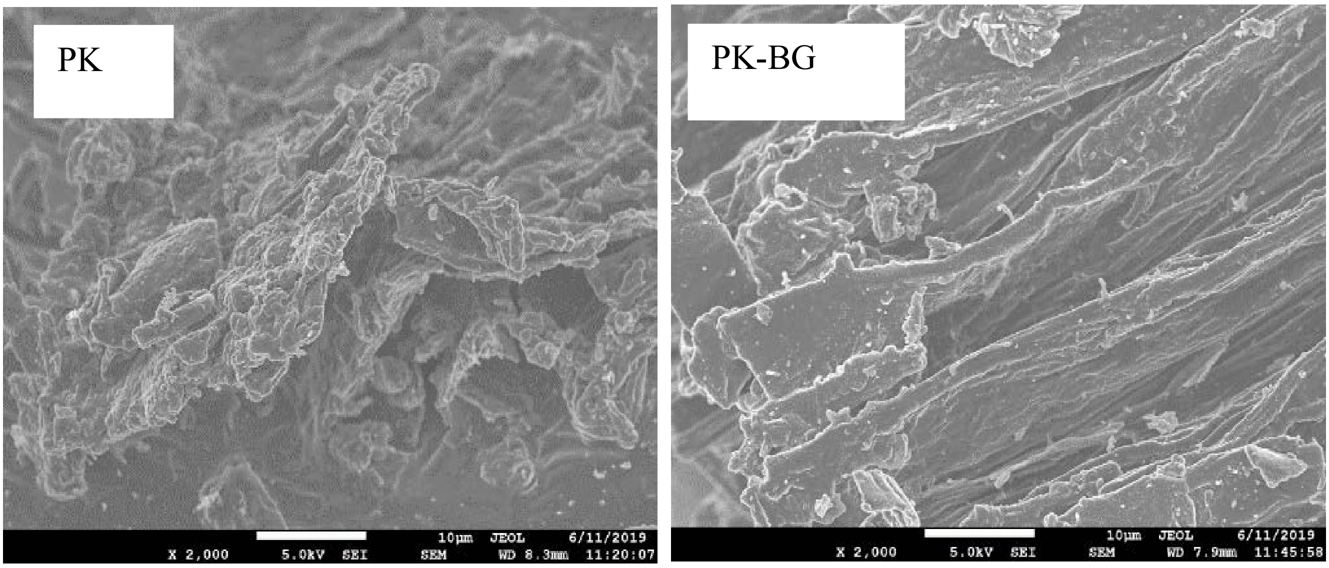

Fig. 2. SEM images of Pakis before and after adsorption of BG at 2,000× magnification.

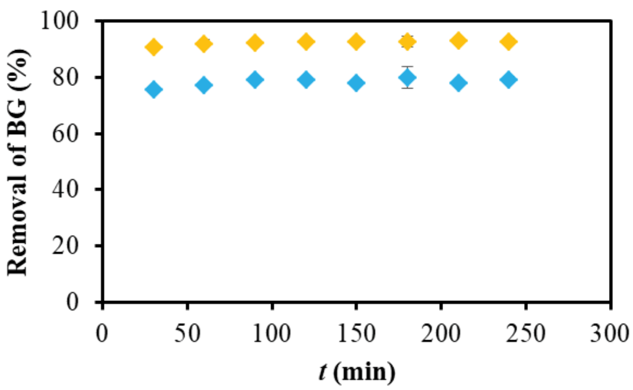

Fig. 3. Effect of contact time on the removal of 100 mg L^{-1} (◆) and 500 mg L^{-1} (◆) BG by Pakis.

can be explained by the fact that the adsorbent's surface carries a fixed number of active vacant sites per unit mass of adsorbent [40,41]. Hence with lower dye concentration, there will be higher availability of these active sites for adsorption to take place thereby resulting in higher percentage removal of dye [26].

3.3. Effects of pH and concentration of NaCl on adsorption of BG on Pakis

It is known that in wastewater, the pH and ionic strength always vary due to various pollutants and electrolytes present. Hence, it is important to study their effects to evaluate an adsorbent's performance with changing conditions. The more tolerant the adsorbent is, the more attractive it would be when applied to wastewater treatment. Additionally, some dyes and adsorbents are quite sensitive to pH since the functional groups present would undergo protonation or deprotonation. In this study, the pH range was kept between 4 and 10, to avoid any structural changes of the dye which would lead to inaccurate results [42].

According to Fig. 4, Pakis still shows a strong tolerance under different pH and NaCl concentrations, yet maintaining a high extent of adsorption of >90% toward BG, demonstrating the great potential of the adsorbent to be applied in wastewater treatment. The ability to maintain strong adsorption characteristics relatively unaffected by solution pH could be the result of the interaction of BG dye molecules with various functional groups present, such as carboxyl and hydroxyl groups, even under ionized conditions. This would probably be possible for organic adsorbates, such as dyes, which would not contribute to ion exchange mechanisms unlike ionic adsorbates, whose adsorption characteristics are highly dependent on the local ionic environment [43]. Further, it has been reported that an increase in ionic strength could cause a shielding effect and suppress electrostatic interactions, influencing ionic adsorbates [44]. Another possibility could be that dye adsorption involves hydrophobic interactions, which are not much affected by the variation of ionic strength of the medium [45]. It has however been reported that many adsorbents show a severe drop in their ability to remove dyes when pH and ionic strength are changed [46,47]. Thus, the stability of Pakis under varying environmental conditions while maintaining its adsorption efficiency is a very attractive feature as a potential adsorbent in wastewater treatment application.

3.4. Adsorption kinetics of BG onto Pakis

Understanding the rate of adsorption and evaluating an adsorbent's performance are important especially when applied to industrial scale wastewater treatment. Application of kinetics models for small-scale batch experiments is the initial step, followed by subsequent steps of investigation of adsorption kinetics under dynamics conditions and proto-type conditions, in order to extend experimental findings toward industrial scale. Kinetics modeling is therefore extremely important, and this

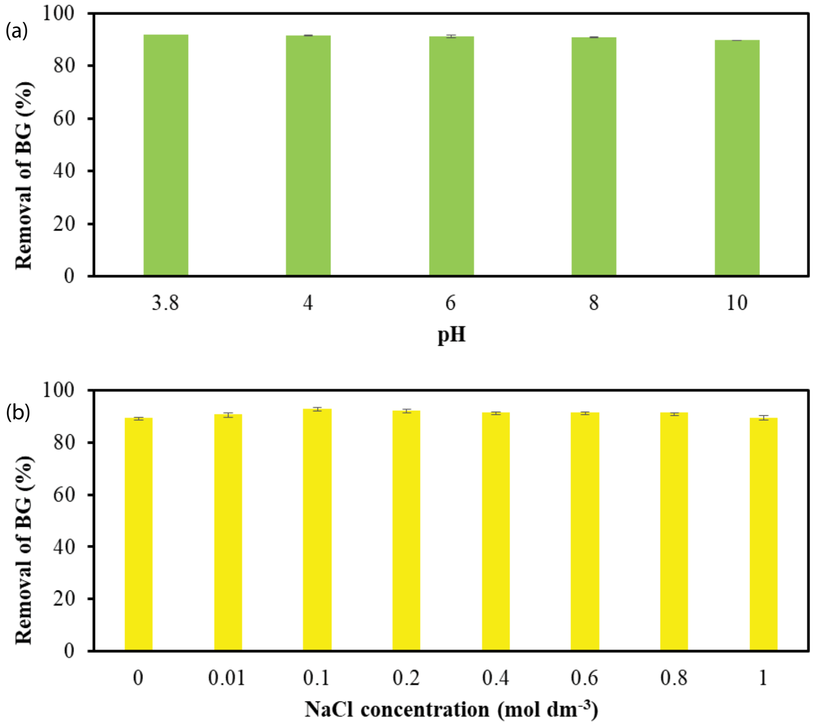

Fig. 4. Effect of adsorption of BG by Pakis in different (a) pH and (b) NaCl concentrations.

should be performed during the initial stage of adsorption before the equilibrium is reached. In this study, adsorption data of BG onto Pakis were fitted to two kinetics models, namely the Lagergren pseudo-first-order [48] and the pseudo-second-order [49], as shown in Table 2. Both these models have been widely reviewed [50,51]. Five error functions were also used: the sum of absolute error (EABS), the average relative error (ARE), the sum square error (SSE), hybrid fractional error function (HYBRID), and chi-square test (χ^2). Their equations are presented in Table 1.

The linear regression method has been widely used in adsorption studies, offering a quick and easy method of analysis. Determination of the best fit model is based on the highest R^2 obtained from the linear plots. However, this has its drawbacks since errors can occur through the transformation of nonlinear into linear equations [52]. Nevertheless, despite inherent bias errors, many recent reports continue to use this method of analysis [53–55]. Studies have shown that nonlinear regression analysis is better and more accurate since the original form of the equation is being retained without any alteration [56–58].

Hereby, the adsorption kinetics data were analyzed using both the linear and nonlinear regression methods and compared. The latter method of analyses was done with the aid of Microsoft Excel Solver add-in and minimizing SSE. Using Eq. (1), the R^2 from nonlinear regression method of each model was calculated.

$$R^2 = \frac{\sum\left(q_{e,\mathrm{cal}} - q_{m,\mathrm{exp}}\right)^2}{\sum\left(q_{e,\mathrm{cal}} - q_{m,\mathrm{exp}}\right)^2 + \left(q_{e,\mathrm{cal}} - q_{m,\mathrm{exp}}\right)^2} \tag{1}$$

where $q_{e,\mathrm{cal}}$ is the calculated amount of adsorbate (mmol g^{-1}); and $q_{m,\mathrm{exp}}$ is the average amount of adsorbate adsorbed from the experiment (mmol g^{-1}).

Table 2
Kinetics models used in this study with linear and nonlinear relationships

Kinetics model	Nonlinear	Linear	Linear plot
Pseudo-first-order	$q_t = q_e\left(1 - e^{-kt}\right)$	$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{k_1 t}{2.303}$	$\log\left(q_e - q_t\right)$ vs. $\log\left(q_e\right)$
Pseudo-second-order	$q_t = \frac{q^2 e^{kt}}{1 + \left(k q_t t\right)}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$\frac{t}{q_t}$ vs. t

k_1 and k_2 are the rate constants of the pseudo-first-order and pseudo-second-order kinetics, respectively; q_e and q_t represent the adsorption capacity at equilibrium and at time t, respectively, and t is reaction time in minutes.

In both methods, the pseudo-second-order model gave the highest R^2 with the lowest error values (Table 3), thereby indicating that it is a more suitable model for adsorption kinetics. Its simulated plot, as shown in Fig. 5, is also closer to the experimental kinetics data than the Lagergren pseudo-first-order which showed a large deviation. Further confirmation of the pseudo-second-order being the best fit model is by comparison of the experimental (q_{exp}) vs. calculated (q_{calc}) adsorption capacity, as tabulated in Table 3.

3.4.1. Linear vs. nonlinear regression analyses in adsorption kinetics of BG onto Pakis

Between the nonlinear and linear regression analyses, the former is preferred in that the errors are much lower and the curve fittings are also better, as seen in Table 3 and Fig. 5b, respectively. Further confirmation of the superiority of nonlinear regression over linear regression can be seen from Fig. 6 wherein the nonlinear regression fits better to the experimental data than the linear regression method. This is especially prominent in the Lagergren pseudo-first-order fit where the linear regression method has highly deviated from the experimental data, which could explain the observed high error values given in Table 3. Further, the very small p-values, especially for the Lagergren pseudo-first-order kinetics model, reject the null hypothesis and clearly indicate that there is a significant difference between the two methods of analyses.

3.5. Adsorption isotherm

Adsorption isotherm provides vital information in relation to the interaction between adsorbent and adsorbate after the establishment of equilibrium. Such information would be much helpful in designing wastewater treatment systems because in some large-scale operations, a sufficient time period is allowed to maximize the extent of removal by then the adsorbate-adsorbent system has reached equilibrium status. Batch adsorption isotherm data obtained were fitted to five isotherm models, that is, Langmuir [59], Freundlich [60], Temkin [61], Redlich–Peterson [62], and Sips [63], whose equations are shown in Table 4. All these isotherm models have been widely discussed [52,64].

3.5.1. Linear regression method

Many adsorption studies make use of linearized isotherm equations to determine the best-fit adsorption isotherm simply because of the simplicity and ease of such a method of analysis. From the linear plots of the five isotherm

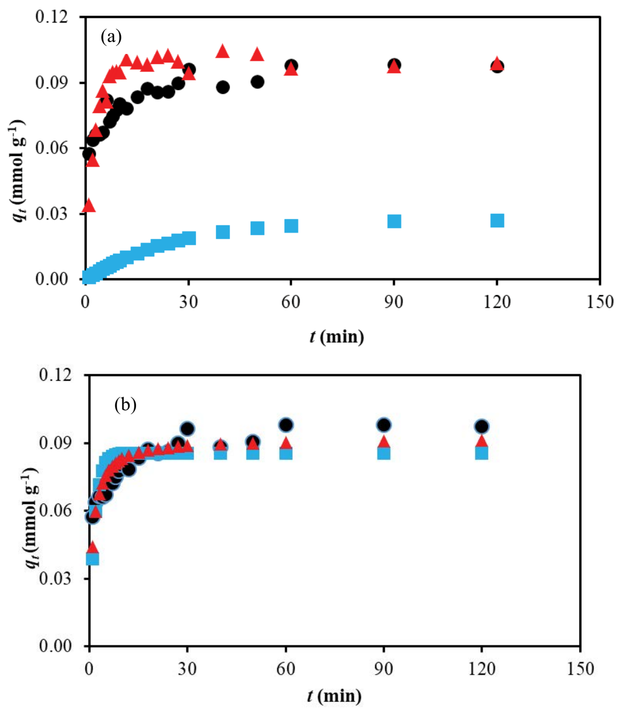

Fig. 5. Comparison of experiment kinetics data (●) with Lagergren pseudo-first-order (■) and pseudo-second-order (▲) models using (a) linear regression and (b) nonlinear regression analyses.

Table 3
Kinetics parameters and error values of Lagergren pseudo-first-order and pseudo-second-order models

Model		R^2	q_{calc} (mmol g^{-1})	ARE	SSE	HYBRID	EABS	χ^2
Linear regression								
Pseudo-first-order		0.682	0.027	85.37	0.104	6.41	1.51	1.280
k_1 (min^{-1})	0.039							
Pseudo-second-order		0.998	0.099	15.88	0.004	0.30	0.27	0.060
k_2 (g mmol^{-1} min^{-1})	4.333							
Nonlinear regression								
Pseudo-first-order		0.884	0.086	6.95	0.0017	0.09	0.16	0.017
k_1 (min^{-1})	0.060							
Pseudo-second-order		0.941	0.092	4.43	0.0007	0.04	0.10	0.007
k_2 (g mmol^{-1} min^{-1})	10.08							
q_{exp} (mmol g^{-1})			0.079					

Table 4
Parameter values and error analyses of the five adsorption isotherm models

Model	Nonlinear	Linear
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$
q_{max} (mmol g^{-1})	0.820	0.888
K_L (L $mmol^{-1}$)	0.024	0.013
R^2	0.7610	0.9138
ARE	108.69	26.48
SSE	0.11	0.19
HYBRID	7.40	3.07
EABS	1.25	1.08
χ^2	1.26	0.72
Freundlich	$q_e = K_F C_e^{\frac{1}{n_F}}$	$\ln q_e = \frac{1}{n_F} \ln C_e + \ln K_F$
K_F (mmol g^{-1} (L $mmol^{-1})^{1/n}$)	0.063	0.019
n	2.303	1.412
R^2	0.6758	0.8135
ARE	185.73	38.44
SSE	0.26	0.73
HYBRID	19.78	8.94
EABS	1.98	2.27
χ^2	3.03	1.08
Temkin	$q_e = \frac{RT}{b_T} \ln K_T C_e$	$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e$
K_T (L $mmol^{-1}$)	0.240	0.224
b_T (kJ mol^{-1})	13.90	13.83
R^2	0.9944	0.9093
ARE	139.96	31.25
SSE	0.11	0.10
HYBRID	15.18	2.41
EABS	1.23	0.98
χ^2	3.52	0.34
Redlich–Peterson	$q_e = \frac{K_{RP} C_e}{1 + a_R C_e^n}$	$\ln\left(\frac{K_{RP} C_e}{q_e} - 1\right) = n \ln C_e + \ln a_R$
K_{RP} (L g^{-1})	0.016	0.013
n	1.342	0.545
a_R (L $mmol^{-1}$)	0.003	0.165
R^2	0.7953	0.7380
ARE	88.28	28.56
SSE	0.08	0.38
HYBRID	5.28	5.84
EABS	1.12	1.67
χ^2	0.61	1.08
Sips	$q_e = \frac{q_m K_s C_e^{\frac{1}{n}}}{1 + K_s C_e^{\frac{1}{n}}}$	$\ln\left(\frac{q_e}{q_{max} - q_e}\right) = \frac{1}{n} \ln C_e + \ln K_s$
q_{max} (mmol g^{-1})	0.660	0.810
K_S (L $mmol^{-1}$)	0.001	0.009
n	0.413	0.821
R^2	0.9987	0.9117
ARE	26.45	23.32
SSE	0.07	0.12
HYBRID	2.58	2.18
EABS	0.72	0.92
χ^2	0.06	0.50

models used, the present study shows that the order of increasing R^2 value (Table 4) is Redlich–Peterson < Freundlich < Temkin < Sips < Langmuir models. This is also in agreement with the simulation plots of each model as shown in Fig. 6a where the Freundlich and Redlich–Peterson clearly deviated from the experimental data. Five error functions, whose equations are shown in Table 1, were also employed in order to address the shortfall arising from inherent bias linearization. The error values as tabulated in Table 4 further helped eliminate both the Freundlich and Redlich–Peterson models. Even though the Langmuir has the highest R^2 value, its overall errors pointed to it being a less suitable isotherm model to describe the adsorption of BG onto Pakis. Of the five isotherm models investigated, the Sips model is deemed the most suitable given its high R^2 value and lower overall error values. The Sips is the best in terms of its highest R^2, lowest error values, and closest fit to the experimental data. This three-parameter isotherm model is sometimes known as the Langmuir–Freundlich model as it tends toward the Langmuir at high adsorbate concentration and follows the Freundlich at low adsorbate concentrations.

3.5.2. Nonlinear regression method

Although analysis using linear regression is one of the most common tools, nonlinear regression analysis was employed in this study since it has been reported that linearization can lead to errors as a result of the change in structure and distribution [58]. Further, nonlinear regression has been found to be more flexible in curve fitting [57]. Another advantage of nonlinear fitting is that the parameter data can be obtained directly from actual equations, without the need to change into the corresponding linearized forms.

Simulation of each model and comparison with experimental data in Fig. 6 clearly show that the two most deviated models are the Freundlich and Temkin models, and this is further confirmed by their high error values (Table 4). Both the Redlich–Peterson and Langmuir models can likely be ruled out based on their low R^2 (<0.8). Of all the isotherm models, the Sips model is the closest fitting to the experimental data with high R^2 close to unity and low error values.

3.5.3. Linear vs. nonlinear regression methods

Comparison of the experiment isotherm data with the two methods of analyses, shown in Fig. 7, indicates that the nonlinear regression fits closer to the experiment data as compared to the linear regression. This is especially so for both the Freundlich and Redlich–Peterson isotherm models, shown in Figs. 7b and d, respectively, where the linear regression is associated with large deviation. Of all the plots, the nonlinear Sips model fits the best to the experimental data, as can be observed from Fig. 7e.

In order to evaluate the two methods, linear vs. nonlinear regression, ANOVA analyses were carried out for each isotherm model. The null hypothesis was used to test if there is a significant difference between the two methods of analysis. All the p-values were >0.005 which indicates that the null hypothesis cannot be rejected, and there is no significant difference between the linear and nonlinear regression methods.

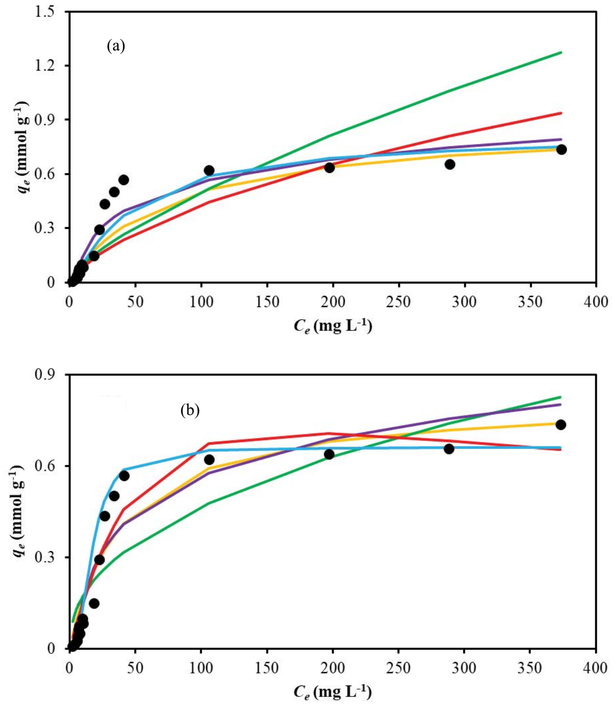

Fig. 6. Comparison of experiment isotherm data (●) with Langmuir (yellow), Freundlich (green), Temkin (purple), Redlich–Peterson (red), and Sips (blue) isotherm models.

Nevertheless, it is clear from the plots in Fig. 7 that the nonlinear regression method of analysis is superior to the linearized isotherm equations, which are in line with literature reports [56,58,65].

The above results using both the linear and nonlinear regression analyses unanimously point to the Sips being the best model for the adsorption of BG onto Pakis, with the nonlinear method being superior compared to the linear method. Based on this isotherm model, the maximum adsorption capacity (q_{max}) of Pakis using nonlinear regression fitting is 318.55 mg g^{-1}, which is much higher than many reported natural adsorbents as shown in Table 5. Its q_{max} also surpassed adsorbents that have been chemically modified or synthesized. In order to qualify as a potential adsorbent to be applied in wastewater treatment, the adsorbent must be easy to prepare and has the ability to demonstrate high adsorption ability. It must be emphasized that Pakis was simply oven-dried at 60°C without any complicated preparation procedures. Surface modification to further enhance its q_{max} is a possibility to be attempted [20,66,67].

3.6. Thermodynamics studies on the adsorption of BG onto Pakis

Thermodynamics also plays an important role in the designing and setting-up of wastewater treatment plants. The thermodynamics parameters would help in the planning and design as the values from the Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) which can be obtained using Eqs. (2)–(5), and further, the van Hoff's plot

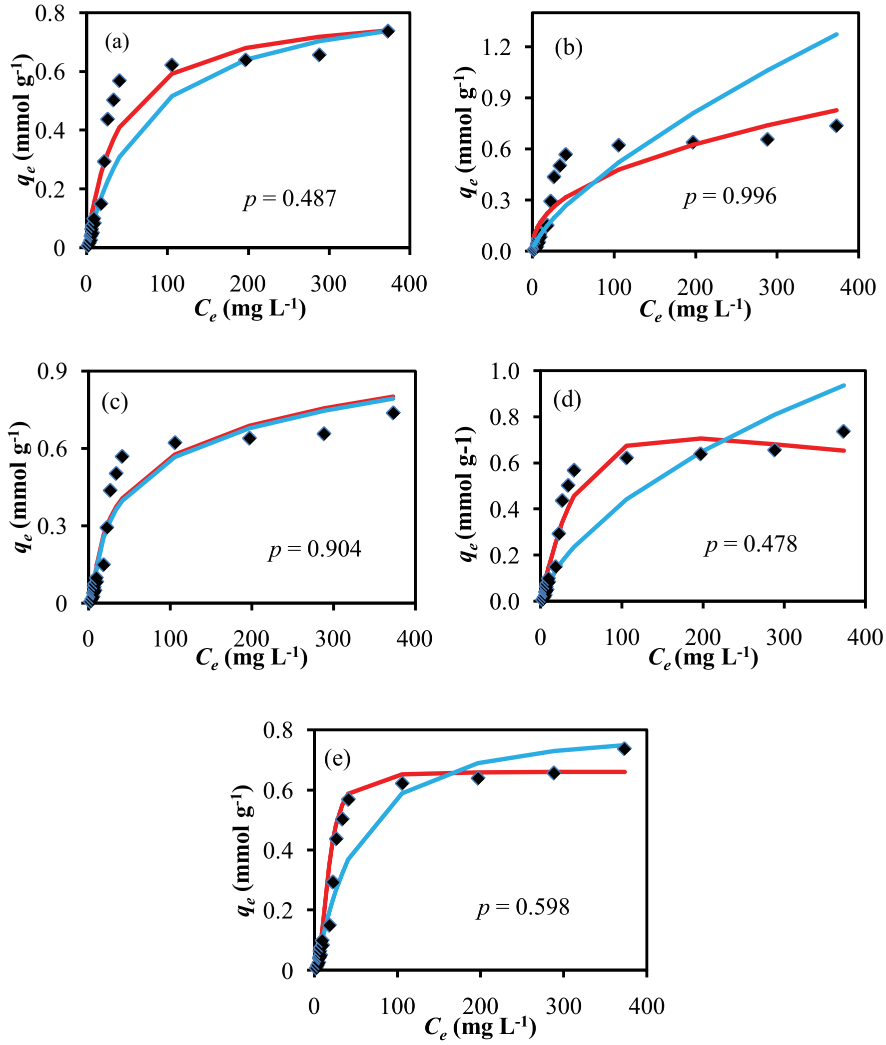

Fig. 7. Comparison of experiment data (◆) for (a) Langmuir, (b) Freundlich, (c) Temkin, (d) Redlich–Peterson, and (e) Sips isotherm models with linear (blue line) and nonlinear (red line) regression analyses with the p values using ANOVA for adsorption of BG onto Pakis.

of ln$K$ vs. 1/T would help provide insight into whether the adsorption process is favorable, spontaneous, endothermic, or exothermic in nature. Thermodynamics studies carried out at five temperatures, ranging from room temperature to 343 K, as shown in Fig. 8, lead to spontaneous adsorption of BG onto Pakis according to negative $\Delta G°$ values, and further, the adsorption process is overall exothermic in nature as shown by the negative $\Delta H°$ value (Table 6).

$$\Delta G° = \Delta H° - T\Delta S° \quad (2)$$

$$\Delta G° = -RT\ln K \quad (3)$$

$$K = \frac{C_s}{C_e} \quad (4)$$

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (5)$$

3.7. Regeneration and reusability of Pakis

Although there have been many reports on the use of adsorbents to remove heavy metals and dyes, reports on recycling and reusing of spent adsorbents are rather limited. This is an important aspect since the ability to regenerate and reuse an adsorbent would contribute to in terms of cost savings when designing wastewater treatment systems [82]. Hence in this study, the feasibility of regenerating and reusability of BG loaded Pakis was investigated. A total of five consecutive cycles were studied, and the spent Pakis, that is, Pakis that has been used to adsorb BG dye, was washed with 1.0 M HCl, 1.0 M NaOH, or distilled water together with control for comparison purpose. This study is important as it provides information on the ability of Pakis to be reused more than once and hence can reduce cost in wastewater treatment. Fig. 9 indicates that only treatment with acid and base show great regeneration ability with the latter showing the highest regeneration ability. This could be due to the capability of the base in removing surface waxes and fats located on the adsorbent and hence making more exposure on the functional groups for the adsorption process. Moreover, the base would lead to deprotonation of carboxylic acid and alcohol functional groups, creating negatively charged surface sites on the adsorbent, promoting cationic BG dye molecules to be more strongly attracted to the adsorbent. Similar observations have also been reported for other adsorbents which have shown a stronger affinity toward positively charged adsorbates after base treatment [83]. However, the optimum concentration of the base would have to be determined in large-scale treatment processes.

Table 5
Maximum adsorption capacity of selected adsorbents toward BG dye

Adsorbent	q_{max} (mg g^{-1})	Reference
Diplazium esculentum (Pakis)	318.55	This work
Peat	265.4	[37]
Kaolin	65.4	[68]
Pomelo skin	325.0	[69]
Rice husk ash	21.6	[70]
Base treated *Eugenia jambolana* leaves	5.2	[71]
Nephelium mutabile (Pulasan) leaves	130.3	[72]
Neem leaves	70.9	[73]
Psidium guajava (Guava) leaves	1.2	[74]
Peganum harmala activated carbon	18.7	[75]
Cempedak durian peel	98.0	[42]
Red clay	125.0	[40]
Lemon peel waste	150.0	[28]
Amine modified tannin gel	20.4	[76]
Acid activated watermelon rind	188.6	[77]
Modified cellulose with metaphosphoric acid	150.0	[27]
Polyurethane foam materials modified with coal	135.0	[78]
LGB/St/Al_2O_3 biocomposite	226.5	[29]
Saklikent mud	9.7	[79]
Artocarpus odoratissimus (Tarap) peel	174.0	[80]
Binary oxidized cactus fruit peel	166.7	[81]
Magnetic composite (Fe_3O_4@SDBS@LDHs)	329.1	[39]
Dimorcarpus longan ssp. malesianus leaves	337.9	[38]

4. Conclusion

Adsorption of Brilliant green (BG) dye onto *D. esculentum* (Paku Pakis), investigated using batch experimental data, shows that this adsorbent has very high adsorption capacity with q_{max} of 318.55 mg g^{-1} based on Sips isotherm model, reaching equilibrium within 2 h of contact time. The pseudo-second-order kinetic model is the best fit for the adsorption process with a fast k_2 of 10.01 g mmol^{-1} min^{-1}.

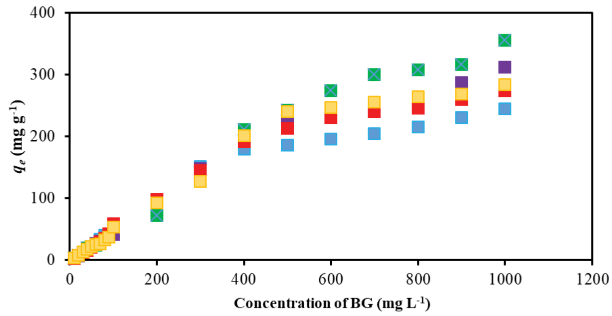

Fig. 8. Adsorption of BG onto Pakis at 298 K (■), 313 K (■), 323 K (■), 333 K (■), and 343 K (■).

Table 6
Thermodynamics data for the adsorption of BG onto Pakis

Temperature (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta H°$ (kJ mol^{-1})	q_{max} (mg g^{-1})
298	–21.675			318.55
313	–25.240			289.59
323	–23.400	54.15	–6.49	337.86
333	–24.948			337.86
343	–24.345			289.59

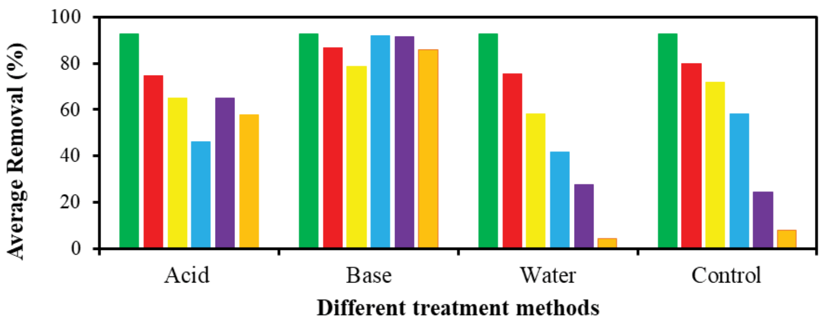

Fig. 9. Regeneration of spent MKL for the adsorption of BG in five consecutive cycles [cycles 0 (■), 1 (■), 2 (■), 3 (■), 4 (■), and 5 (■)].

The adsorbent also exhibits high tolerance to changes in pH solution or salt concentration, whereby the high adsorption towards BG can be maintained. The regeneration experiments reveal that the reusability of the adsorbent is possible through acid and base treatments. The adsorbent can maintain dye adsorption even after five consecutive cycles, with the base performing better than acid. Taking into consideration all of the above-obtained results, as well as being readily available throughout the year, this adsorbent would have good potential for the removal of BG dye from aqueous systems. Its practical applicability would be feasible owing to being low-cost and having strong adsorption characteristics; however, optimization of parameters for dynamic scale and prototype measurements would be a necessity for large-scale removal of BG dye.

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