Adsorption of brilliant green dye on *Nephelium mutabile* (Pulasan) leaves

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Abstract

The main objective of this study is to investigate the ability of *Nephelium mutabile* (Pulasan) leaves (PL) in removing toxic brilliant green (BG) dye using the adsorption method. Batch experiments were conducted on the adsorption of BG dye using PL with a contact time of 3.5 h. Adsorption isotherm studies were analysed using six isotherm models, namely Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R), Redlich-Peterson (R-P) and Sips, and the results showed that Sips is the model that best fits the experimental data, with a maximum adsorption capacity (a_{max}) of 130.3 mg g^{-1}. The point of zero charge (pH$_{PZC}$) of PL was found to be at pH 5.29. Regeneration studies showed that PL can be recovered and reused, especially after treatment with NaOH. This study demonstrates that PL can be considered as a reasonably good and cost-effective biosorbent for BG under our experimental conditions.

Index Terms: Nephelium mutabile, adsorbent, adsorption isotherm, brilliant green dye

1. Introduction

Dye is generally used to colour substances, either by soaking the material in a solution impregnated with a dye or directly on the fiber. In the latter case, a mordant is required in order to improve the fastness of the dyeing process.[1] Dyes can be from natural or synthetic sources. Both dyes and pigments are coloured because they absorb only some wavelengths of visible light. Dyes are usually soluble in water whereas pigments are insoluble. Some dyes can be rendered insoluble with the addition of salt to produce a lake pigment.[2] The majority of natural dyes are derived from plant sources: roots, berries, bark, leaves, and wood, fungi, and lichens.[3] However, the discovery of man-made synthetic dyes in the late 19th century ended the large-scale market for natural dyes.[4] Synthetic dyes are made from petroleum, sometimes in combination with mineral-derived components.[1] Many dyes are organic compounds.[5] The dyes are classified according to their solubility and chemical properties. There are different types of dyes: acidic, basic, mordant, reactive and dispersive dyes.[6] These dyes are produced and applied in large quantities by many different industries. Therefore, it is a challenge to treat dye effluents because of their synthetic origins and complex aromatic structures, which are biologically non-degradable and could be harmful to health.

Nephelium mutablie, often called Pulasan or wild rambutan, belongs to the family Sapindaceae, which is a tropical seasonal fruit closely allied to the *Nephelium lappaceum* (rambutan). The fruits are quite popular as it is sweeter than the rambutan and lychee, but it is very rare outside Southeast Asia. Pulasan is a seasonal fruit and, during the period of this study, the Pulasan fruits were not in season. So instead of using the fruit peel, Pulasan leaves (PL) were chosen as the adsorbent. Furthermore, the leaves are in abundance throughout the year, a necessary criterion for a low-cost adsorbent. Because of this, this project utilized PL in the adsorption of a selected dye, *viz.* brilliant green (BG) dye.

BG is one of the triarylmethane dyes with the chemical formula $C_{27}H_{33}N_2.HO_4S$ and a molecular weight of 482.64 g mol^{-1}. When

dissolved in water, it gives a blue-coloured solution with a maximum absorbance at a wavelength of 624 nm. BG is used widely in many industries to colour silk and wool. Even the dilute alcoholic solution of BG is sold in Eastern Europe and Russia as a topical antiseptic due to its effectiveness against Gram-positive bacteria.[7,8] The main advantage of BG over more common antiseptics such as iodine is that it does not irritate mucous membranes as harshly. However, if swallowed, BG can induce vomiting and it can be toxic upon ingestion. If BG comes in contact with the eyes, it can cause corneal opacification and lead to bilateral blindness.[9] Hence, the potential of PL as a low-cost adsorbent in the removal of BG from aqueous solutions is worth investigating.

2. Experimental approach

2.1 Sample preparation and chemical reagents
The Pulasan leaves (PL) were freshly plucked from a tree and washed with water for several times to remove dust on the surface. Then they were thoroughly rinsed with distilled water and dried in an oven at 80°C for about a week, to remove all moisture, until a constant mass was obtained. The dried sample was blended using a blender and sieved using a laboratory metal sieve to obtain a particle size of less than 355 μm. The sieved sample was stored in a zip-lock plastic bag to prevent moisture build-up and avoid contamination.

Brilliant green (BG) dye with a percentage purity of 90% was purchased from Sigma Aldrich Corporation, and was used without further purification. 1000 mg L^{-1} of BG stock solution was prepared by dissolving 1 g of the dye in distilled water in a 1 L volumetric flask. To obtain solutions of different concentrations, this stock solution was appropriately diluted by adding distilled water.

2.2 Calibration curve
For the calibration curves of the BG dye, 2, 4, 6, 8 and 10 mg L^{-1} concentrations of standard solutions were prepared.

2.3 Instrumentation
To measure the absorbance of the BG solutions, a Shimadzu UV-1601PC spectrophotometer was used at a wavelength of 624 nm. Also, a Stuart Scientific Flask Shaker SF_1 was used to mix the adsorbent with the dye solution at 250 rpm. In order to identify the functional groups present in the PL, a Shimadzu IRPrestige-21 spectrophotometer (FTIR) Scanning Electron Microscope (SEM) was used to observe the morphology of the adsorbent's surface.

2.4 Adsorption studies
Similar procedures as reported by Lim *et al.*[10] were followed in this study to investigate the effects of contact time, pH, and ionic strength on the adsorption of BG onto the PL. However, there were slight changes to the methods cited above, as the concentration of BG used to test the effects of contact time was 100 mg L^{-1} and an additional three salts were used to test the effects of ionic strength, namely NaCl, NaNO$_3$ and KCl, as well as KNO$_3$.

For regeneration studies of the spent adsorbent, 0.4 g of the adsorbent was placed into a 500 mL conical flask containing 200.0 mL of 100 mg L^{-1} dye solution. The ratio of the volume of dye to the mass of adsorbent was 1:500, as 1 g of sample was mixed with 500.0 mL of dye. The flask was then shaken using a shaker at 250 rpm at room temperature for an optimum shaking time. After filtration, the solid residues were collected and dried in an oven at around 60 °C overnight, while the filtrate was diluted to 10 mg L^{-1} for the analysis of absorbance using the UV-Vis spectrophotometer.

The dried solid residues were weighed and divided into five portions in 250 mL labelled conical flasks for treatment purposes. The residual solids were treated with HCl (0.1 M), NaOH (0.1 M), distilled water (shake and rinse) and a control was also set up. In the treatments with acid, base and distilled water, the volumes used were chosen to give a 1:20 ratio. After being washed with desorbing agents, the residues were placed back in the oven to dry. This alternation of

adsorption and desorption steps was continued for five consecutive cycles.

3. Characterization of PL

The point of zero charge (pH$_{PZC}$) was used to determine the pH at which the adsorbent's surface has zero charge. *Figure 1* shows that the pH$_{PZC}$ of the PL was determined to be pH 5.29. This value can be determined from the point of intersection of the plot of ΔpH against the initial pH at which the ΔpH is zero (see *Figure 1*). When the pH is less than pH$_{PZC}$, the adsorbent's surface will be predominantly positively charged due to protonation and hence will attract anions from the solution. By contrast, at pHs greater than the pH$_{PZC}$, the adsorbent's surface will be predominantly negatively charged due to deprotonation and hence attract cations from the solution. In this case, when pH < 5.29 the PL's surface is expected to be positively charged, and negatively charged when pH > 5.29. At pH = 5.29 the PL's surface has zero net charge.
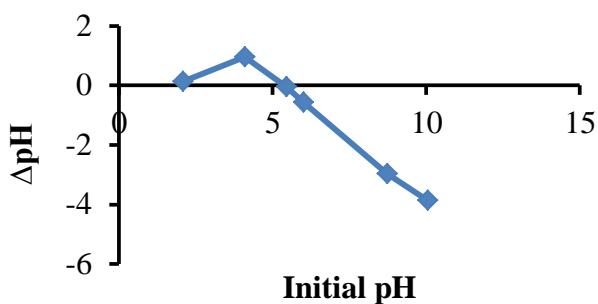

Figure 1. Plot to determine the point of zero charge of PL. (Mass of adsorbent: 0.05 g; volume of KNO$_3$: 25.0 mL; conc. of KNO$_3$: 0.1 mol L^{-1}; room temperature; pH: 2-10)

The SEM images of the PL, before and after adsorption with BG, are shown in *Figure 2* with a magnification of 800x. Untreated PL, as shown in *Figure 2 (a)*, have a rough, undulating surface with many folds. However, after adsorption of BG, there was a distinct change in the surface morphology of the PL, indicating that BG was adsorbed, as shown in *Figure 2 (b)*.
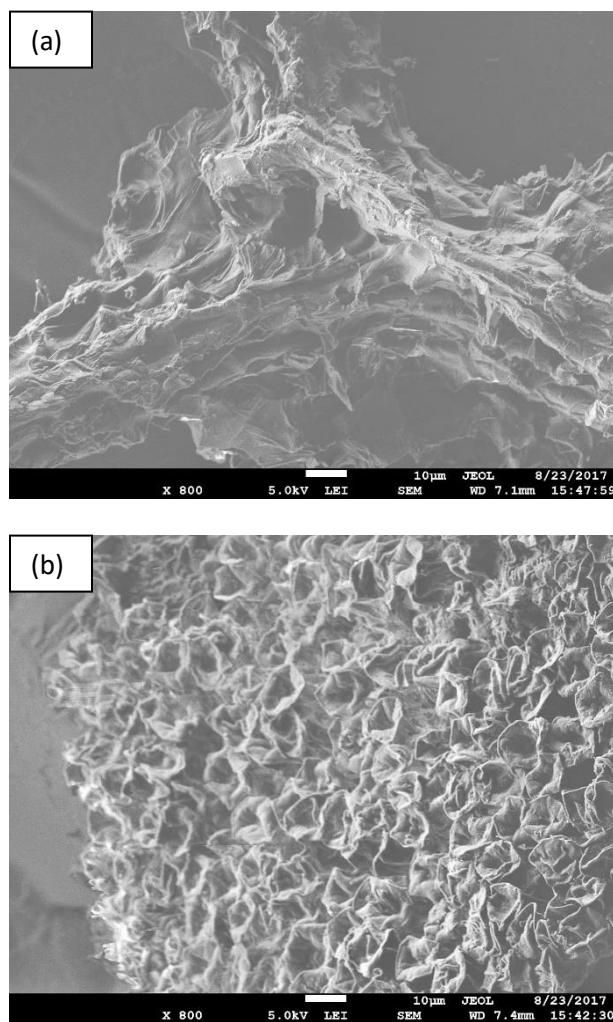

Figure 2. SEM images of the PL (a) untreated and (b) treated with BG at 800x magnification

Figure 3 shows the FTIR spectra of the untreated PL and the BG-loaded PL. As can be observed from the spectrum of the untreated PL (in black), functional groups such as alkenes (C=C) at 1621 cm^{-1}, C=O at about 1724 cm^{-1}, alkyls (CH) at 2926 cm^{-1}, and amines (NH) and hydroxyls (OH) at 3309 cm^{-1} are present. After being treated with BG, the spectrum (in blue) indicated shifts in the amino, hydroxyl, alkene and carboxyl groups, which suggests that these groups could be involved in the adsorption of BG dye.
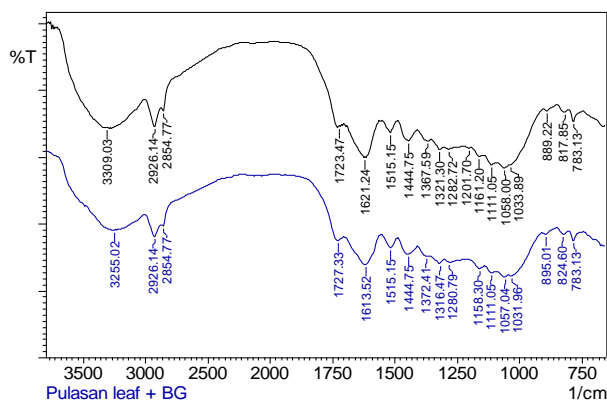
Figure 3. FTIR spectra of the untreated PL (black) and the PL treated with BG (blue)

4. Results and Discussion.

4.1 Effect of contact time

Figure 4 shows the extent of the adsorption of BG by the PL adsorbent over four hours. Approximately 65% of the BG dye was adsorbed by the PL and equilibrium was reached within 210 minutes. It can be observed that there was a rapid adsorption of BG dye for the first 30 minutes of the contact time. This was due to the availability of vacant sites on the surface of the adsorbent, together with the high concentration of the dye. After some time, the rate of adsorption slowed down until it reached equilibrium, once all the sites on the adsorbent were occupied by dye molecules. Hence the contact time used for the rest of the study was set at 3.5 hours to ensure that complete equilibrium was reached.

4.2 Effects of pH

In real-life situations, the actual pH of the wastewater may be more acidic or basic than the ambient pH, thus there is a need to study the effects of pH.[11] Investigation of the effects of the pH of the dye solution on the adsorption capacity of PL should consider possible changes in both the degree of ionization of the dye and its surface properties.[12] As a result of these changes, the ability of an adsorbent to adsorb dye will vary with the pH of the aqueous solution. A study of the adsorption process was therefore performed using different pHs of BG, and the results are shown in ***Figure 5***.
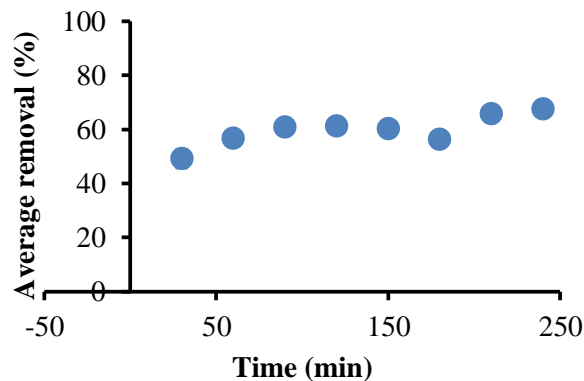

Figure 4. Effect of contact time on the removal of BG (Mass of adsorbent: 0.050 g; volume of BG: 25.0 mL; conc. of BG: 100 mg L^{-1}; room temperature; ambient pH)
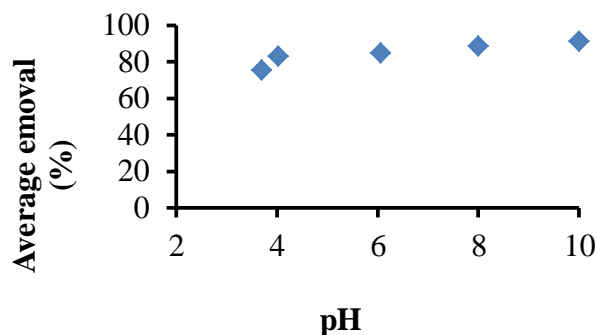

Figure 5. The effect of pH on the adsorption of BG onto the PL (Mass of adsorbent: 0.050 g; volume of BG: 25.0 mL; conc. of BG: 100 mg L^{-1}; room temperature; pH: ambient (3.69), 4.02, 6.06, 8 and 10)

A previous report by Chieng *et al.*[13] has shown that BG is unstable at extreme pHs. Hence, this study was limited to pHs between 3.7 and 10. The recorded untreated (ambient) pH of BG was 3.69, and at this pH removal of about 75% of BG dye was observed. Above this pH, from pH 4.02 to 10.0, there was a slight increase in the removal of BG dye which was probably due to a decrease in the concentration of H$^+$ ions in the aqueous solution and also due to the electrostatic attraction between the adsorbent and the dye molecules. This study shows that the PL has the ability to adsorb BG over a wide range of pHs. Unlike adsorbents such as *Luffa cylindrica* sponge[14] and some reported agriculture wastes,[15] which show a decrease in adsorption of BG at

higher pHs, PL are resilient to changes in the pH of the medium. This is an advantage especially in real-life applications of wastewater treatment, where the pH varies.

4.3 Adsorption isotherm of BG onto the PL

Batch adsorption isotherm was carried out at room temperature using BG concentrations ranging from 0 to 1000 mg L^{-1}. The experimental data obtained were fitted to six different isotherm models, namely Langmuir,[16] Freundlich,[17] Temkin,[18] Dubinin-Radushkevich (D-R),[19] Redlich-Peterson (R-P)[20] and Sips,[21] the linear equations for which are shown in **Table 1**. Six error functions (shown in **Table 2**) were used to help in identifying the best-fit model, especially in situations where all the models were in close agreement with the experimental data.

Table 1. Brief descriptions of the types of isotherm used.[16-21] [Here, C_e is the equilibrium concentration of dye solution (mg L^{-1}); q_e is the equilibrium dye concentration on the bio-sorbent (mmol g^{-1}); q_{max} is the maximum adsorption capacity of the PL for BG; K_L, K_F, K_T, K_R and K_S are the Langmuir, Freundlich, Temkin, Redlich-Peterson and Sips adsorption constants respectively; n (in the Freundlich model) is an empirical parameter related to the adsorption capacity and is typically in the range $0 < n < 1$; b_T is the Temkin constant related to the heat of adsorption; R is the gas constant; and T is the temperature (in Kelvin) at which the adsorption takes place.]

Isotherm Model	Linearized Equation	Linear Plots
Langmuir	$\dfrac{C_e}{q_e} = \dfrac{1}{q_{max}} C_e + \dfrac{1}{q_{max}}\left(\dfrac{1}{K_L}\right)$	$\dfrac{C_e}{q_e}\,vs.\,C_e$
Freundlich	$\log q_e = \dfrac{1}{n}\log C_e + \log K_F$	$\log q_e\,vs.\,\log C_e$
Temkin	$q_e = \left(\dfrac{RT}{b_T}\right)\ln K_T + \left(\dfrac{RT}{b_T}\right)\ln C_e$	$q_e\,vs.\,\ln C_e$
Dubinin-Radushkevich (D-R)	$\ln q_e = \ln q_{max} - \beta\varepsilon^2$ where β is the D-R constant, Polanyi potential: $\varepsilon = RT\ln\left(1 + \dfrac{1}{C_e}\right)$ Mean free energy: $E = \dfrac{1}{\sqrt{2\beta}}$	$\ln q_e\,vs.\,\beta\varepsilon^2$
Redlich-Peterson (R-P)	$\ln\left(\dfrac{K_R C_e}{q_e} - 1\right) = n\ln C_e + \ln a_R$	$\ln\left(\dfrac{K_R C_e}{q_e} - 1\right)vs.\,\ln C_e$
Sips	$\ln\left(\dfrac{q_e}{q_{max} - q_e}\right) = \dfrac{1}{n}\ln C_e + \ln K_S$	$\ln\left(\dfrac{q_e}{q_{max} - q_e}\right)vs.\,\ln C_e$

Figure 6 shows simulated plots of the six chosen isotherm models together with the experimental data. The linear regression coefficients (R^2) and error values of the six isotherm models used are shown in **Table 3**. Based on the simulation plots, it is clear that the D-R model deviates from the experiment data and hence can be ruled out. All the other five models are in good agreement with the experimental data. Even though the Sips model does not give the highest R^2 value, it was chosen as the best isotherm model since it has the lowest overall error values when compared to the other models, and its R^2 value is good (> 0.95). The Langmuir model, which describes monolayer adsorption, gives the highest R^2 value, but its overall errors are much higher.

The maximum adsorption capacity (q_{max}) of the PL based on the Sips and Langmuir models is 130.3 mg g^{-1} and 102.6 mg g^{-1}, respectively, as shown in **Table 3**. In comparison with the other selected adsorbents (see **Table 4**), PL have a higher q_{max} than some natural adsorbents (e.g. Luffa sponge, kaolin) and even adsorbents that have undergone modification with an acid (almond peel) or a base (saw dust). However, their q_{max} is lower than some reported adsorbents such as peels of pomelo and *Artocarpus odoratissimus.* Nevertheless, PL have a good q_{max}, making it a potentially useful adsorbent for real-life wastewater treatment.

4.4 Effects of ionic strength
In a real-life situations, the wastewater produced by industrial processes may be polluted with different kinds of cations and anions with different concentrations.[11] In this study, the effects of ionic strength were investigated to see if increasing the concentrations of NaCl, NaNO$_3$, KCl or KNO$_3$ (0, 0.01, 0.1, 0.2, 0.4, 0.6, 0.8 and, 1.0 mg L^{-1}) influences the adsorption of 100 mg L^{-1} of BG on the PL.

Figure 7 shows the effects of varying ionic strengths on the adsorption of BG dye. It can be observed that as the concentration of all the salts increases from 0 to 1.0 mg L^{-1}, the percentage removal of the BG dye decreases. Initially, the presence of the salts tends to affect the interactions between the PL and BG through competition between the cations from the salts (Na$^+$ and K$^+$) with the cationic BG for the available active sites on the PL.[30-31] The increase in the salt concentrations also indirectly disturbs the equilibrium, which can affect the operation of the adsorption of BG onto the PL.[32]

Table 2. The six error functions used. [Here, $q_{e,meas}$ and $q_{e,calc}$ are the experimental and calculated values respectively; n is the number of experimental data points and p is the number of parameters in the model.]

Type of errors	Equations
Average relative error (ARE)	$\dfrac{100}{n}\displaystyle\sum_{i=1}^{n}\left\| \dfrac{q_{e,meas}-q_{e,calc}}{q_{e,meas}} \right\|_i$
Sum square error (SSE)	$\displaystyle\sum_{i=1}^{n}(q_{e,calc}-q_{e,meas})_i^2$
Hybrid fractional error function (HYBRID)	$\dfrac{100}{n-p}\displaystyle\sum_{i=1}^{n}\left[\dfrac{(q_{e,meas}-q_{e,calc})^2}{q_{e,meas}}\right]_i$
Sum of Absoulte Error (EABS)	$\displaystyle\sum_{i=1}^{n}\left\|q_{e,meas}-q_{e,calc}\right\|$
Marquardt's percent standard deviation (MPSD)	$100\sqrt{\dfrac{1}{n-p}\displaystyle\sum_{i=1}^{n}\left(\dfrac{q_{e,meas}-q_{e,calc}}{q_{e,meas}}\right)_i^2}$
Non-linear Chi-Square (x^2)	$\displaystyle\sum_{i=1}^{n}\dfrac{(q_{e,meas}-q_{e,calc})^2}{q_{e,meas}}$

4.5 Regeneration studies
A regeneration study of the adsorbent is important because it helps in the recovery of the adsorbates, especially where precious metals are involved, and the reusability of adsorbents reduces the costs of wastewater treatment. In this study, three solvents (HCl, NaOH and distilled water) were used to treat the BG-loaded adsorbent, and the study was carried out for five consecutive cycles. A control experiment was also carried out for comparison purposes.

The spent PL adsorbent can be reused while retaining similar adsorption capabilities even in the fifth cycle, as shown by the control experiment shown in *Figure 8*. Furthermore, successive treatment of the PL with HCl, NaOH or distilled water all showed that the spent PL

were still able to remove BG well, even after the fifth cycle. Both acid and base treatments were able to enhance the adsorption capacity of the PL, with NaOH being the most effective method of regeneration.

5. Conclusion.
In conclusion, PL have the potential to be used as a low-cost adsorbent for the removal of BG, as they have a high maximum adsorption capacity for the removal of BG. The adsorption of BG is best described by the Sips isotherm model. The presence of high concentrations of salts in the aqueous solution seems to have a great influence on the adsorption of BG. Nonetheless, the ability to regenerate and be reused further enhances the potential of the PL as a possible adsorbent for removing BG.

Table 3. The adsorption isotherm constants, linear regression coefficient (R^2) and error functions for the six isotherm models used to describe the adsorption of BG onto the PL.

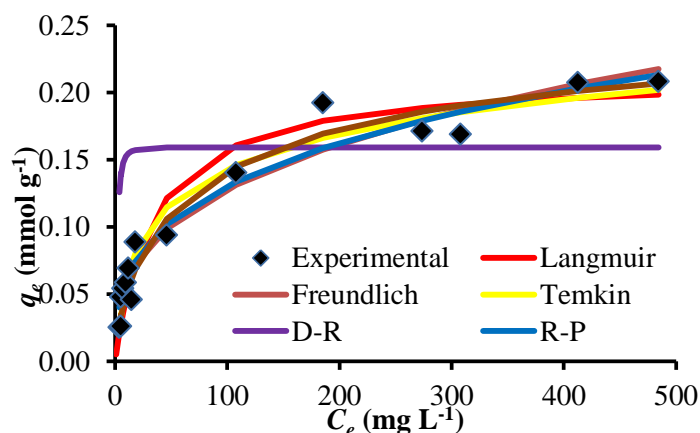| Model		R^2	Error functions					
			ARE	SSE	HYBRID	EABS	MPSD	$\varkappa^2$
Langmuir		0.9833	16.71	0.0041	0.32	0.23	22.21	0.049
q_{max} (mmol g^{-1})	0.21							
q_{max} (mg g^{-1})	102.63							
K_L (L mmol^{-1})	0.03							
Freundlich		0.9366	16.73	0.0034	0.36	0.17	31.88	0.055
K_F (mmol g^{-1})	0.03							
K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	13.13							
n	2.97							
Temkin		0.9603	13.87	0.0029	0.25	0.17	21.28	0.037
K_T (L mmol^{-1})	0.47							
b_T (kJ mol^{-1})	66.45							
Dubinin-Radushkevish		0.8895	115.25	0.084	12.56	0.99	187.52	1.89
q_{max} (mmol g^{-1})	0.16							
q_{max} (mg g^{-1})	76.87							
B (J mol^{-1})	7.29x10^{-7}							
E (kJ mol^{-1})	827.94							
Redlich Peterson		0.9821	15.94	0.0031	0.35	0.17	30.45	0.048
K_R (L g^{-1})	0.05							
α	0.70							
a_R (L mmol^{-1})	1.48							
Sips		0.9518	14.52	0.0029	0.24	0.18	20.10	0.034
q_{max} (mmol g^{-1})	0.27							
q_{max} (mg g^{-1})	130.32							
K_S (L mmol^{-1})	0.05							
n	1.45							

Figure 6. Simulation plots of the six isotherm models, together with the experimental data for the adsorption of BG onto the PL (Mass of adsorbent: 0.050 g; volume of BG: 25.0 mL; conc. of BG: 0-1000 mg L^{-1}; room temperature; ambient pH)

Table 4. Maximum adsorption capacity (q_{max}) of the PL and other reported adsorbents for the removal of BG.

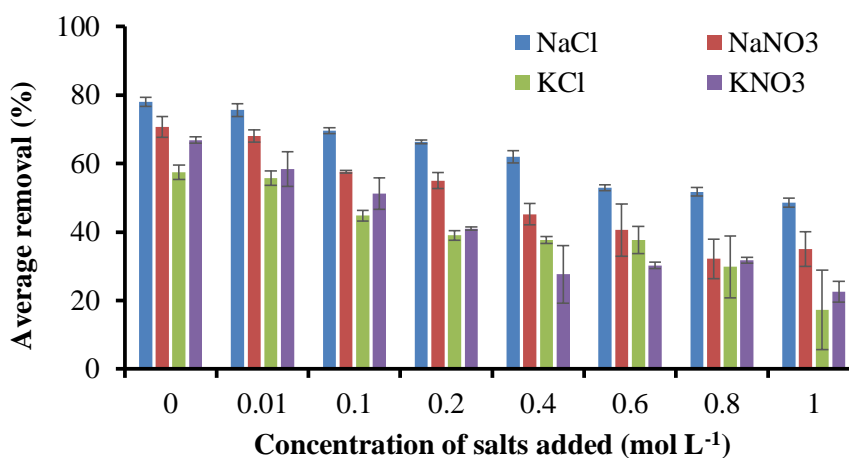| Adsorbent	q_{max} (mg g^{-1})	Reference
Nephelium mutabile (pulasan) leaves	130.3 (Sips)	This study
	102.6 (Langmuir)	
Peat	265.0	[13]
Luffa cylindrica sponge	18.2	[14]
Acid treated almond peel	30.0	[22]
NaOH treated saw dust	58.5	[23]
Kaolin	65.4	[24]
Red clay	125.0	[25]
Pomelo skin	325.0	[26]
Rice straw biochar	111.1	[27]
Artocarpus odoratissimus peel	174.0	[28]
Cempedak durian peel	98.0	[29]

Figure 7. The effect of ionic strength on the adsorption of BG using four salts (Mass of adsorbent: 0.05 g; volume of BG: 25 mL; conc. of BG: 100 mg L^{-1}; room temperature; pH: ambient; types of salt: KCl, NaCl, KNO$_3$, NaNO$_3$; conc. of salt: 0 to 1 mol L^{-1})
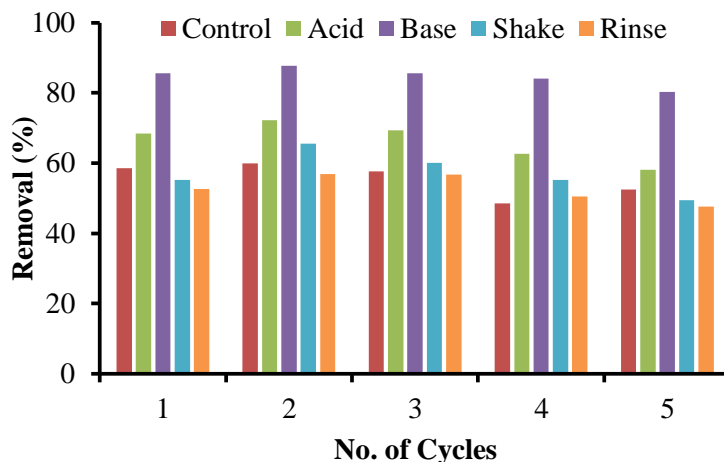
Figure 8. Regeneration of PL for five consecutive cycles with different desorbing agents (Ratio of mass of adsorbent and volume of BG: 1 g: 500 mL; conc. of BG: 100 mg L^{-1}; room temperature, pH: ambient; desorbing agents: HCl, NaOH, water; ratio of mass of adsorbent and volume of desorbing agents: 1 g: 50 mL; conc. of HCl and NaOH: 0.1 mol L^{-1})

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