

Adsorption characteristics of pomelo skin toward toxic Brilliant Green dye

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Abstract

Pomelo skin was investigated for its adsorption ability toward Brilliant Green dye. Experimental conditions used in this study were 2 h contact time; PS dosage = 0.04 g and ambient temperature. No adjustment of medium pH was required throughout the study and pomelo skin was able to maintain good adsorption capability under various ionic strengths. Of the three isotherm models (Langmuir, Freundlich and Sips) used to fit the experimental data, the adsorption was best described by the Freundlich model, indicating multi-layer adsorption onto a heterogeneous surface, followed by the Sips and the Langmuir models. Adsorption was exothermic in nature and kinetics was best described by the pseudo second order and pore diffusion was found to be not the rate determining step. Successful regeneration and reusability of spent pomelo skin, coupled with high maximum adsorption capacity (q_{max}) of 325 mg/g (Langmuir) and 400 mg/g (Sips) at 25 °C compared with many reported adsorbents, make pomelo skin a potential candidate to be considered in real life application of wastewater remediation.

Index Terms: pomelo skin, low-cost adsorbent, adsorption isotherm, brilliant green dye

1. Introduction

Industrialisation and exponential growth in the world's population have resulted in severe environmental pollution, thereby causing global concern. Irresponsible dumping of wastes into the water systems has caused severe damage to aquatic organisms and plants. The past couple of decades have seen the emergence of various adsorbents for the remediation of wastewater. These adsorbents ranged from industrial¹⁻³ to agricultural wastes,⁴⁻⁸ synthetic materials⁹ to natural biosorbents,¹⁰⁻¹³ as well as surface modified adsorbents¹⁴ and many others^{15, 16}.

Brilliant green (BG) dye, also known as malachite green G, belongs to the triarylmethane dyes. It is known to be toxic when ingested and can cause vomiting.¹⁷ This dye has also been reported to cause corneal opacification when 1% of this dye solution came in contact with the eye.¹⁸

In this study, we report the use of pomelo skin (PS) as a low-cost natural adsorbent for the removal of BG. The skin of the fruit is inedible and often discarded as waste. As such, PS can be obtained easily and at abundance making it an ideal sample to be used as an adsorbent. Reports have shown that PS has been successfully utilised as an adsorbent for the removal of heavy metals such as Cu(II),¹⁹ Pb(II),²⁰ Cd(II),²¹ as well as dyes such as methylene blue,²² reactive blue 114,²³ and acid blue 15.²⁴ PS has also been reported to clean up oil spill from simulated seawater.²⁵ These studies along with the fact that PS is easily available and abundant make it a good low-cost adsorbent. To the best of our knowledge, the use of PS for the removal of BG has not been investigated.

2. Experimental

2.1. Sample preparation and chemicals

Pomelo fruits were purchased from the supermarket and had their skin separated from the

flesh. The skin was dried in an oven at 70 °C until constant mass was obtained. The dried skin was then blended using normal household blender and sieved to obtain particle size of 355-850 µm and was stored in airtight plastic bag.

Brilliant green dye, IUPAC name 4-([4-(diethylamino)phenyl](phenyl)methylene)-N,N-diethyl-2,5-cyclohexadien-1-iminium hydrogen sulfate (molecular formula C₂₇H₃₄N₂O₄S and M_r=483 g/mol), was purchased from Sigma-Aldrich. Sodium hydroxide (Univar) and nitric acid (AnalaR) were diluted and were used in adjusting the solution's pH. Stock solution of potassium nitrate (Sigma-Aldrich) was prepared and diluted to different concentrations. All reagents were used without further purification and distilled water was used throughout the experiment.

2.2. Experimental setup

The experiment was done using batch experiment method. PS was mixed with BG solution and agitated using Stuart orbital shaker at 250 rpm for predetermined time. The filtrate was collected and analysed using UV-visible (UV-vis) Jenway 6320D spectrophotometer at wavelength 624 nm. The adsorption capacity of PS, q_e (mg/g) and the percentage removal are calculated as follow:

$$q_e(\text{mg/g}) = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$\text{Removal (\%)} = \frac{(C_i - C_e) \times 100 \%}{C_i} \quad (2)$$

where C_i is the dye concentration initially (mg/L), C_e is the filtrate dye concentration (mg/L), V is the dye volume used (L) and m is the mass of PS (g).

2.2.1. Effect of contact time

PS (0.4 g) was weighed into 13 conical flasks and 100 mg/L BG solution (20.0 mL) was added into each of the flasks. The mixtures were then agitated at 250 rpm at room temperature (25 °C). One flask was taken at the interval of 5, 10, 15, 20, 25, 30, 60, 90, 120, 150, 180, 210 and 240 min. The filtrate was then analysed using UV-vis spectrophotometer.

2.2.2. pH effect

The pH of 10 mg/L BG solution (20.0 mL) was adjusted to 4, 6, 8 and 10 using NaOH and HNO₃ and measured using Thermo-Scientific pH meter. Each of the pH adjusted BG solution was then mixed with PS (0.4 g) and agitated at 250 rpm for 2 h. The filtrate was collected and analysed using UV-vis spectrophotometer.

2.2.3. Point of zero charge

0.1 mol/L KNO₃ solutions (20.0 mL) were prepared and their pH was adjusted to 2, 4, 6, 8 and 10. These solutions were then mixed with PS (0.4 g) and agitated at 250 rpm for 24 h. The final pH was measured and the plot of ΔpH (final pH - initial pH) vs initial pH was used for the determination of PS's point of zero charge.

2.2.4. Effect of ionic strength

10 mg/L BG solutions (20.0 mL) containing various concentration of KNO₃ (0.01, 0.1, 0.2, 0.4, 0.6 and 0.8 mol/L) solutions were prepared and mixed with PS (0.4 g). These mixtures were then agitated at 250 rpm for 2 h and the dye content was analysed.

2.2.5. Adsorption isotherm

A series of BG solution (20.0 mL) ranging from 10 – 1000 mg/L was prepared and mixed with PS (0.4 g). The mixtures were agitated for 2 h at 250 rpm before the filtrate was collected and analysed.

2.2.6. Thermodynamic studies

PS (0.4 g) was mixed with 50 mg/L BG solution and the mixture was agitated at 25, 40, 50, 60 and 70 °C. The filtrate was collected and analysed.

2.2.7. Regeneration

Spent PS was collected from the agitation of PS with 100 mg/L BG solution and washed with distilled water to remove excess dye. It was then divided into three parts where one part was mixed with distilled water (50.0 mL); the other was mixed with 0.1 mol/L HNO₃ (50.0 mL) and the final part was mixed with 0.1 mol/L NaOH (50.0 mL). These mixtures were agitated for 2 h at 250 rpm before they were filtered and further washed using distilled water until the filtrates were near neutral. The treated PSs were then dried in an oven

overnight before mixing them with fresh 100 mg/L BG and the dye content was analysed using UV-vis spectrophotometer. This is considered as one cycle and the regeneration experiment was done for 5 cycles.

3. Results and Discussion

3.1. Adsorption parameters

Parameters such as contact time for the adsorbent-adsorbate system to reach equilibrium, effects of medium pH and ionic strength on BG removal were investigated. As shown in **Figure 1**, rapid removal of BG was observed during the first half an hour which then gradually slowed down to a plateau when full equilibrium is reached. This observation can be attributed to initial presence of a large number of active vacant sites on the surface of PS which allowed rapid adsorption of BG. However, over time as these sites began to be filled by dye molecules, the rate gradually decreased and eventually reached equilibrium. In this study, the best contact time was taken as 2 hours and all subsequent experiments were carried out using this contact time, unless otherwise stated.

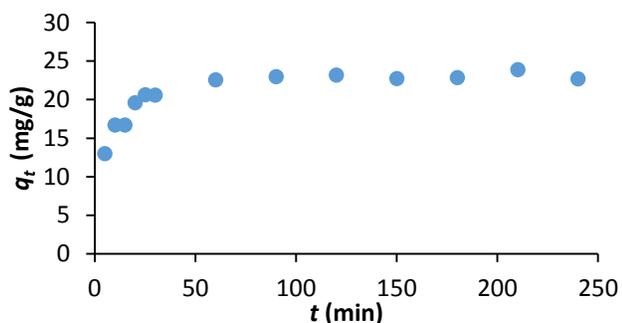


Figure 1. Effect of contact time for the removal of BG onto PS [dye concentration = 100 mg/L; dye volume = 20.0 mL; mass of PS = 0.04 g; ambient pH; stirring rate = 250 rpm and room temperature]

When the effect of medium pH was tested over the range of pH 4 to 10, the adsorbent showed a reduction of 40% BG removal at high pH, while at pH 4 a slight reduction of 8% was observed (**Figure 2**).

The point of zero charge (pH_{pzc}) of PS was found to be at pH 3.53, as shown in **Figure 3**. Any $\text{pH} > \text{pH}_{\text{pzc}}$ will result in deprotonation of the surface

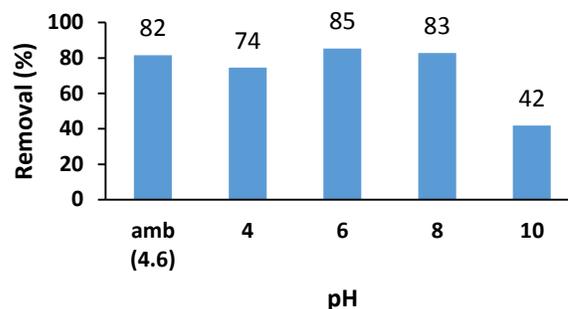


Figure 2. Effect of medium pH on the adsorption of BG onto PS [contact time = 2 h; dye concentration = 10 mg/L; dye volume = 20.0 mL; mass of PS = 0.04 g; stirring rate = 250 rpm and room temperature].

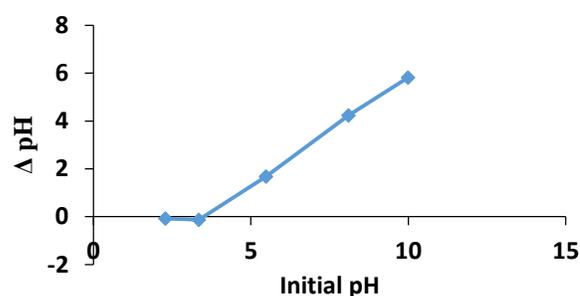


Figure 3. Point of zero charge of PS [contact time = 24 h; salt solution volume = 20.0 mL; mass of PS = 0.04 g; stirring rate = 250 rpm and room temperature].

functional groups of PS, causing the surface to be predominantly negative in charge. Since BG is a cationic dye, this will enhance attraction between the dye molecules and the negatively charged surface, resulting in higher removal of BG as shown by the increase in percentage removal from pH 4 to 6. From pH 8 to 10, a drastic reduction was observed. Cheing et al.²⁶ reported that BG is unstable at $\text{pH} < 3$ and $\text{pH} > 10$. From their study, it was also shown that the absorbance of BG was greatly reduced at pH 10 due to alkaline fading,²⁷ which could explain the 40% reduction observed in this study. While at low pH, the formation of BGH^{2+} also causes the fading of the dye colour intensity. Further, when $\text{pH} < \text{pH}_{\text{pzc}}$, both the surface of PS and BG will be positively charged due to protonation taking place and this results in an electrostatic repulsion between the adsorbate and the adsorbent. Hence, a decrease in the dye removal. Similar finding was reported for kaolin.²⁸

Since the removal of BG by PS was 82% at untreated (ambient) pH, which was comparable to that of pH 6 with the highest observed percentage removal of 85%, no medium pH adjustment was deemed necessary and the ambient pH was used throughout this study.

The effect on ionic strength using 0 to 0.8 mol/L KNO_3 showed that PS was resilient to change in salt concentration (**Figure 4**). It was able to maintain good adsorption of BG over the range studied with only 9% reduction being observed at 0.1 mol/L KNO_3 . Many reported adsorbents such as duckweed,²⁹ breadnut peel,²⁹ leaf¹¹ and stem axis of *Artocarpus odoratissimus*,³⁰ showed drastic reduction of more than 30% in adsorption capacity towards adsorbates with increasing salt concentration. Since salts are usually present in wastewater, the fact that PS was still able to maintain good adsorption capacity indicates its potential as an adsorbent in wastewater remediation.

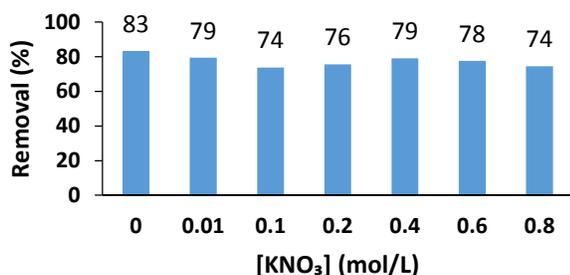


Figure 4. Effect of ionic strength on the adsorption of BG onto PS at different $[\text{KNO}_3]$ PS [contact time = 2 h; dye concentration = 100 mg/L; dye volume = 20.0 mL; mass of PS = 0.04 g; ambient pH; stirring rate = 250 rpm and room temperature].

3.2. Adsorption isotherm of BG onto PS

Adsorption isotherm was carried out for BG dye concentrations ranging from 0 – 1000 mg L^{-1} and the experimental data was fitted to the Langmuir,³¹ Freundlich³² and Sips³³ isotherm models, whose linearised equations are shown below:

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}} \quad (3)$$

$$\text{Freundlich: } \ln q_e = \frac{1}{n_F} \ln C_e + \ln K_F \quad (4)$$

$$\text{Sips: } \ln \left(\frac{q_e}{q_{max} - q_e} \right) = \frac{1}{K_{LF}} \ln C_e + \ln K_S \quad (5)$$

where q_{max} (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the Langmuir constant, K_F ($\text{mg/g}(\text{Lmg}^{-1})^{1/n}$) is the adsorption capacity, n_F value (between 1 and 10) indicates favourability of the adsorption process, K_S (L/g) is the Sips constant and K_{LF} is the exponent.

The Langmuir model assumes a monolayer adsorption where once the active sites are being occupied by the dye molecules, no more adsorption will take place. The Freundlich model, on the other hand, assumes that even though the active sites have been occupied by dye molecules, more adsorption is still possible through multi-layer adsorption. Unlike the Langmuir and the Freundlich models which are two parameter models, the Sips model is a three parameter model which is often known as the Langmuir-Freundlich model. As the name implies, the Sips is a combination of the Langmuir and Freundlich models where at high adsorbate concentration, it follows Langmuir model and follows Freundlich model at low adsorbate concentration.³⁴ Based on the coefficient of determination (R^2), as shown in **Table 1**, the order of best fit model for the adsorption of BG onto PS is Freundlich > Sips > Langmuir. The adsorption is also favorable as indicated by $n_F > 1$, which is further confirmed by $1/n$ lying between 0 and 1 showing adsorption is favorable and heterogeneous. The suitability of the isotherm models was also analysed using two error functions *i.e.* Marquart's percent standard deviation (MPSD) (**Equation 6**) and Chi-test (χ^2) (**Equation 7**). Relying on just the R^2 can be inaccurate as there have been many reports where isotherm models with high R^2 values gave high errors as well. From the error values as shown in **Table 1**, it can be seen that the Freundlich model gave the lowest values, followed by the Sips model, with the Langmuir model giving the highest error values.

$$\text{MPSD: } 100 \sqrt{\frac{1}{n-2} \sum_{i=1}^n (q_{e,meas} - q_{e,calc})^2} \quad (6)$$

$$\chi^2 : \sum_{i=1}^m \frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \quad (7)$$

where $q_{e,meas}$ is the experimental value while $q_{e,calc}$ is the calculated value and n is the number of data in the experiment. Smaller values of these error analysis indicates the better curve fitting.³⁵

Table 1. Adsorption isotherm models and their parameters

Models	Parameters	Values
Langmuir	q_{max} (mg/g)	324.98
	b (L/mg)	0.003
	R^2	0.835
	MPSD	20.35
	χ^2	26.21
Freundlich	$K_F[(\text{mg/g})(\text{L/mg})^{1/n}]$	2.988
	n_F	1.472
	$1/n$	0.679
	R^2	0.993
	MPSD	11.55
Sips	q_{max} (mg/g)	400.00
	K_S (L/g)	0.005
	K_{LF}	1.17
	R^2	0.971
	MPSD	18.78
	χ^2	21.37

The maximum adsorption capacity (q_{max}) of PS for adsorption of BG is 400 mg/g and 325 mg/g based on the Sips and Langmuir isotherm models, respectively. When these values were compared to other reported adsorbents for the removal of BG, PS is indeed a very good low-cost adsorbent as shown by its high q_{max} value in **Table 2**.

Table 2. Maximum adsorption capacity of BG by various adsorbents.

Adsorbent	q_{max} (mg/g)	References
Pomelo skin	400	This work
Peat	266	26
Cempedak durian peel	98	36
Red clay	125	37
Rice straw biochar	111	38
<i>Luffa cylindrical</i> sponge	18	39
Neem leaves	134	40

3.3. Thermodynamics and kinetics studies on the adsorption of BG onto PS

Thermodynamics studies were carried out at temperatures ranging from 298 – 343 K and the

data were fitted into Van't Hoff equation shown below:

$$\Delta G^\circ = -RT \ln K \quad (8)$$

$$K = \frac{C_s}{C_e} \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

Inserting **Equation 8** into **Equation 10**:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

where K is the distribution coefficient for adsorption, C_s is the dye concentration adsorbed on PS (mg/L), R is the gas constant (J/mol K) and T is the absolute temperature (K).

In **Table 3**, it was found that the amount of BG adsorbed decreases as the temperature is raised, indicating an exothermic nature of the adsorption process. This was confirmed by the negative enthalpy (ΔH°) of -16.42 kJ/mol. Negative entropy (ΔS°) and decreasing negativity of the Gibbs energy (ΔG°) point to the adsorption process showing less freedom of movement of molecules and less spontaneous as the temperature increases.

Table 3. Thermodynamics parameters for the adsorption on BG onto PS.

Temp (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	q_e (mg/g)
298	-1.999	-16.418	-48.089	18.41
313	-1.407			16.90
323	-1.038			15.84
343	0.196			12.89

Kinetics study was carried out using 100 mg/L BG at room temperature. The experimental data was fitted using the Lagergren first order⁴¹ and pseudo second order⁴² models, whose equations are as follow:

Lagergren first order:

$$\log(q_e, \text{expt} - q_t) = \log q_e, \text{expt} - \frac{t}{2.303} k_1 \quad (12)$$

Pseudo second order:

$$\frac{t}{q_t} = \frac{1}{q_{e,expt}^2 k_2} + \frac{t}{q_{e,expt}} \quad (13)$$

where t is the time shaken (min), q_t is the adsorbate adsorbed per gram of adsorbent (mg/g) at time t , k_1 is the Lagergren first order rate constant (1/min), k_2 is pseudo second order rate constant (g/mg min).

From **Figure 5** and **Table 4** the data clearly show that of the two kinetics models used, the Lagergren first order model even though has a high R^2 is not the suitable model since the experimental $q_{e,expt}$ of 23.91 mg/g is far from the calculated $q_{e,calc}$ of 8.42 mg/g. On the other hand, the pseudo second order kinetics gave a higher R^2 which is very close to unity. Its $q_{e,calc}$ (23.57 mg/g) is also in good agreement with the $q_{e,expt}$. Hence, it is concluded that the adsorption of BG onto PS follows the pseudo second order kinetics with rate constant k_2 of 0.011 g/mg min.

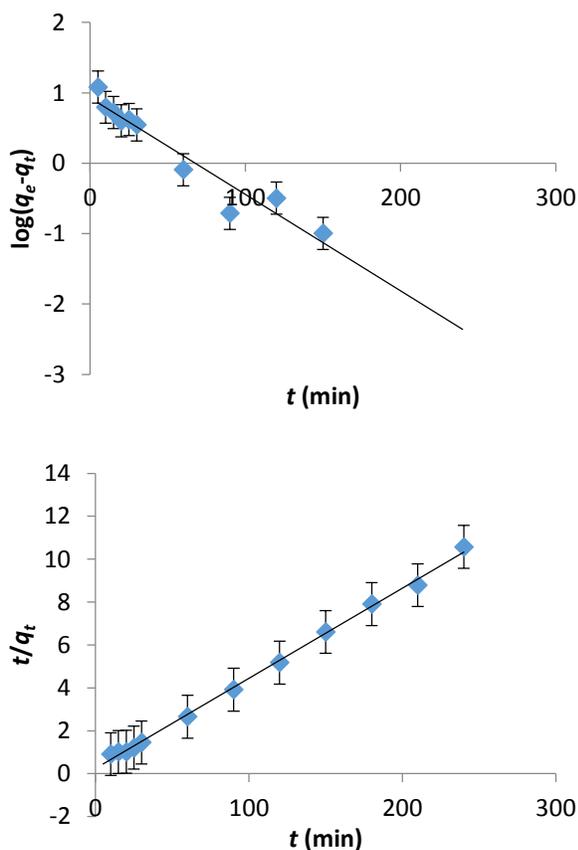


Figure 5. Adsorption kinetics based on the Lagergren first order (top) and the pseudo second order (bottom).

Table 4. Kinetics parameters for the adsorption of BG onto PS.

Lagergren first order			
$q_{e, expt}$ (mg/g)	$q_{e, calc}$ (mg/g)	k_1 (1/min)	R^2
	8.42	0.032	0.931
pseudo second order			
$q_{e, calc}$ (mg/g)	k_2 (g/mg min)	R^2	
23.91	23.57	0.011	0.997
Intra-particle diffusion			
	k_3 (mg/g min ^{1/2})	C	R^2
Region 1	2.396	8.20	0.934
Region 2	0.055	22.35	0.115

Further investigation of the adsorption kinetics using the Weber Morris intra-particle diffusion⁴³ (**Equation 14**), showed that pore diffusion was not the rate determining step since the plot did not pass through the origin as shown in **Figure 6**.

Weber Morris intra-particle diffusion:

$$q_t = k_3 t^{1/2} + C \quad (14)$$

K_3 is the intraparticle diffusion rate constant (mmol/g min^{1/2}) and C is the slope that represents the thickness of the boundary layer.

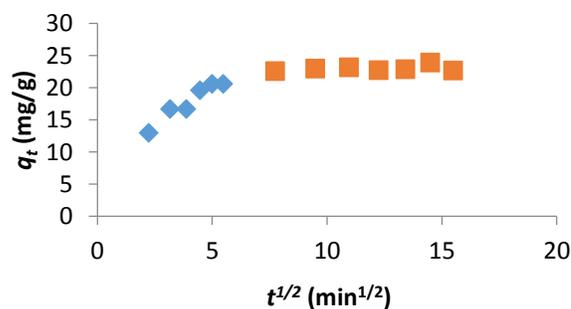


Figure 6. Adsorption kinetics based on the Weber Morris intra-particle diffusion model.

3.4. Regeneration of PS

In order to test the reusability of spent-PS, regeneration studies were carried out using three methods of washing after each adsorption i.e. washing with distilled water, acid and base. Under the experimental conditions used, all three methods gave higher removal of BG even after 4 consecutive cycles (**Figure 7**). However, a

reduction of about 20% in removal of dye was observed for washing with water in the 5th cycle compared to the spent-PS. Nevertheless both acid and base wash were able to maintain high removal of BG even at the 5th cycle, with the base being a more superior method of treatment. The reason could be that base treatment is known to remove the surface fats and waxes⁴⁴ thereby exposing the functional groups on the surface which in turn will enhance adsorption with the dye molecules.

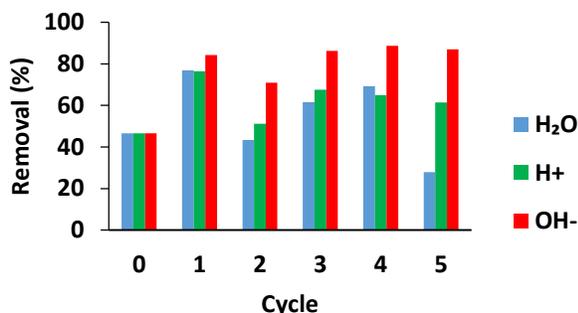


Figure 7. Regeneration of spent PS using water, base and acid treatment PS [contact time = 2 h; dye concentration =100 mg/L; dye volume = 20.0 mL; mass of PS =0.04 g; ambient pH; stirring rate =250 rpm and room temperature].

4. Conclusion

This study has shown that pomelo skin, which is often discarded as waste and of no economic value, can be converted to a valuable adsorbent for the removal of Brilliant green dye. Fast contact time to reach equilibrium, resilient to ionic strength, high maximum adsorption capacity together with the ability to regenerate and reuse the spent pomelo skin make it a potential and attractive low-cost candidate as an adsorbent in real life application for the treatment of wastewater.

Acknowledgements

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