Research Article

Brilliant Green Dye Elimination from Water Using *Psidium guajava* Leaves and *Solanum tuberosum* Peels as Adsorbents in Environmentally Benign Way

Rabia Rehman, Tariq Mahmud, and Maria Irum

Institute of Chemistry, University of the Punjab, Lahore 54590, Pakistan

Correspondence should be addressed to Rabia Rehman; rabia.chem@pu.edu.pk

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The aim of this study is to check the feasibility of *Psidium guajava* (Guava) leaves and peels of *Solanum tuberosum* (Potato) as biosorbents in removal of Brilliant Green (BG) in batch mode. Surface analysis of biosorbents was done by FT-IR and quantitatively analyzed by Boehm titration. The removal of dye was confirmed by UV-VIS spectroscopy. Isothermal modeling was studied by using Langmuir, Freundlich, and Temkin isotherms. Various isothermal parameters for adsorption of Brilliant Green such as $q_m = 1.075 \text{ mg/g}$, $1.173 \text{ mg/g}$, $\Delta G^\circ = -3.397$, and $-2.397 \text{ KJ/mol}$ were noted for *Solanum tuberosum* peels (PP) and *Psidium guajava* leaves (GL), respectively. Similarly pH, moisture content, and various metals were quantitatively analyzed. Results showed that leaves of *Psidium guajava* were more effective for removal of Brilliant Green.

1. Introduction

Dyes and pigments have worldwide applications in various industries while discharge of these stuffs is posing serious threats to natural environment. Water pollution is one of the major sources of environmental pollution nowadays. Various synthetic dyes are directly released into natural environments which are potentially harmful. Although in low concentrations, these are undesirable for domestic use. However, the aromatic structures of dyes provide them with greater stability and are not degraded easily. The treatment of such synthetic dyes is very difficult, as these are dead set against aerobic digestion. Moreover, these cannot be oxidized by application of various oxidizing agents. It is roughly estimated that various different types of synthetic dyes and pigments are commercially synthesized which have extensive applications in textile industry as well as in rubber, leather, plastics, and paper industries. Thus effluents from these industries block sunlight which is necessary for many biological activities of plants such as photosynthesis [1].

Brilliant Green (Figure 1) is an odorless green crystalline solid which is used as biological stain, dermatological agent, and an additive to poultry feed to prevent formation of parasites and fungus. It is also extensively used in textile dying and paper printing. It causes irritation to the gastrointestinal tract; symptoms include nausea, vomiting, diarrhea, irritation to the respiratory tract, leading to cough and shortness of breath in humans. It may also cause dermatitis upon skin contact with redness and pain.

Various methods have been used to build up effective methodologies for removal of BG dye. However, no single technique is being suitable yet for treatment of wide range of this synthetic dye [2]. Different physicochemical processes like coagulation/flocculation, ion-exchange, electrochemical oxidation, and photo-catalytic degradation have been found significantly successful in dealing these wastewaters; however, there are few limitations of later described methods. Coagulation leads to huge amount of waste products with high disposal costs. Ion-exchange method is expensive and cannot be used with such a wide range of dyes. Conventional biological methods are expensive so they cannot be used to treat the wide range of wastewater containing dyes. Thus adsorption through various biosorbents provides an attractive alternative, particularly if the adsorbent is low.
cost. This technique is becoming popular and promising technology in most of the developing countries because of its ease, simplicity of action, minimum sludge formation, and maximum regeneration of biosorbent. Adsorption is economically feasible which brings complete removal of impurities with no environmental hazards [3]. Activated carbons have been used for adsorption studies due to their properties such as surface area, micro porous composition, and high adsorption capacity. But the high cost of activated carbon leads to search low cost adsorbents such as those derived from biological materials.

Currently more focus has been given to use low cost, reusable, easily available, and biodegradable adsorbent mainly obtained from natural sources. Natural and modified clays, sugar industry mud, peels of various fruits, and vegetables have been used to reduce the pollution of wastewaters [4]. Previously, PP were used for removal of dyes such as methylene blue, reactive black 5, and reactive red 198, while metal ions such as Ni, Cu, and As were also effectively removed while GL were used for removal of malachite green, crystal violet, methylene blue dyes, and zinc.

The main objective of this study is to develop resourceful adsorbent from PP and GL and check their feasibility for effective removal of BG. Biosorbents were characterized through FT-IR. Various biosorption factors were studied such as temperature, pH, biosorbent dose, and time. This fundamental study will be helpful for further application in forming an adsorbent for the treatment of wastewater containing dye using a local biosorbent such as PP and GL.

2. Materials

2.1. Chemicals. Brilliant Green (C.I. = 42040, chemical formula = C35H34N2O4S, molecular weight = 482.62 g/mol, dye content 85%, λ max = 625 nm) was purchased from Riedel-De Haen A G Seezle Hannover. It has its maximum absorbance at a wavelength of 625 nm. NaOH (Merck, molecular weight = 40 g/mol) and HCl (Merck II.6 M) were used for maintaining pH. Surface functional groups of adsorbents were quantitatively analyzed by NaHCO3, Na2CO3, phenolphthalein, and methyl orange which were purchased from Friends Chemical Laboratory, Ltd. Distilled water was employed for the preparation and dilution where ever required.

2.2. Instruments. FT-IR spectrophotometer (IR Prestige-21 SHIMADZU, DRS-8000), electric balance (HX-T), electric grinder (Moullinex), pH meter (GL-21 Crison), electric shaker digital timer, and spectrophotometer-721 model (UV-Vis Double Beam UVD-3500 Labomed) were used.

2.3. Preparation of Adsorbents. PP were collected from waste baskets of cafe and household domestic waste, whereas GL were collected from home garden and trees grown at home institute. Both the adsorbents were washed in order to remove dust particles and impurities and then dried in sunlight for one week followed by oven drying at 70°C for two hours. These were the sample of the untreated biosorbents. Biosorbents were chemically treated with acetone by dipping 100 g of dried powder into 400 mL of acetone solution for 24 hours. After filtration, it was again dried out in oven at 70°C for two hours.

The Boehm titration method was used for calculation of oxygen containing functional groups. The number and type of acidic sites were calculated as NaOH neutralizes carboxylic, lactonic, and phenolic groups, Na2CO3 is used for neutralization carboxylic and lactonic groups, and NaHCO3 neutralizes carboxylic groups only. Carboxylic groups were then calculated by direct titration with NaHCO3. The differences between the groups titrated with Na2CO3 and those titrated with NaHCO3 were supposed to be lactones and that titrated with NaOH and Na2CO3 were characterized as phenolic groups. Basic sites were examined by titration with HCl. Various characteristics of adsorbents are given in Tables 1–3.

2.4. Biosorption Studies. Batch experiments were carried out for adsorption study. Stock of dye was prepared by dissolving 1 g of BG in 1000 mL of distilled water. Standard solutions of required concentration were prepared by further dilution of the Stock. For studying the effect of various parameters, pH was varied from 1 to 9. In order to study the effect of biosorbent dose, it was varied from 0.1–1.0 g/100 mL with dye concentration 25 ppm. Effect of temperature was studied by...
Table 3: Determination of various metal ions.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>PP</th>
<th>GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.96</td>
<td>0.54</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.01</td>
<td>0.11</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1.14</td>
<td>0.98</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.17</td>
<td>0.04</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>1.28</td>
<td>0</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.09</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>0.16</td>
<td>0</td>
</tr>
</tbody>
</table>

varying temperatures (10–80 °C). Time was varied from 10 to 60 minutes.

Isothermal study was done by taking optimum values of optimized conditions and adsorption data was validated using Langmuir, Freundlich, and Temkin isotherm. The equilibrium adsorption capacity was calculated by using (1) [8]:

\[
q_e = \frac{V (C_o - C_e)}{m},
\]

where \( V \) = volume of dye solution, \( m \) = mass of biosorbent (g), \( C_o \) = initial concentration (ppm), and \( C_e \) = equilibrium concentration (ppm). The percentage removal of dye was calculated by (2):

\[
\% \text{ Removal of dye} = \frac{(C_o - C_e)}{C_o} \times 100.
\]

3. Results and Discussion

3.1. Characterization of Adsorbents. The adsorbents were characterized by FT-IR showing the activity of –OH, –CO, –COOH C-C, and –NH groups which may act as possible active sites for adsorption and structural changes which occur after chemical treatment. Absorption peaks were recorded in Tables 4 and 5. The spectra of untreated and treated GL before adsorption of dye at 3309.85 and 3321.42 cm⁻¹ showed stretching vibrations and bands at 1618.28 and 1527.62 cm⁻¹ and 1625.99 showed deformation vibrations could be of –NH group while the bands at 2924.09 and 2922.16 cm⁻¹ could be due to stretching of –OH group. The bands at 1728.22 in untreated GL and 1730.15 cm⁻¹ in treated GL were showing the stretching of –C=O of ester. Moreover, bands observed at 1244.09 and 1236.37 cm⁻¹ in untreated GL and 1240.23, 1155.36, and 1004.91 cm⁻¹ in treated GL showed stretching frequency of C–O which could be of ester. The spectra are shown in Figures 2 and 3.

Similarly the FT-IR spectra of untreated and treated GL after adsorption of BG showed stretching vibrations bands at 3329.14, 3315 cm⁻¹, while deformations bands at 1635.64, 11625.99, 1525.69, and 1529.55 cm⁻¹ due to –NH group. The bands obtained at 2924.09 and 2922.16 cm⁻¹ might be stretching frequency of –OH group. The bands at 1730.15 and 1728.22 cm⁻¹ showed stretching of –C=O group and the bands at 1240.23, 1157.29, 1008.77 cm⁻¹, 1155.36, and 1004.91 cm⁻¹ showed stretching due to C–O group. Other bands for cyanide group were obtained at 1319.31 and 1321.24 cm⁻¹. Band at 2357.01 was observed in treated GL which showed the stretching could be due to silane (Si–H) that was shifted to lower wave number, that is, 2355.08, in treated GL after adsorption of BG. Below 1000 cm⁻¹ is known as fingerprint region which does not interact with dye appreciably. The spectra are shown in Figures 4 and 5, respectively.

FT-IR spectrum of untreated PP before adsorption of dyes showed bands at 3300.20, 1639.49, and 1537.27 cm⁻¹ among which some were shifted to high wave number at 3304.06 in treated PP while others were shifted to lower wave number at 1637.56 and 1531.48 cm⁻¹ which could be stretching and deformation due to –OH group. Bands at 2924.09 showed stretching due to –OH in untreated PP which was shifted to high wave number at 2926.01 in treated PP. Bands at 1244.09 and 1149.57 cm⁻¹ showed stretching due to carbonyl group in untreated PP which was shifted to lower wave number at 1242.16 and higher wave number at 1151.50 cm⁻¹ in treated PP. The results are shown in Figures 6 and 7, respectively.

Bands at 3305.99, 1643.35, and 1529.55 cm⁻¹ were due to stretching and deformation of N–H group in treated PP which were shifted to lower wave number at 3298.28 and 1641.42 cm⁻¹ while no change occurred in band at 1529.55 cm⁻¹ in treated PP after adsorption of BG, respectively. Band at 2926.01 cm⁻¹ was observed due to stretching..
Table 4: Characteristic FTIR adsorption frequencies of functional groups of Guava leaves.

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Untreated GL</th>
<th>Treated GL</th>
<th>Untreated GL with BG</th>
<th>Treated GL with BG</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_{(N-H\text{str})})</td>
<td>3309.85 (w)</td>
<td>3321.42 (w)</td>
<td>3329.14 (w)</td>
<td>3315.63 (w)</td>
</tr>
<tr>
<td>(\nu_{(O-H\text{str})})</td>
<td>2924.09 (s)</td>
<td>2922.16 (s)</td>
<td>2924.09 (s)</td>
<td>2922.16 (s)</td>
</tr>
<tr>
<td>Silane (\nu_{(Si-H\text{str})})</td>
<td>—</td>
<td>2357.01</td>
<td>—</td>
<td>2355.08</td>
</tr>
<tr>
<td>(\nu_{(C=O\text{str})})</td>
<td>1728.22 (s)</td>
<td>1730.15 (s)</td>
<td>1730.15 (s)</td>
<td>1728.22 (s)</td>
</tr>
<tr>
<td>(\nu_{(N-H\text{def})})</td>
<td>1618.28 (m)</td>
<td>1625.99 (m)</td>
<td>1635.64 (m)</td>
<td>1625.99 (m)</td>
</tr>
<tr>
<td>(\nu_{(C-N\text{str})})</td>
<td>1321.24 (s)</td>
<td>1319.31 (s)</td>
<td>1321.24 (s)</td>
<td>1319.31 (s)</td>
</tr>
<tr>
<td>(\nu_{(C-O\text{str})})</td>
<td>—</td>
<td>1157.29 (s)</td>
<td>1157.29 (s)</td>
<td>1155.36 (s)</td>
</tr>
<tr>
<td>(\nu_{(C-O\text{str})})</td>
<td>1010.70 (s)</td>
<td>1008.77 (s)</td>
<td>1008.77 (s)</td>
<td>1004.91 (s)</td>
</tr>
</tbody>
</table>

Table 5: Characteristic FT-IR adsorption frequencies of functional groups of PP.

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Untreated PP</th>
<th>Treated PP</th>
<th>Untreated PP with BG</th>
<th>Treated PP with BG</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_{(N-H\text{str})})</td>
<td>3300.20 (w)</td>
<td>3304.06 (m)</td>
<td>3305.99 (w)</td>
<td>3298.28 (w)</td>
</tr>
<tr>
<td>Silane (\nu_{(Si-H\text{str})})</td>
<td>—</td>
<td>—</td>
<td>2364.73 (s)</td>
<td>2360.87 (s)</td>
</tr>
<tr>
<td>(\nu_{(O-H\text{str})})</td>
<td>2924.09 (w)</td>
<td>2926.01 (m)</td>
<td>2926.01 (w)</td>
<td>2926.01 (w)</td>
</tr>
<tr>
<td>(\nu_{(N-H\text{def})})</td>
<td>1639.49 (m)</td>
<td>1637.58 (m)</td>
<td>1643.35 (m)</td>
<td>1641.42 (m)</td>
</tr>
<tr>
<td>(\nu_{(C-N\text{str})})</td>
<td>1537.27 (s)</td>
<td>1531.48 (s)</td>
<td>1529.55 (s)</td>
<td>1529.55 (s)</td>
</tr>
<tr>
<td>(\nu_{(C-O\text{str})})</td>
<td>1244.09 (s)</td>
<td>1242.16 (s)</td>
<td>1242.16 (s)</td>
<td>1242.16 (s)</td>
</tr>
<tr>
<td>(\nu_{(C-O\text{str})})</td>
<td>1149.57 (s)</td>
<td>1151.50 (s)</td>
<td>1151.50 (s)</td>
<td>1151.50 (s)</td>
</tr>
</tbody>
</table>

s = strong, m = medium, w = weak signal.

Figure 4: FT-IR spectrum of untreated GL after adsorption of BG.

Figure 5: FT-IR spectrum of treated GL after adsorption of BG.

Figure 6: FT-IR spectrum of untreated PP.

Figure 7: FT-IR spectrum of treated PP.
of O–H in untreated and treated PP after adsorption of BG, respectively. Bands at 1244.09 cm$^{-1}$ and 1149.57 cm$^{-1}$ were observed due to stretching of C–O group in untreated PP which were shifted to lower shift at 1242.16 and 1151.50 cm$^{-1}$ in treated PP and then not change after adsorption of BG, respectively. Band at 2360.87 cm$^{-1}$ was observed due to silane which was shifted to higher wave number at 2364.73 cm$^{-1}$.

The spectra are given in Figures 8 and 9, respectively.

3.2. Optimization of Biosorption Parameters

(i) Biosorbent Dose. The effect of biosorbent dose was studied by changing its amounts, that is, 0.1–1.0 g. The adsorption of Brilliant Green shows an increasing trend with increasing adsorbent dosage of both the adsorbents first which then decreases up to 0.2 g in case of both the adsorbents on which it then decreases up to certain amount, that is, 0.6 g of GL and 0.8 g of PP, and then becomes constant. The results have shown that adsorption capacity of GL is 99.36% at 0.2 g and 99.07% at 0.6 g of PP. As the adsorbent dose is increased, the adsorption capacity is also increased. As the number of active sites is increased, adsorption showed an increasing trend [9, 10]. The effect of biosorbent dose is shown in Figure 10.

(ii) Effect of $pH$. $pH$ may increase or decrease the uptake of dye which is due to the surface charge of the adsorbent. As $pH$ increases, the adsorption capacity decreases and then becomes constant. Increasing $pH$ increases the number of hydroxyl groups which infers that as the number of negatively charged sites is increased, the interaction between dye and biosorbent is also increased. Generally, the net positive charge decreases with increasing $pH$. This leads to the decrease in repulsion between the adsorbent surface and the dye; thus adsorption is increased [6, 11].

The percentage removal of BG was gradually increased at $pH = 1.0–2.0$ in case of GL which then started decreasing and then became constant up to $pH = 3.0–6.0$. It means that slightly acid conditions favour the adsorption of BG by GL due to increase in negative surface charges on GL and protonation of dye molecules in solution. Adsorption was increased at $pH = 4.0$. While it showed a decreasing trend for PP first at $pH = 2.0$, then it increased and became constant. All of a sudden again it decreased at $pH = 7.0$ and then increased at $pH = 8.0$ and again decreased. Thus from the course of study $pH = 4.0$ was taken as optimal $pH$ for GL and $pH = 8.0$ for PP. The percentage removal was 99.68% for GL while 83.6% for PP. The effect of $pH$ is shown in Figure 11.

(iii) Contact Time. In order to check the effect of contact time on the adsorption, it was studied by batch process whereby varying the time of adsorbents from 10 to 60 minutes. Percentage removal firstly increased with increasing time which then started decreasing and then became stable. The optimum adsorption capacity was observed at 30 minutes for PP and 40.0 minutes for GL. The comparative graph is shown in Figure 12.

(iv) Effect of Temperature. Temperature is also another important parameter along with other optimization factors in adsorption study. It shows the nature of adsorption process whether exothermic or endothermic. It was found that the adsorption of dye increased as the temperature was increased in the range of 10–20°C for GL which dropped at 30°C and again increased at 40°C which became constant as shown in Figure 13. This indicates that it was an exothermic process in nature. But a decreasing trend was observed for the PP
at 20°C and then an increasing trend was observed at 30–40°C which suddenly decreased at 50°C thereby showing maximum adsorption at 60°C and then again decreased and became constant; thus the adsorption was said to be endothermic \[5,12\].

3.3. Equilibrium Study for Adsorption of Brilliant Green. Adsorption isotherms are used to describe how pollutants interact with adsorbent. Batch study was carried out by changing the dye concentration from 5 to 30 ppm. The batches were studied with adsorbent amount taken as 0.2 g GL and 0.6 g PP and the contact time of 30.0 minutes for PP and 40.0 minutes for GL whereas pH was maintained at pH 4.0 for GL and pH 8.0 for PP while temperature was kept constant at 60°C for PP and 40°C for GL.

3.4. Langmuir Isotherm. It is the most commonly used adsorption isotherm and is shown in

\[
\frac{1}{q_e} = \frac{(1/bq_m)}{C_e} + \frac{1}{q_m},
\]

where \(q_e\) = adsorption capacity at equilibrium (mg/g), \(C_e\) = final concentration of dye solution (ppm), \(q_m\) = maximum adsorption capacity (mg/g), and \(b\) = adsorption energy (L/mg). The Langmuir constants can be obtained by plotting a graph between \(1/q_e\) and \(1/C_e\) which can be expressed by a separation factor. It is shown in

\[
R_L = \frac{1}{1 + bc},
\]

where \(R_L\) is dimensionless constant which shows the nature of adsorption and its value lies in the range of 0-1. Adsorption capacity \(q_m\) was calculated from the linear plot of Langmuir model \[7, 13, 14\]. The results are shown in Figure 14 and Table 6.

3.5. Freundlich Isotherm. Freundlich gave an empirical adsorption relation for a nonideal system in 1906 for single layer adsorption onto heterogeneous surfaces. The mathematical expression is given as

\[
\log q = \frac{1}{n} \log C_e + \log K_f,
\]
Table 6: Adsorption isothermal parameters of Langmuir isotherm.

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>Slope</th>
<th>Intercept</th>
<th>( R^2 )</th>
<th>( B ) (Lg(^{-1}))</th>
<th>( q_m ) (mg/g)</th>
<th>( \Delta G^\circ ) (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0.236</td>
<td>0.932</td>
<td>0.961</td>
<td>0.99</td>
<td>1.075</td>
<td>−3.397</td>
</tr>
<tr>
<td>GL</td>
<td>2.235</td>
<td>0.852</td>
<td>0.935</td>
<td>0.38</td>
<td>1.173</td>
<td>−2.397</td>
</tr>
</tbody>
</table>

where \( K_f \) = adsorption capacity and \( 1/n \) = adsorption intensity. The values of these constants can be calculated from the linear plot of Freundlich model as \((1/n)\) corresponds to the slope and \( \log K_f \) gives the value of intercept. The results for adsorption on PP and GL are shown in Figure 15 and Table 7 [15–17].

3.6. Temkin Isotherm. This isotherm assumes that heat of adsorption is linearly decreased and uniform distribution of binding energies favours adsorption. Its equation is

\[
q = B_T \ln A + B_T \ln C_e.
\]  

(6)

The equilibrium relationship describes the behavior of many adsorption systems on the heterogeneous surface. Using slope and intercept of graph of \( q \) versus \( \ln C_e \), Temkin constants \( B_T \) and \( A \) were determined [2, 18]. Here “\( A \)” = equilibrium binding constant (L mol\(^{-1}\)) and \( B_T \) = heat of adsorption. The results are being shown in Figure 16 and Table 8.

3.7. Comparison of Various Adsorbent for Adsorption of BG. A comparison of different adsorbents for removal of BG has been given in Table 9 which shows that the proposed adsorbents are comparable to other adsorbents. The feasibility of PP and GL can be predicted in terms of adsorption rate with exothermic adsorption. These adsorbents are appropriate for the adsorption of BG. This elementary study of batch biosorption of BG will be helpful for the wastewater treatment of dye which is being directly discharged from industries in natural environment without proper treatment.

4. Conclusion

In the present course of research study, low cost adsorbents such as leaves of \textit{Psidium guajava} and peels of \textit{Solanum tuberosum} were used for the batch biosorption of Brilliant Green. Characterization of these biosorbers was carried out...
by FT-IR and functional groups were calculated by Boehm titration. Moreover, isothermal modeling was studied by using Langmuir, Freundlich, and Temkin isotherm.

Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

References


