

## REMOVAL OF BRILLIANT GREEN AND PROCION RED DYES FROM AQUEOUS SOLUTION BY ADSORPTION USING SELECTED AGRICULTURAL WASTES

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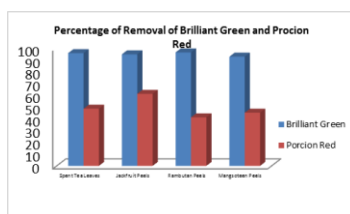
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### Graphical abstract



### Abstract

Approximately 10-15 % of usage synthetic textile dyes are released to waste streams meanwhile the effluent release from wastewater treatment plant contribute 20 %. Adsorption being a physical process, inexpensive and less time consuming, is widely accepted to eliminate dyes from wastewater. An experiment was carried out to observe the adsorption of Brilliant Green and Procion Red dye. The experiment is to identify the most effective adsorbent to remove the colour of Brilliant Green and Procion Red. Both dyes were mixed with the agricultural wastes, spent tea leaves, jackfruit peels, rambutan peels, and mangosteen peels. The percentage of removal and adsorption capacity of the dyes were examined. Rambutan peels were the most effective adsorbent to remove Brilliant Green which is 96.42 % with 9.64 mg/g adsorption capacity, whereas for Procion Red, jackfruit peels were recorded as the highest percentage of removal, 61.2 % with 6.12 mg/g adsorption capacity in 24 hours. Based on FESEM and FTIR results, the effectiveness of adsorbents was affected by the structure of the adsorbent, presence of pores and functional groups. Functional group of carbonyl and carboxyl helps in the adsorption process and will form bonds with the dyes and thus remove them from the solution.

**Keywords:** Adsorption, synthetic dyes, agricultural wastes, brilliant green, procion red

### Abstrak

Lebih kurang 10-15 % penggunaan pewarna sintetik tekstil dilepaskan ke sungai manakala pelepasan dari loji rawatan air menyumbang sebanyak 20 %. Penjerapan merupakan proses fizikal, tidak mahal mahupun makan masa, telah diterima secara meluas bagi penyingkiran pewarna dari air sisa. Eksperimen dijalankan untuk mengenalpasti tahap penjerapan bagi Brilliant Green dan Procion Red. Kedua-dua pewarna kemudiannya bercampur dengan sisa pertanian iaitu daun teh, kulit nangka, kulit rambutan, dan kulit manggis. Pewarna yang mempunyai penyingkiran yang paling tinggi dan penjerap yang paling berkesan dikenalpasti. Kulit rambutan menjadi penjerap yang paling berkesan untuk menghapuskan Brilliant Green dengan kadar 96.42 % serta dengan 9.64 mg/g kapasiti penjerapan manakala bagi Procion Red, kulit nangka telah direkodkan sebagai peratusan penyingkiran yang tertinggi sebanyak 61.2 % dengan 6.12 mg/g kapasiti penjerapan dalam tempoh 24 jam. Berdasarkan FESEM dan FTIR, dapat ditunjukkan bahawa keberkesanan sesuatu penjerap itu dipengaruhi oleh struktur penjerap sendiri seperti dengan wujudnya liang-liang dan dengan adanya kumpulan berfungsi tertentu. Kumpulan berfungsi carbonyl dan carboxyl sangat membantu dalam proses penjerapan

dan kumpulan berfungsi ini akan membentuk bon bersama pewarna sintetik dan seterusnya menyingkirkan pewarna tersebut keluar daripada larutan.

*Kata kunci:* Penjerapan, pewarna sintetik, sisa pertanian, brilliant green, procion red

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## 1.0 INTRODUCTION

Recently, the rapid development in industry gave big impression to the environmental society. Among many industries, textile contribute the highest in utilize dyes for coloration of fiber. The effluent from textile industry carries a huge number of dyes and added with other additives throughout the colouring process [1]. The discharge of coloured effluents, although frequently less toxic than many colourless effluents, is resented by the public on the ground that colour is an indicator of pollution [2]. Owing to its colour, it is the most easily recognizable pollutants. Therefore, public must aware with the usage of dye concentration in mineral water because it can cause mankind unfit from health aspect. Anually the production of dyestuff can reach 700 000 tonnes and 100 000 types of dyes. The dyes were categorized based on their structure as anionic and cationic [3].

The elimination of dyes is necessity before they are released into the environment. This is because we have to follow the tight restrictions on the organic content. Most of the dyes are carcinogenic and toxic in nature and when discharged into the water they pose serious hazards to the aquatic biota. Among a number of different techniques for dye removal such as coagulation and flocculation, ultrafiltration, electrochemical degradation and ion exchange method, it was reported that the adsorption technique has proved one of the best technology and showed good result in removal of different coloring materials from the water system. Adsorption can be consider a potential method to remove dye from industrial effluents [4, 5]. Thus, many studies, come out with natural material as alternative adsorbent which are low-cost, reliable resources and environment-friendly in order to replace commercial activated carbon adsorbent [6, 7, 8, 9]. Adsorbent is referring to the adsorbing material which contains many elements that capable for pollutant removal [10].

The use of activated carbon has a lot of disadvantages, it is costly, ineffective and non-selective against disperse and vat dyes [11]. Therefore, in order to save the waste water from being polluted and protect the environment, developing alternative and economical adsorbents to treat the synthetic dyes has attracted a great interest in recent years. Thus, the aim of the research is to come out with a suitable and low cost method for the removal of dye from agricultural wastes. Agricultural wastes also became the source for the production of activated carbon [12]. The effectiveness of the reaction

between both dye and agricultural wastes was also investigated.

## 2.0 EXPERIMENTAL

To determine the adsorptive capacity of the materials, there are some experiments that will be conducted which is the Batch Test and Time-Adsorption relationship test. These tests are done to observe the adsorptive capacity and effectiveness of adsorbents to decolourise brilliant green and procion red dyes.

Spent tea leaves, jackfruit peels, rambutan peels and mangosteen peels were prepared and the materials were then cut into small pieces and put into four separate trays respectively. Next, the collected materials were washed several times with running water in order to remove dust before they were washed again with distilled water. Sample that had been clean were then put into the oven for about 24 hours at 110 °C. After ensuring that the materials were completely dried out, they were then grind until becoming fine powder.

Agricultural wastes were weighed for about 5 g and poured 50 ml of the brilliant green and procion red stock solution respectively into the conical flask containing 5 g of spent tea leaves. The prepared solution was then being shake on the shaker with 120 rpm speed for almost 24 hours.

The solution was then filtered and left for few minutes to get the filtered solution ready. Next, all the sample was diluted. 1 ml of the filtered mixture and 9 ml of distilled water was poured into a measuring cylinder. Shake the measuring cylinder slowly to mixed them up. After that, all of the samples were tested by using the UV-Vis spectroscopy to determine the percentage of removal and adsorption capacity for each of the sample. Below are the equation used to identify the percentage of removal and adsorption capacity of the sample:

$$\text{Colour removal (\%)} = \frac{C_0 - C_x}{C_0} \times 100 \quad (1)$$

$$\text{Adsorption capacity} \left( \frac{\text{mg}}{\text{g}} \right) = \frac{C_0 - C_x}{M} \times \text{Vol} \quad (2)$$

Where  $C_0 \left( \frac{\text{mg}}{\text{l}} \right)$  is the concentration of adsorbent + dye at 1000 mg/L,  $C_x \left( \frac{\text{mg}}{\text{l}} \right)$  is the diluted concentration of adsorbent + dye, M (g) is the mass of adsorbent used and Vol (l) is the volume of dye concentration.

### 3.0 RESULTS AND DISCUSSION

This experiment was conducted on two types of dyes, brilliant green and procion red. Both with the concentration of 1000 mg/L with only using the batch test. Four different adsorbent was used for each of the dye, which are spent tea leaves, jackfruit peels, rambutan peels and mangosteen peels.

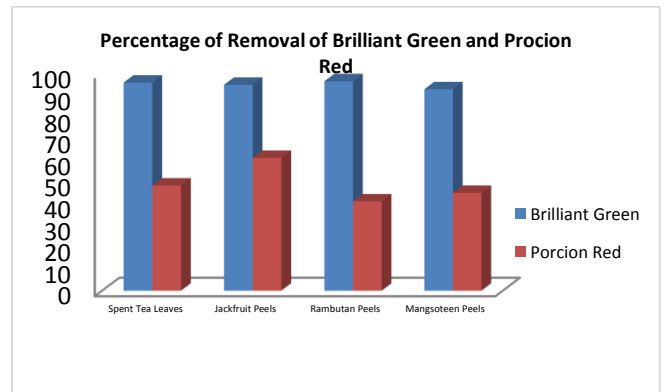
From the uv analysis, we know that the maximum absorbance for brilliant green dye at 621 nm while procion red at 538 nm.

**Table 1** Percentage of removal and adsorption capacity of brilliant green and procion red

| Adsorbent        | Brilliant Green           |                            | Porcion Red               |                            |
|------------------|---------------------------|----------------------------|---------------------------|----------------------------|
|                  | Percentage of Removal (%) | Adsorption Capacity (mg/g) | Percentage of Removal (%) | Adsorption Capacity (mg/g) |
| Spent Tea Leaves | 95.78                     | 9.57                       | 48.55                     | 4.8                        |
| Jackfruit Peels  | 94.78                     | 9.47                       | 61.22                     | 6.12                       |
| Rambutan Peels   | 96.42                     | 9.64                       | 41.20                     | 4.12                       |
| Mangosteen Peels | 92.74                     | 9.27                       | 45.17                     | 4.51                       |

Based on Table 1 and Figure 1, for brilliant green dye, it is found that percentage of removal for spent tea leaves is 95.78 %. Jackfruit peels recorded about 94.78 % of removal towards brilliant green. Moreover, rambutan peels have the highest percentage of decolorization among the other adsorbents which is 96.42 % and lastly is 92.74 % of removal from mangosteen peels, which is also the least percentage of removal for brilliant green. From the overall result, we can see that the percentage of removal between each sample is not that obvious, and all of them still can be assume having an effective adsorption, this is because all the removals are around 90 % and above.

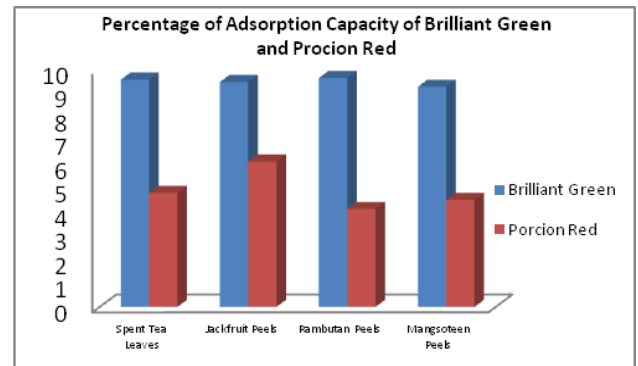
For procion red dye, the highest percentage of removal for is from jackfruit peels which is 61.2 %. On the other hand, rambutan peels give the least percentage that are 41.2 %. For spent tea leaves, they decolorize procion red for about 48.55 %, whereas 45.17 % of removal recorded from mangosteen peels. In this case, the percentage of removal from one sample to another variable. Thus, we can say that jackfruit peels are the most effective adsorbents for procion red dye.



**Figure 1** Percentage removal of brilliant green and procion red

Figure 2 show the adsorption capacity for both of the dyes used in this experiment, brilliant green and procion red. According to For brilliant green dye, it can be seen that rambutan peels have the highest adsorption capacity which is 9.64 mg/g. Next is 9.57 mg/g, and the adsorbent is spent tea leaves. Jackfruit peels come third, the adsorption capacity is 9.47 mg/g and the least adsorption capacity for brilliant green is recorded by mangosteen peels, 9.27 mg/g. To conclude, rambutan peels have reached at one limit which is 9.64 mg/g, further prolong of time, there is no more increase in the adsorption capacity. This theory is applied for all of the adsorbents.

Based on Figure 2, for procion red dye, 6.12 mg/g is the highest value of adsorption capacity recorded by jackfruit peels. Followed by spent tea leaves, 4.85 mg/g and mangosteen peel, 4.51 mg/g. Lastly is rambutan peels and the adsorption capacity is 4.12 mg/g. As a conclusion, jackfruit peels can reach the highest 6.12 mg/g of adsorption capacity before they become optimum throughout the graph. This is also can be applied for the other three adsorbents used.

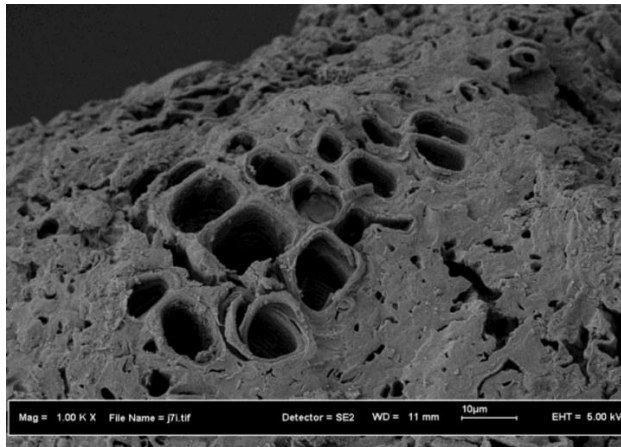


**Figure 2** Percentage of adsorption capacity of brilliant green and procion red

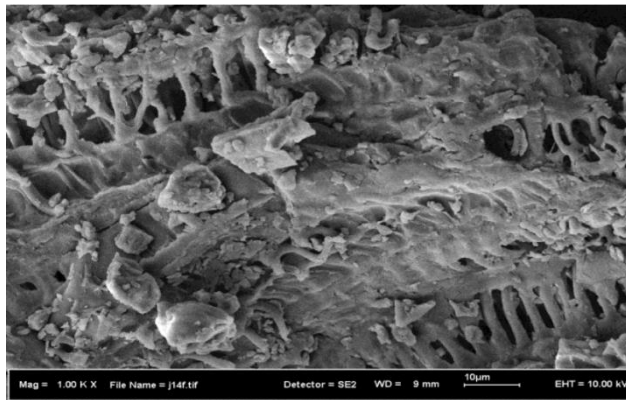
Field Emission Scanning Electron Microscopy (FESEM) is used to investigate molecular surface structures and their electronic properties in materials. The microscopy was used in order to obtain real space magnified images of a surface. Crystallography, surface morphology and surface composition can be analyzed using microscope. The image from Figure 3(a) and Figure 3(b) show the surface structure of spent tea leaves and rambutan peels. The images show heterogeneous surface structure of them, which have hilly and valleys like structure. Plus, the surface is porous and have a lot of pores. These pores function to help in adsorption. Thus, by having these criteria, they help to increase in the percentage of removal.

In Figure 3(c), it displays the surface structure of jackfruit peels. As we can see, jackfruit peels has perforated surface structure. The perforated type of surface can help in trapping the dye particles within them. Hence, percentage of dye removal the adsorbent can become higher.

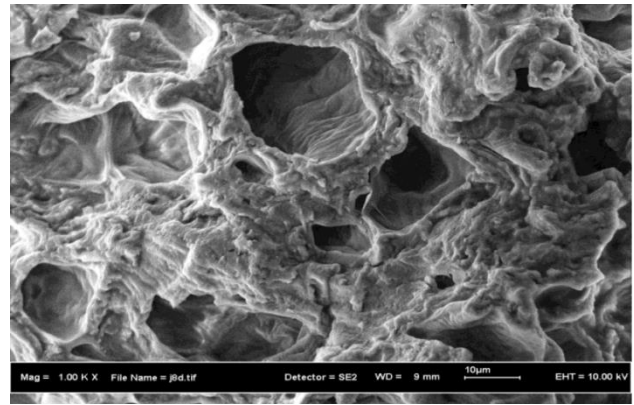
Figure 3(d) shows the FESEM image of mangosteen peels. It can be seen that the surface of mangosteen peels is rough and irregular in shape. Porous surface indicate that there is an adequate morphology (study of shape) for dye adsorption. Since they are irregular in shape, there is high possibility that the dye can be trapped by them and causes the removal of dye from the solution.



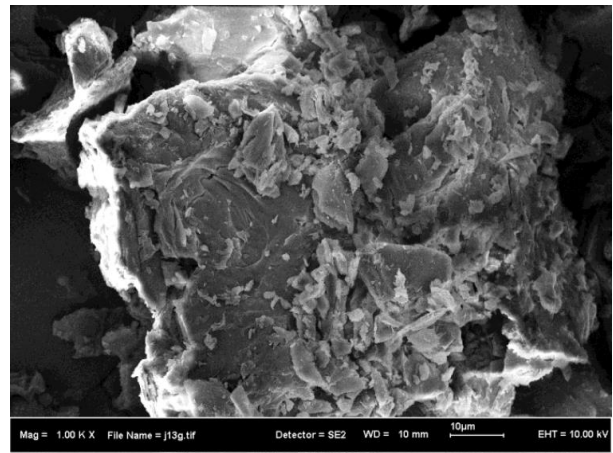
(a)



(b)



(c)



(d)

**Figure 3** FESEM image for (a) Spent Tea Leaves (b) Rambutan Peels (c) Jackfruit Peels (d) Mangosteen Peels

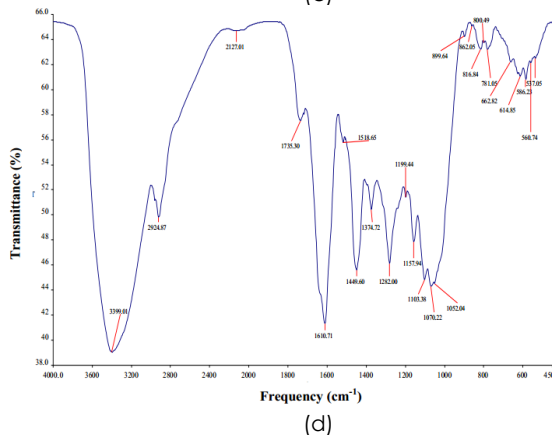
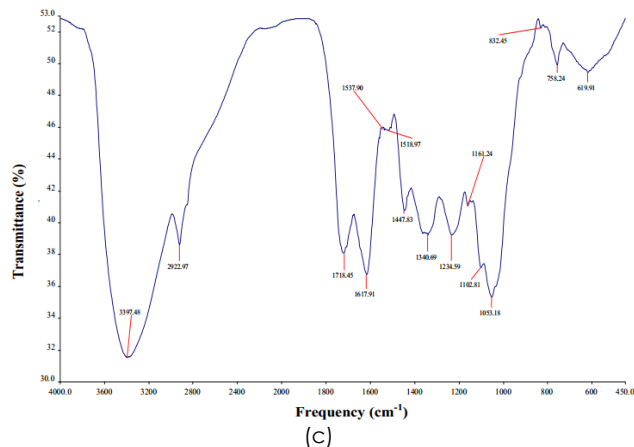
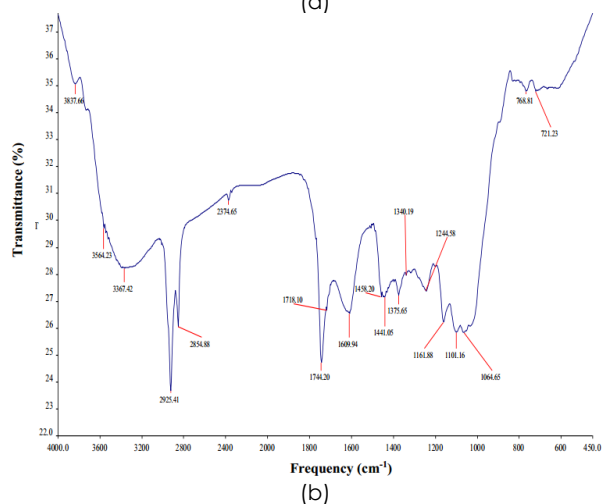
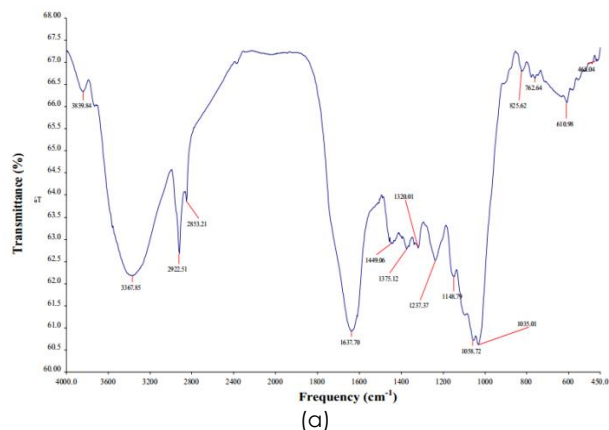
The Fourier Transform Infrared (FTIR) is an important method to prepare and identify the functional group that causes adsorption to occur. The infrared spectrum peaks show the types of functional group presents. Each adsorbent may have varies functional group, hence causes their adsorption capacity to be different. The functional group may either help or prevent the adsorption process. These functional groups help to bind and trap the dye molecules.

In those adsorbents, there are presence of the functional group carbonyl and carboxyl group. Carboxyl group has high affinity towards pollutants and also heavy metals. Carbonyl group can form hydrogen bonds with the dye and hence adsorbing them.

Figure 4(a) shows the FTIR of spent tea leaves, containing many adsorption peaks. The exhibition of the peak at  $3367.85\text{ cm}^{-1}$  is caused by functional group of alcohols and phenols which consist of O-H stretch and H-bonded. Peak at  $2922.51\text{ cm}^{-1}$  shows the present of carboxylic acids with C-H stretch. At  $1637.70\text{ cm}^{-1}$ , there are N-H bend which in the functional group of  $1^\circ$  amines. Whereas at  $1035.01\text{ cm}^{-1}$ , there exist functional group of aliphatic amines having the C-N stretch.

Figure 4(b) shows the infrared spectrum of jackfruit peels. O-H stretch and H-bonded with functional group alcohols, phenols are found at  $3367.42\text{ cm}^{-1}$ . At frequency of  $2925.41\text{ cm}^{-1}$ , it shows there is alkanes group with C-H stretch. While at  $1744.20\text{ cm}^{-1}$ , esters, saturated aliphatic functional group exist with C=O stretch. On the other hand, at  $1609.94\text{ cm}^{-1}$ , there is  $1^\circ$  amines with N-H bend. At  $1161.88\text{ cm}^{-1}$ , bond C-N stretch bond with functional group of aliphatic amines is shown. Based on the FTIR of rambutan peels, Figure 4 (c), peak at  $3397.48\text{ cm}^{-1}$  there is functional group of alcohols and phenols which consist of O-H stretch and H-bonded. Peak at  $2922.97\text{ cm}^{-1}$  shows the present of alkane group with C-H stretch. At  $1617.91\text{ cm}^{-1}$ , there are N-H bend which in the functional group of  $1^\circ$  amines. Whereas at  $1053.18\text{ cm}^{-1}$ , there are functional group of aliphatic amines having the CN stretch bond exists.

Figure 4(d) shows the FTIR analysis for mangosteen peels. Alcohol, phenol group with O-H stretch and H-bonded exists at  $3399.01\text{ cm}^{-1}$ . Alkanes group present at frequency of  $2924.87\text{ cm}^{-1}$ . At  $1610.71\text{ cm}^{-1}$ , there is functional group of  $1^\circ$  amines with N-H bend. Whereas at peak  $1449.60\text{ cm}^{-1}$ , there is functional group of aromatics group. Aromatics amines with C-N stretch appears at  $1282.00\text{ cm}^{-1}$ .



**Figure 4** FTIR for (a) spent tea leaves (b) rambutan peels (c) jackfruit peels (d) mangosteen peels

## 4.0 CONCLUSION

This experiment presents the efficiency of low cost agricultural adsorbents for dye removal. From this experiment, the results show between those four adsorbents, which are spent tea leaves, jackfruit peels, rambutan peels and mangosteen peels, rambutan peels have the highest efficiency for colour removal of brilliant green dye which is 96.42%. On the other hand, rambutan peels recorded 9.64 mg/g for adsorption capacity. Next, for procion red dye, jackfruit peels show the highest percentage of removal which is 61.2% with 6.12 mg/g adsorption capacity.

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