Biointerface Research in Applied Chemistry
Platinum Open Access Journal (ISSN: 2069-5837)

*Article*
**Volume 11, Issue 1, 2021, 8564 - 8576**
https://doi.org/10.33263/BRIAC111.85648576

# Adsorption of Phenol Red and Remazol Brilliant Blue R by Coconut Shells (*Cocos nucifera*) and Ambarella Peels (*Spondias dulcis*)

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**Received: 5.07.2020; Revised: 30.07.2020; Accepted: 1.08.2020; Published: 2.08.2020**

**Abstract:** The potential of agricultural waste materials for the removal of synthetic dye, Phenol Red (PR) and Remazol Brilliant Blue R (RBBR) from aqueous solution was investigated. One of the major pollutants of water pollution, dyes, which not only result in enormous damage to the water body but also impact the organism's health, as it is highly toxic and carcinogenic by nature. Agricultural wastes are sustainable adsorbents since they are availability and low cost, which can also replace the traditional activated carbon. Therefore, this study investigated the removal of PR and RBBR from dye solution by adsorption onto the treated adsorbent. Two best out of ten adsorbents were chosen through a screening process using RBBR as a tested dye. Coconut shells (*Cocos nucifera*) and ambarella peels (*Spondias dulcis*) were selected as the main adsorbent of this study since they achieved the highest removal rate compared to others. With the selected adsorbent, the experiment was continued to study the effect of different initial dye concentration, adsorbent dosage, contact time, pH, and particle size on dye adsorption. Results show that different parameters can affect the removal rate and adsorption capacity of adsorbent in a different way. The adsorption of dye from aqueous solution onto adsorbent was evaluated using Fourier transform infrared spectroscopy (FTIR) to investigate the functional groups of adsorbent before and after the adsorption process, and it found that the functional group would affect the effectiveness or removal rate and adsorption capacity of adsorbents. The present study indicates that 99.82% of PR with an adsorption capacity of 1.05 mg/g can be removed by 5-gram ambarella peels. While coconut shells had removed 75.78% of RBBR with an adsorption capacity of 7.96 mg/g for 21 hours. The results proved that these agricultural waste were promising materials as an alternative adsorbent for the removal of dye from aqueous solution.

**Keywords:** Adsorption; Coconut shells (*Cocos nucifera*); ambarella peels (*Spondias dulcis*); Phenol Red; Remazol Billiant Blue R.



## 1. Introduction

Water pollution can affect the organism's lives in many aspects; one of the distinct aspects affects the health of humans through drinking. The study indicates that nearly 1.7 million children under 5 years old die from access to clean water every year. This clearly shown how significant clean water is. Pollution of wastewaters have come from many sources, and they can be categorized into two main sources which are the non-point source and point source. Industrial, agricultural and residential wastes are the three major sources that pollute the river in developing countries [1-4]. Synthetic dyes have been widely utilized throughout the world, there have more than 100,000 commercial dyes with various range of colors in the market, and over seven hundred thousand tonnes of dyes are produced every year [5]. The reasons for them have been largely produced, and widely used are due to they are much cheaper, have a high wet fastness profile, great structural diversity, vibrant shades of color, and apply easily [6,7]. The effluents discharged by the textile industry mostly contain the dyes that are highly toxic and recalcitrant to microbial degradation, which can form suspected carcinogens. This results in increasing in concentration of a pollutant in a food chain and organism, which name as bioaccumulation and biomagnification effects [8].

PR is frequently used as a pH indicator in the cell biology laboratory. It provides a visual assessment of pH by changing in color. For example, purple or bright pink color represents the basic condition, and the yellow color represents the acidic condition. RBBR is one of the most common, recognizable, and significant reactive dyes used in the textile industry. It frequently acts as a preliminary material in polymeric dyes production. RBBR also is an anthraquinone-based dye that indicates highly toxic and recalcitrant pollutants. The dyes wastewater that discharge by dye-utilizing industries has clearly visible and threat the life of the organism; this drawn the awareness to the researcher to solve the problem. Through the various study, research, and experiment, many treatment methods have been indicated and proposed to treat the dyes in the wastewater. The treatment method mainly can be categories into three methods, which are biological methods, chemical methods, and physical methods, as well as nanotechnology [9-13].

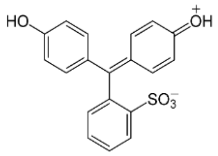
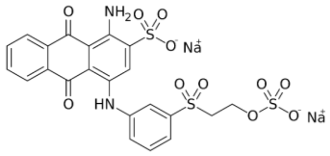
The adsorption process is a cheap process of removing a substance from either liquid or gaseous. It has played a significant role in the treatment of wastewater by decolorizing the color in the dye effluents. Agriculture which also known as farming is a production process to produce food, fiber, feed, and other goods by raising poultry or livestock and cultivation of crops. Agricultural products have not only acted as a food supplier for many thousands of years but also an essential sector of economics throughout the centuries prior to now. Previously, many types of research have proven the agricultural waste has a high potential in removing the dyes from wastewater [6,14]. Besides, it is very cost-effective and easy to obtain. Thus it can replace the high cost activated carbon for the wastewater treatment process. As different agricultural waste has different adsorption ability, so the test needed to carry to investigate for different agricultural waste. The aim of this study and research was to identify and investigate the most effective adsorbent to decolorize or remove adsorbate (dyes) by adsorption methods. The adsorption isotherm and kinetic studies were also investigated.

## 2. Materials and Methods

### *2.1. Dye solution and adsorbent.*

Phenol red (PR) and remazol brilliant blue r (RBBR) were obtained from Sigma–Aldrich with high laboratory grade. The physicochemical characteristics of the dye are shown in Table 1. The stock solution was made by dissolving 1 g of dye in 1 liter of distilled water. The series of 100, 200, 400, 600, and 800 mg/L of dye concentration was provided from this main dye solution. The stink bean was collected from a local market and cleaned by tap water to remove the dirt. The adsorbent was ground and dried in the oven at 105$^{o}$C for 24h, and sieved through 600 µm siever to obtain a similar average size of the adsorbent powder and stored it in an airtight container at room temperature.

**Table 1.** Physical and chemical characteristics of PR and RBBR.

| Parameter | PR | RBBR |
|---|---|---|
| Chemical Structure |  |  |
| Synonyms | Phenolsulfonphthalein | Reactive Blue 19 |
| Molecular Formula | $C_{19}H_{14}O_5S$ | $C_{22}H_{16}N_2Na_2O_{11}S_3$ |
| Molecular Weight | 354.376 g/mol | 626.54 g/mol |
| Appearance in Solid Stage | Red Crystal Powder | Crystalline Powder |
| Appearance in Liquid Stage | Reddish Orange Coloured Solution | Blue to Black |
| Physical State | Solid | Solid |
| Composition | Dye Content 90% | Dye Content ~ 50% |
| Solubility | Slightly Soluble in Water | Soluble in Water |
| Melting Point | 285˚C or 545˚F | ~ 305˚C or ~ 581˚F |
| $\lambda_{max}$ | 435 nm | 590 nm |

*2.2. FTIR.*

Fourier Transform Infrared Spectroscopy (FTIR) (Agilent Model: Cary 630) analysis was performed to determine the surface functional groups of adsorbents. It was recorded in the spectral range varied from 650 $cm^{-1}$ to 4000 $cm^{-1}$.

*2.3. Equilibrium study.*

Adsorption experiment was conducted in 100-ml Erlenmeyer flasks containing 50 ml solution and dried powder of dye (5 g). The flask was sealed and agitated using a mechanical shaker (100 rpm) at room temperature (±27$^o$C). This test was conducted for the five proposed effect parameters, which included concentration, contact time, adsorbent dosage, molecular size, and pH. In order to obtain a reliable result, the test was conducted for each parameter would repeat two to three times. The kinetics was studied in a duration of up to 24 hr. The sample solution was filtered by using The Advantech filter paper, and the removal of dye was measured by calculating the decrease of absorbance at 435 nm (PR) and 590 nm (RBBR) on the UV spectrum (Perkin Elmer).
The dye removal (%) and adsorption capacity $q_e$ (mg/g), was calculated by:

$$\text{Colour removal (\%)} = \frac{C_i - C_f}{C_i} \times 100$$

$$\text{Adsorption capacity (mg/g)} = \frac{C_i - C_f}{M} \times V$$

where $C_i$ is the initial concentration of dye solution (mg/L), $C_f$ is the final concentration of dye solution after adsorption (mg/L), M is the mass of adsorbent (gm), and V is the volume of dye solution (L).

*2.4. Isotherm and kinetic studies.*

Two models were used in the isotherm study of this research, which is Langmuir isotherm and Freundlich isotherm. Langmuir isotherm was used to contrast and quantify the adsorption ability of adsorbents also describe the adsorption in the gas-solid phase. It considers the surface coverage by balancing the dynamic equilibrium and adsorption relative rates.

Freundlich isotherm has high correlation coefficients and widely applicable to the adsorption process that takes place on the heterogonous surface (mainly organic compound) and multilayers with non-uniform adsorption heat distributions. The variation of the slope for adsorption intensity is in between 0 to 1, the closer the value to 0 means, the more heterogeneous it is. The equation of that isotherm is presented as following [15]:

Langmuir equation : $\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$

Freundlich : $\log q_e = \log K_F + 1/n \log C_e$

where $C_e$ is the concentration of adsorbate at equilibrium (mg/g), $q_e$ is the amount of adsorbate at equilibrium (mg/g), $q_m$ is equal to $q_e$ and $K_L$ is Langmuir constant related to adsorption capacity (L/mg), $K_F$ is adsorption capacity (mg/g), and 1/n is adsorption intensity.

The two models (pseudo-first-order and pseudo-second-order) was used to analyze the kinetics of the adsorption process as follows:

Pseudo-first-order rate law : $\text{In } [q_e - q(t)] = \text{In } q_e - k_1 t$

Pseudo-second-order rate law :

$$\frac{t}{q(t)} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$$

where $q_e$ is adsorption capacity at equilibrium time (mg/g), q(t) is the amount of adsorbate adsorbed at contact time t (mg/g), $k_1$ is the pseudo-first-order rate constant ($min^{-1}$), and t is contact time with the adsorbent (min), and $k_2$ is the pseudo-second-order rate constant (g/ (mg min)).

## 3. Results and Discussion

*3.1. Screening of adsorbent.*

This screening process was conducted by using Remazol Brilliant Blue R (RBBR) as the tested dyes to choose the best two that have the highest removal percentage among ten adsorbents. The available adsorbent including coffee (*Coffea*) dregs, tea (*Camellia sinensis*) dregs, coconut (*Cocos nucifera*) shells (*Endocarp*), pineapple (*Ananas comosus*) peels, ambarella (*Spondias dulcis*) peels, longan (*Dimocarpus longan*) peels, lemon (*Citrus limon*) peels, honeydew (*Cucumis melo*) peels, banana (*Musa acuminata*) peels and langsat (*Lansium domesticum*) peels. 50 ppm concentration of dye solution was added with 0.5 grams of different adsorbent in different conical flask respectively and placed in an orbital shaker at 120 rpm for 4 hours under room temperature. Coconut shells and ambarella peels have achieved the best two results among ten of the adsorbents, with the removal rate of 62.73% and 58.32%, respectively (Fig. 1). Although the tea dregs adsorbent has achieved more than 50% of removal rate, it is lower compare to coconut shells and ambarella peels. The lowest removal rate goes to banana peels, which is 10.62%. At the same time, the rest of the adsorbents is less than 50% of the removal rate. The same goes for adsorption capacity; adsorbent that has the highest capacity were coconut shells and ambarella peels, which is 6.59 mg/g and 6.12 mg/g. The lowest adsorption capacity the same goes to banana peels, which is 1.12 mg/g, and the rest of the adsorbents is below 6 mg/g. This test had been carried out to evaluate the effect of initial dye concentration on the adsorption process for coconut shells and ambarella peels in removing Phenol Red (PR) and Remazol Brilliant Blue R (RBBR) dyes. It was conducted by adding 0.5

grams of adsorbents to the various initial concentration of dye (10 ppm, 30 ppm, 50 ppm, 70 ppm, 100 ppm, and 150 ppm). Those samples were shacked mechanically at 120 rpm for 4 hours. Other parameters were kept constant, and finally, the percentage of removal was calculated.

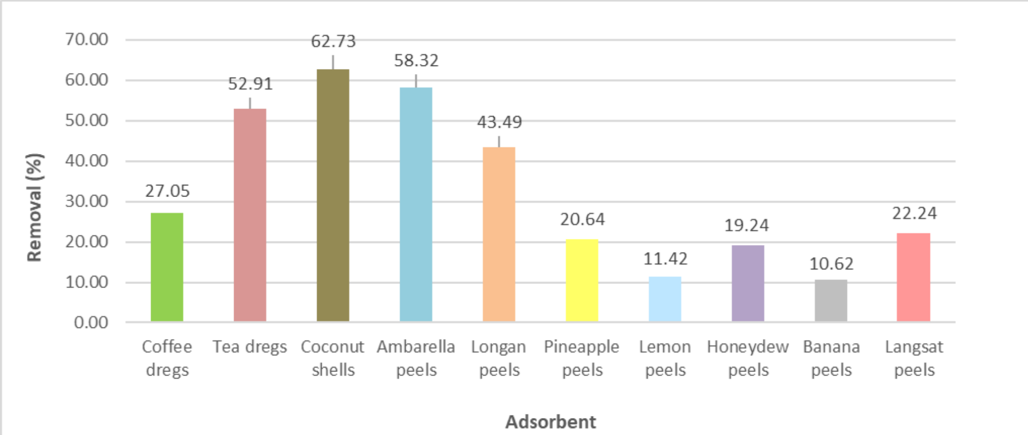



**Figure 1.** Graph of removal rate for a different type of adsorbents.

*3.2. Batch studies.*

Based on the results shown in Fig. 2, it is possible to conclude that the removal rate of dyes decreases with increasing initial dye concentration for both adsorbents. For coconut shells, as the initial PR and RBBR concentration increased from 10 to 150 ppm, the percentage of removal rate decreased from 85.64% to 71.32% and 65.11% to 53.12%, respectively. Whilst for ambarella peels, as the initial PR and RBBR concentration increased from 10 to 150 ppm, the percentage of removal rate decreased from 98.34% to 81.07% and 63.25% to 47.19% respectively. However, with the increase in dye concentration, the actual amount of dye adsorbed per unit mass of carbon ($q_t$) increased. The phenomenon above can actually be explained in terms of active surface sites of the adsorbent. At low concentration, the amount of unoccupied active sites is high, which means the ratio of surface active sites to the total dye molecules in solution is high. Therefore, in the interaction of dye molecules or ions with adsorbent, those molecules occupy the active sites on the carbon surface and can be removed from the solution [16,17]. Yet with the increase in dye concentration, the active sites of adsorbent were saturated and not enough to accommodate dye molecules, and hence the percentage of removal decreased.

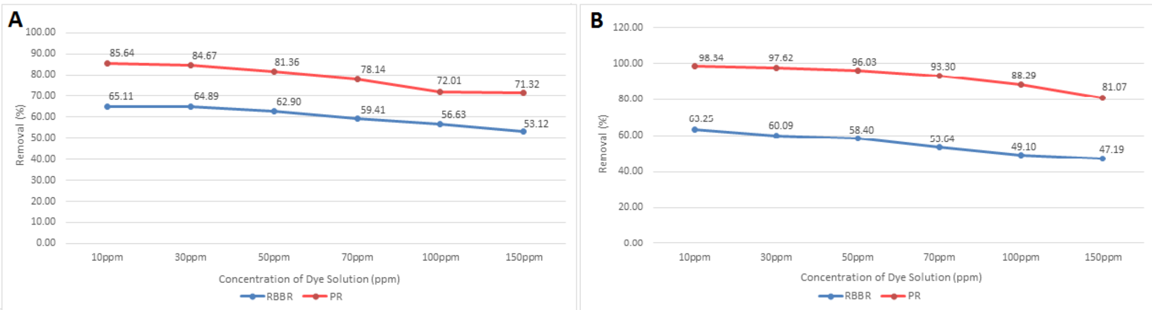



**Figure 2.** Effect of dye concentration on RBBR and PR removal by coconut shells (A) and in ambarella peels (B).

Figure 3 shows the effect of adsorbent dosage on the adsorption process for coconut shells and ambarella peels in removing phenol red and remazol brilliant blue r dyes. It was conducted by adding a various amount of adsorbent to 50 ppm concentration of dye solution. The amount of both adsorbents used to add to the solution were 0.5 gram, 1 gram, 3 gram, and 5 grams. Those samples were be shacked mechanically at 120 rpm for 4 hours. Other parameters were kept constant, and finally, the percentage of removal was calculated. It can be observed that the removal rate of PR increased linearly as the dosage of coconut shell increased. For 0.5 grams of coconut shell resulted in 81.21% of removal PR and 62.13% of removal RBBR. Besides, for 1 gram of coconut shell resulted 88.65% of removal PR and 63.62% of removal RBBR. Meanwhile, 3 grams of coconut shell resulted 92.60% of removal PR and 68.96% of removal RBBR. Lastly, 5 grams of coconut shell resulted 95.54% of removal PR and 73.43% of removal RBBR. Thus, the highest removal rate of coconut shells for both PR and RBBR resulted in 5-gram phase. As a result, shown in, the percentage of removal increases with increasing the dosage of ambarella peels from 0.5 grams to 5 grams. For 0.5 gram of ambarella, peels resulted 96.80% of removal PR and 56.44% of removal RBBR. Besides, for 1 gram of ambarella peels resulted 97.51% of removal PR and 59.43% of removal RBBR. Meanwhile, 3 grams of ambarella peels resulted 99.03% of removal PR and 67.37% of removal RBBR. Lastly, 5 grams of ambarella peels resulted 99.82% of removal PR and 73.13% of removal RBBR. Thus, the highest removal rate of ambarella peels for both PR and RBBR also resulted in 5-gram phase. Overall, most of the results show that the removal rate of dye increased as the adsorbent dosage increased. This can be explained as the study on the effect of dye concentration before, which by available active sites. With the increasing of adsorbent dosage, the total number of active sites of adsorbent increased as well as the greater availability of specific surfaces of the adsorbents [10,17,18].

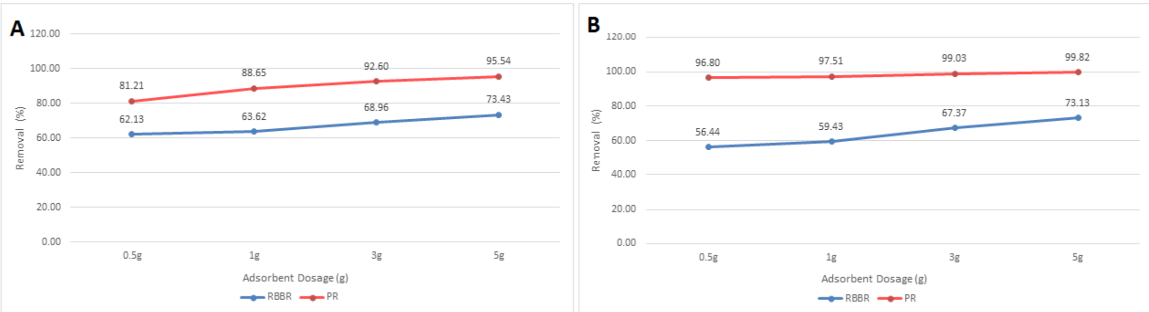



**Figure 3.** Effect of adsorbent dosage on RBBR and PR removal by coconut shells (A) and in ambarella peels (B).

Figure 4 shows the effect of contact time for adsorbent and dye solution. The objective of this test is to investigate the most appropriate duration of time for adsorbent to decolorize the dye solution. It was carried out by adding 0.5 grams of adsorbent to 50 ppm concentration of dye solution. Those samples were be shacked mechanically at 120 rpm for 4 hours. The absorbance result was recorded every 3 hours; each reading was repeatedly scanned three times; then, the average value was calculated in order to obtain an accurate result. Figure 4A shows the PR and RBBR removal rates of the coconut shells with 24 hours contact time. The removal rate of PR and RBBR were increased gradually in the first 18 hours and 21 hours respectively, after that both results were decreased slightly. Therefore, the suitable duration for coconut shells to remove PR and RBBR were 18 hours and 21 hours with a result showing that those were the highest removal rate compared to other durations. The highest percentage of PR and RBBR removal for coconut shells was 89.76% and 75.78%, respectively, as clearly shown in the figure above. Figure 4B shows the PR and RBBR removal rate of the ambarella peels with 24 hours contact time. The removal rate of PR and RBBR were increased gradually in the first 12 and decreased slightly after the maximum peak. Therefore, the suitable duration for ambarella peels to remove PR and RBBR were 12 hours with a result showing that those were the highest removal rate compared to other durations. The highest percentage of PR and RBBR removal for ambarella peels was 97.28% and 68.60%, respectively, as clearly shown in the figure above. By comparing all the results, it can be concluded that both coconut shells and ambarella peel adsorbents were more efficient in removing PR, since the removal rate of PR for both adsorbents was higher than the removal rate of RBBR. Moreover, the percentage of removal was found to be increased initially but decreased after a certain contact time. This is because the attractive forces between adsorbent and dye molecules were strong enough, and the time was sufficient for them to interact with each other [10,17]. However, due to equilibrium was not achieved between the amount of dye molecule adsorbed by adsorbent and the amount of dye molecule remain in the solution, this causes decreasing in removal rate. As a result, the active site of adsorbent was not fully bound with dye molecule, once the adsorbent reaches their limit, the ability for it to absorb the dye molecule would also decrease. The amount of dye molecule adsorbed decreased the attractive force of functional groups on the surface of the adsorbent, and the dye molecule was weaker, so the dye molecule left in the solution [6,19]. As longer the contact time of adsorption, the bigger the collision between particle of adsorbent and adsorbate.

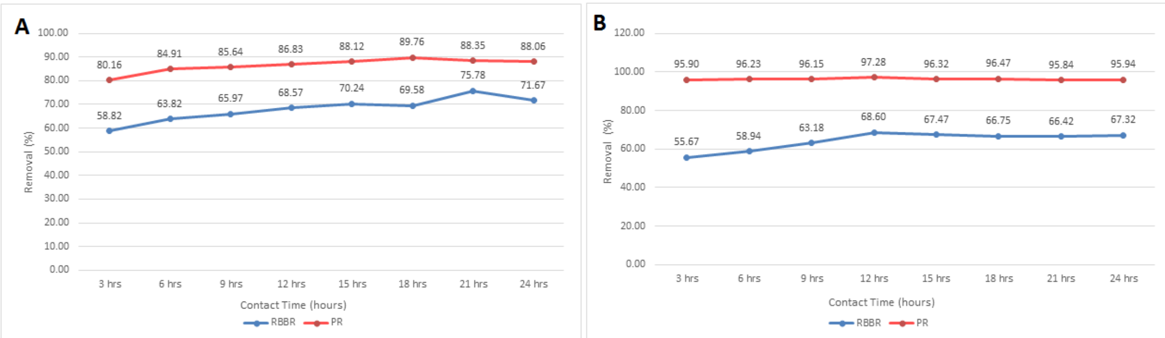



**Figure 4.** Effect of contact time on RBBR and PR removal by coconut shells (A) and in ambarella peels (B).

Figure 5 shows the effect of pH on the adsorption process for coconut shells and ambarella peels in removing PR and RBBR dyes. It was conducted by adding 0.5 grams of adsorbent to various pH of 50 ppm dye solution. The pH of the dye solution was adjusted by adding Hydrochloric acid, HCl, and Sodium Hydroxide, NaOH. Various pH samples decided to used were pH 2, pH 5, pH 7, pH 9, and pH 12. Those samples were be shacked mechanically at 120 rpm for 4 hours. Other parameters were kept constant, and finally, the percentage of removal was calculated. From the result in Figure 5A, the highest removal rate of coconut shells in PR and RBBR were both resulted in an acid medium with a score of 79.49% and 56.97%, respectively. Whilst the highest removal rate of ambarella peels in PR and RBBR resulted in acid and neutral medium with a score of 69.96% and 58.58%, respectively. The neutral condition means there is no positive or negative charge predominate the surface of the adsorbent. As the pH of the dye solution increased until the alkalinity level, the percentage of removal decreased. This phenomenon can be explained by the surface properties of the adsorbents and dissociation or ionization of the adsorbate molecules. Low pH leads to an increase in hydrogen ($H^+$) ion concentration; the adsorbent will possess a positive charge by adsorbing $H^+$ ions. As the surface of adsorbent is positively charged at low pH, a significantly strong electrostatic attraction appears between the dye molecule and positively charged adsorbent surface, leading to higher adsorption. As the pH of the dye solution increased, the negatively charged sites increased, and positively charged sites decreased. A negatively charged surface site on the adsorbent does not favor the adsorption of dye molecules due to the electrostatic repulsion [16,18].

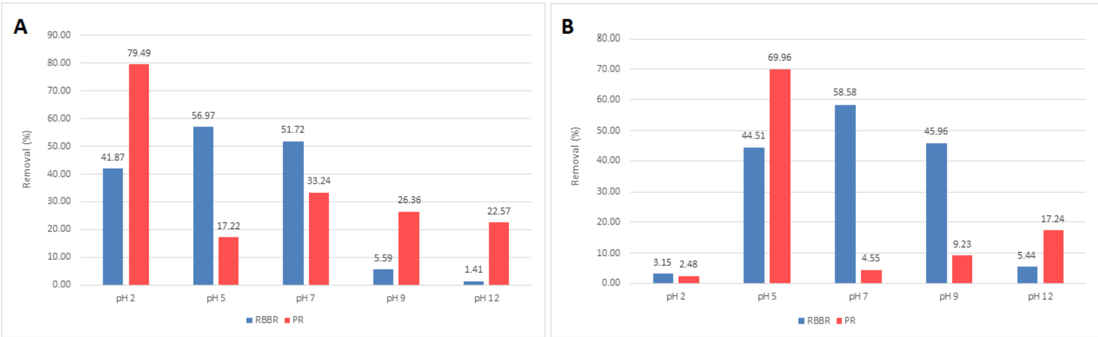



**Figure 5.** Effect of pH on RBBR and PR removal by coconut shells (A) and in ambarella peels (B).

Figure 6 shows the effect of particle size of adsorbent on the adsorption process for coconut shells and ambarella peels in removing PR and RBBR dyes. It was conducted by adding two different sizes of adsorbent to 10 ppm concentration of dye solution. The particle size of adsorbent was 150 µm and bigger than 150 µm. Those samples were be shacked mechanically at 120 rpm for 4 hours. Other parameters were kept constant, and finally, the percentage of removal was calculated. The 150 µm adsorbent was found to remove more of the dye. The relatively higher adsorption capacity with smaller adsorbent particles was due to the greater surface area for adsorption per unit mass or larger surface retention and greater accessibility to pores of adsorbent [20].

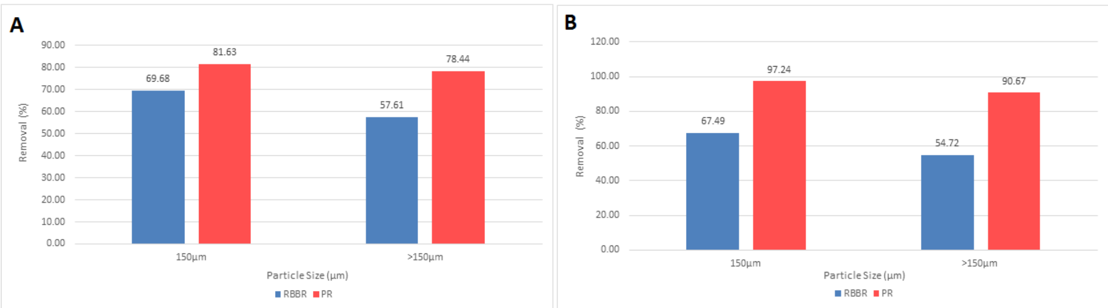



**Figure 6.** Effect of particle size on RBBR and PR removal by coconut shells (A) and in ambarella peels (B).

*3.3. FTIR.*

The chemical reactivity of the functional group at the adsorbent surface could affect the adsorption capacity. Different adsorbents have different functional groups, which cause the difference in adsorption capacity. Figure 7A shows the infrared spectrum for raw coconut shell, the exhibition of the peak at the 3272.60 $cm^{-1}$ was caused by hydroxyl functional group of alcohols which have O-H stretch. At peak 2922.23 $cm^{-1}$, it shows the existence of CH stretching that causes vibration of CH, $CH_2$, and $CH_3$ groups. While at 1595.30 $cm^{-1}$ and 1237.48 $cm^{-1}$ show the characteristic of C═C bonds in aromatic rings. There was a strong variable bond with peak 1028.75 $cm^{-1}$; this shows that a group of silicate which has Si-O stretch existed. The same functional group of alcohols also existed in Figure 7B and Figure 7C at peaks 3332.24 cm$^{-1}$ and 3324.79 cm$^{-1}$. The major deviations of these peaks are assigned to the vibrations of N-H and O-H functional groups. At the same time, other major changes that can be seen are at the increments in the C-O carboxyl bands from 1632.57 cm$^{-1}$ to 1244.93 cm$^{-1}$ and 1625.12 cm$^{-1}$ to 1244.93 cm$^{-1}$ for decolorization of PR and RBBR respectively. Usually, the activity of carboxyl oxygen atoms causes alterations in these band areas. The peaks at 1028.75 cm$^{-1}$ show that there was a silicate group which attributed to Si-O bending and stretching, but it becomes sharp due to the stretching of the carboxyl group beside it.

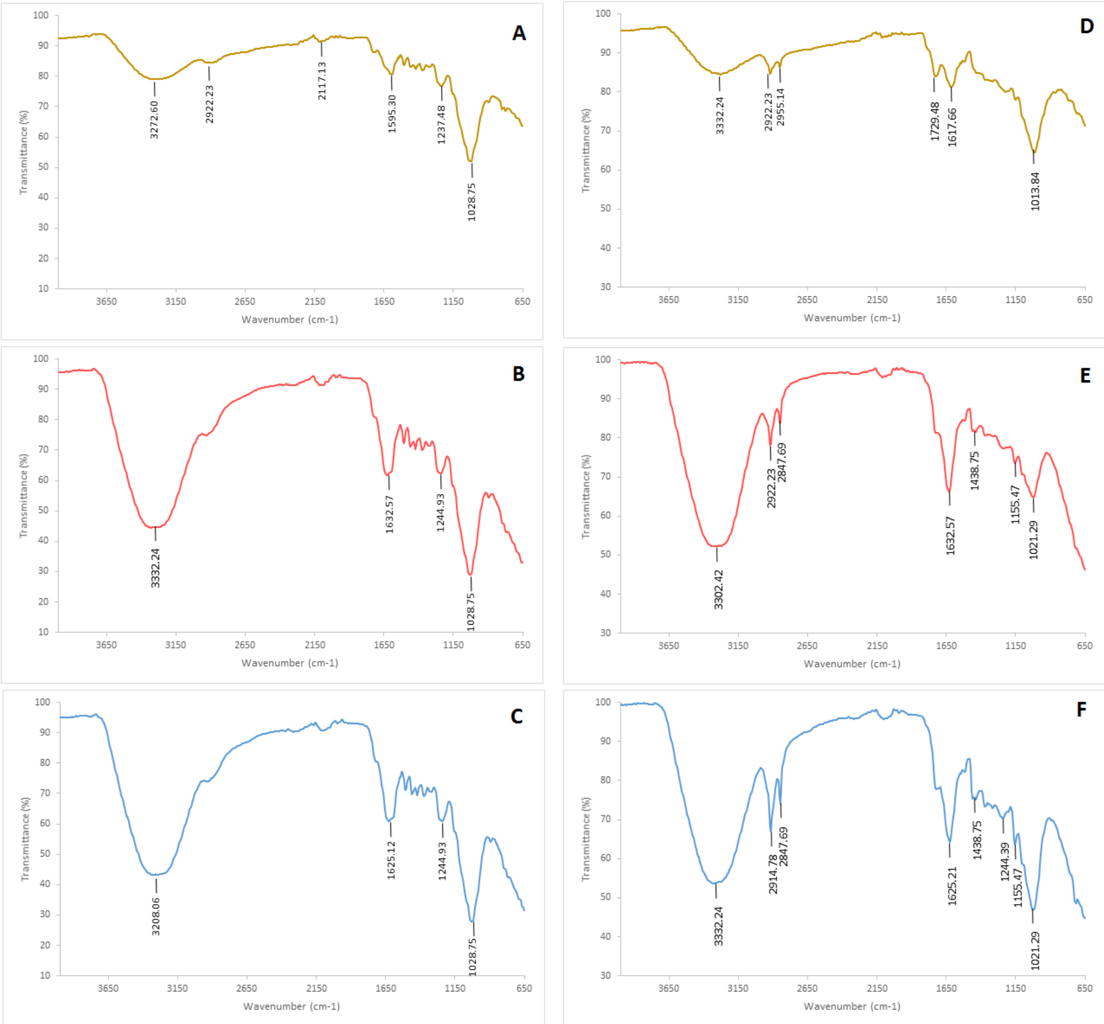



**Figure 7.** FTIR spectra of coconut shell: raw (A), PR decolorization (B), RBBR decolorization (C); and amabrella peel: raw (D), PR decolorization (E), RBBR decolorization (F).

Ambarella is an acidic fruit with some terpene-like and astringency flavor [19]. The first peak observed from Figure 7D was peak 3280.06 cm$^{-1,}$ which was polyurea, amide, and alcohol group with stretching of NH, CH, and OH, which also probably contributed by the carboxylic acid that has COOH functional group. Next, CH stretching causes the vibration of CH and $CH_2$ present at the peak of 2922.23 cm$^{-1}$ and 2855.14 cm$^{-1}$. While at peak 1729.48 cm$^{-1}$ and 1617.66 cm$^{-1}$ show the characteristic of stretch vibration of NH and C=O from a carboxylic acid. Lastly, at peak 1013.84 cm$^{-1}$ was a C-O carboxyl band. Significant peaks observed after the decolorization of PR and RBBR from Figure 7E and Figure 7F were 3302.42 cm$^{-1}$ and 3332.24 cm$^{-1,}$ respectively, both peaks were caused by strong NH and CH stretch. Whereas at 2914.78 cm$^{-1}$, 2847.69 cm$^{-1}$, 2922.23 cm$^{-1,}$ and 2947.69 cm$^{-1}$ show the existence of CH stretching that causes vibration of CH and $CH_2$. Lastly, at peaks, 1632.57 cm$^{-1}$ and 1625.12

cm$^{-1}$ show the presence of a functional group of ketone and amide with C=O stretch. In the overall view of the pattern of before and after decolorization FTIR spectra, changes can be noticed for both coconut shells and ambarella peels adsorbents. Therefore, it can be said that the chemical functional group of both adsorbents was involved in the adsorption process. This means the dye has been successfully adsorbed by coconut shells and ambarella peels, which change the character of the adsorbent.

### *3.4. Isotherm and kinetic studies.*

The adsorption capacity and initial concentration of dye parameter for adsorption of PR and RBBR on coconut shells and ambarella peels were evaluated using Langmuir and Freundlich isotherm models; the results are presented in the figure and table above. The linear plots of $C_e/q_e$ versus $C_e$ revealed that the adsorption obeys Langmuir isotherm model for all adsorbents. The $q_m$ and $K_L$ were determined for all adsorbents from the intercept and slopes of the linear plots present in Figure 8. Langmuir isotherm models have been shown using mathematical calculations that parameter $R_L$ indicates the nature of the adsorption process [17].

**Table 2.** Intraparticle diffusion rate parameter and diffusion coefficient at various initial PR and RBBR concentration.

| Initial dye concentration (ppm) | PR | | RBBR | |
|---|---|---|---|---|
| | Coconut shells | Ambarella peels | Coconut shells | Ambarella peels |
| 10 | 0.7762 | 0.2902 | 0.9281 | 0.9125 |
| 30 | 0.5366 | 0.1199 | 0.8114 | 0.7767 |
| 50 | 0.4096 | 0.0756 | 0.7207 | 0.6761 |
| 70 | 0.3314 | 0.0552 | 0.6483 | 0.5985 |
| 100 | 0.2576 | 0.0393 | 0.5634 | 0.5106 |
| 150 | 0.1878 | 0.0265 | 0.4625 | 0.4103 |

From Table 2, it is observed that $R_L$ values for both adsorbents fall in the range of 0−1, which is an indication of a favorable adsorption process. Besides, the high value of correlation coefficient $R^2$ (0.9597, 0.8894, 0.9145, 0.9743) indicates the applicability of Langmuir isotherm, which assumes a monolayer coverage and uniform activity distribution on the adsorbent surface. On the other hand, according to the adsorption data, the Freundlich isotherm model showed well-fitting $R^2$ (0.9949, 0.9885, 0.9952, and 0.9709). The plot of log $q_e$ versus log $C_e$ is a straight line with the interception at the y-axis representing the value of log $K_F$ with slop 1/n. The linear plot showed the applicability of Freundlich isotherm to both adsorbents and both dyes. The value of 1/n, which closer to 0 means the adsorption is more heterogeneous, 1/n below 1 indicates a normal Freundlich isotherm while 1/n lies between 0 and 1 are indicative of cooperative adsorption. In this case, all the value of 1/n (0.7574, 0.5113, 0.8738, and 0.8185) is within 0 to 1, in which the adsorption is considered as favorable and heterogeneous [10,22].

The data for adsorption of PR and RBBR on coconut shells and ambarella peels were applied to pseudo-first and second-order kinetic models, and the results are presented in Table 3. All the plot of pseudo-first and second-order give a linear relationship, from which the value of $k_1$, $k_2$, and $Q_e$ can be determined from the slope and intercept. The correlation coefficient of the second-order kinetic model (1.0000 and 0.9978) is greater than the first-order kinetic model (0.9969 and 0.9894). This confirmed that the rate-limiting step is chemisorption, involving valence of forces through sharing or exchange of electrons [21].

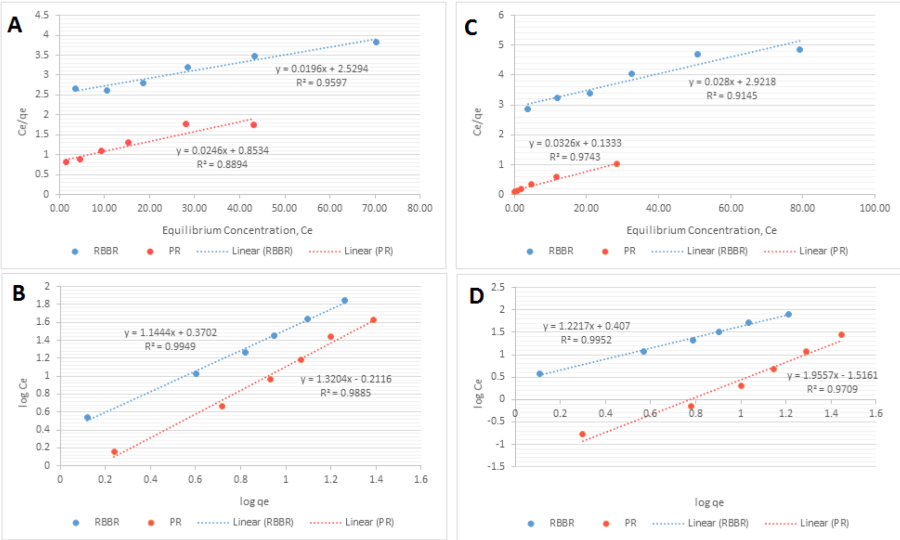



**Figure 8.** Isotherm model coconut shell: Langmuir (A), Freundlich (B); and ambarella peel: Langmuir (C), Freundlich (D).

In addition, it was found that the calculated equilibrium adsorption capacity ($Q_e$) for the pseudo-first-order kinetic model (1.3828 mg/g, 6.5719 mg/g, 2.0065 mg/g, and 4.8545 mg/g) was significantly lower than the pseudo-second-order kinetics calculated value of $Q_e$ (9.4518 mg/g, 10.1112 mg/g, 7.6805 mg/g, and 7.1124 mg/g). Therefore, it was presumed that the pseudo-second-order model provides a better correlation of adsorption fit than the pseudo-first-order model for both adsorbents, ensuring that the rate-limiting step may be of chemisorption type [10,23].

**Table 3.** Kinetic parameters for the adsorption of PR and RBBR onto adsorbents.

| Kinetic | Coconut shells | | | Ambarella peels | | |
|---|---|---|---|---|---|---|
| | $k_1$ or $k_2$ ($min^{-1}$) | $Q_e$ (mg/g) | $R^2$ | $k_1$ or $k_2$ ($min^{-1}$) | $Q_e$ (mg/g) | $R^2$ |
| PR<br>Pseudo-first-order model | − 0.0023 | 1.3828 | 0.9628 | − 0.0006 | 6.5719 | 0.9969 |
| Pseudo-second-order model | 0.0042 | 9.4518 | 0.9999 | 1.8486 | 10.1112 | 1.0000 |
| RBBR<br>Pseudo-first-order model | − 0.0012 | 2.0065 | 0.9154 | − 0.0006 | 4.8545 | 0.9894 |
| Pseudo-second-order model | 0.0203 | 7.6805 | 0.9994 | 0.0228 | 7.1124 | 0.9978 |

## 4. Conclusions

In this study, the most effective adsorbent to remove the PR and RBBR was identified to replace activated carbon in the adsorption process. The positive results showed that low-cost agricultural waste tested such as coffee dregs, tea dregs, coconut shells, ambarella peels, longan peels, pineapple peels, lemon peels, honeydew peels, banana peels, and langsat peels can be used as adsorbents in removing the dye. However, the best two selected from screening with the use of dye Phenol Red were coconut shells and ambarella peels that have a percentage of removal of 79.57% and 95.58%, respectively. From the study of two adsorption isotherms, Langmuir and Freundlich isotherm, it was observed that Freundlich isotherm with a better fitting model than Langmuir isotherm also had higher correlation coefficient, $R^2$ for both adsorbent graphs. This confirmed that the adsorption is heterogeneous and occurred through physical-chemical interactions. At the same time, the rate of adsorption was found to obey the pseudo-second-order kinetics model with a good correlation coefficient.

## Funding

This research was partially funded by The World Academic of Sciences, grant number 2017/2.

## Acknowledgments

This research has no acknowledgment.


## Conflicts of Interest

The authors declare no conflict of interest.

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