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Research Article

Biosorption Study of Methylene Blue (MB) and Brilliant Red Remazol (BRR) by Coconut Dregs

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Water pollution has become a major issue in many countries, including Malaysia. Malaysia is one of the countries that suffers from this detrimental influence on water resource sustainability. Adsorption has been discovered to be a cost-effective and efficient method of removing contaminants such as pigments, dyes, and metal impurities. Many biomass-based adsorbent materials have been successfully used for the removal of dyes from aqueous solutions. In this study, the potential use of coconut dregs as the new biosorbent for the removal of Methylene Blue (MB) (basic dye) and Brilliant Red Remazol (BRR) (acidic dye) was investigated. The effects of adsorption time, adsorbent dosage, pH, and initial dye concentration on coconut dregs adsorption for MB and BRR dye were investigated using 2-Level Factorial Design of Design-Expert 7.1.5. The results indicated that the amount of dye adsorbed on the coconut dregs increased with increasing dye concentration, adsorbent dosage, and adsorption time. However, both MB and BRR dyes favor different pH for the adsorption process. The adsorption capacity of MB dye increased with increasing pH, while the adsorption capacity of BRR dye increased with decreasing pH. Removal of MB was optimum at pH 11, contact time of 240 min, a dosage of 0.25 g adsorbent, and an initial dye concentration of 50 mg/L. Meanwhile, for BRR dye, the optimum condition was pH 2, contact time of 180 min, the dosage of 0.25 g adsorbent, and an initial dye concentration of 50 mg/L. The equilibrium data for both dyes fitted very well with the Langmuir Isotherm equation giving a maximum monolayer adsorption capacity as high as 5.7208 mg/g and 3.7636 mg/g for Methylene Blue Dye and Brilliant Red Remazol dye, respectively. This study shows that coconut dregs can be one of the potential and low-cost biosorbents for the treatment of industrial dyes soon.

1. Introduction

Water pollution is one of the most serious forms of pollution in the world, and it has generated a slew of issues for both humans and the environment. Industries utilize dye to impart desired color products, such as the textile industry [1], which is one of the leading contributors to other water pollution. Cosmetics, paints, leather, and printing inks are among the businesses that employ dyes in addition to the textile industry [1]. It is estimated that 20 kg of wastewater will be generated from 1 kg of synthetic dyed cotton which will take a long time to decompose [2]. Since wastewater-containing dyes are chemicals that may be dangerous to aquatic life, several approaches have been used to remediate them in recent years. Not only that, but these dyes may be resistant to biological deterioration in the natural world. The

common strategies for removing dyes from wastewater include adsorption, oxidation-ozonation, biological treatment, coagulation or flocculation, and membrane processing [3, 4].

Along with its simplicity and cost-effectiveness, the adsorption technique is the most successful approach for dyes treatment [5, 6]. Adsorption is a chemical reaction in which a material in a gas or liquid binds to a solid. Because of its high adsorption capacity and a high degree of surface reactivity, activated carbon is the most extensively employed adsorbent [7–9]. However, carbon adsorption is a costly method due to the high cost of commercially available activated carbons [7]. As a response, numerous investigations have been conducted to find a less expensive adsorbent. Low-cost materials, primarily derived from agricultural waste material, have been tested as alternatives to activated carbon to lower treatment costs. Bio-adsorption is the term for the process of adsorption of contaminants utilizing materials [5]. Palm oil fibre [1], wasted tea leaves [2], cotton plant wastes [3], sunflower seed shells [7], sawdust [7], and 'waste' coir pith [10] have all been utilized as biosorbents, although the most effective and cost-effective biosorbent is still being explored.

The materials being investigated as possible biosorbents must possess a number of key features. For instance, the material should be easier to obtain; most likely, there will be plenty in nature, lowering the material cost. Not only are the resources less expensive, but the usage of abundant biomass will also alleviate pollution issues created by discarded biomass. However, some treatment methods for agricultural waste are required before it may be employed as an adsorbent. If it is not treated further, these components will have catastrophic effects [11].

Coconut dregs, also known as *'hampas kelapa'*, are the residual fibre from coconut milk that can be used as a potential biosorbent. Coconut milk [12] is a sweet, creamy white culinary foundation made from mature coconut meat. After oil palm, rubber, and rice, coconut production is expected to reach 62 million tonnes in 2019, making it Malaysia's fourth most significant crop in terms of acreage [13]. However, the industrialization of coconut oil manufacturing produces a significant amount of coconut dregs, with 1.9 million metric tonnes produced in 2019. To make coconut milk, 19.50 kg of coconut dregs were produced per 100 coconuts. According to reports, the local coconut-based processing sectors are seeing an increase in demand for local consumption [14]. As coconut is readily available in Malaysia, the dreg of coconut was used as the adsorbent in this investigation. The purpose of this study is to determine the adsorption capacity of coconut dregs as a new biosorbent and to investigate their potential as a new biosorbent for dye removal.

2. Materials and Methods

2.1. Sample Collection. The coconut dregs used in this study were obtained from local shops located in Bintong, Perlis before being treated physically using chemicals. The dyes used for this study were Brilliant Red Remazol 3BS (BRR) dye and Methylene Blue (MB) dye supplied in powder form. BRR dye was purchased from A.R. Alatan Sains (K) Sdn. Bhd, Malaysia, and MB dye were purchased from HmbG Chemicals, Hamburg, Germany.

2.2. Biosorbent Preparation. The coconut dregs were dried in an oven at 60°C for 48 hours and were ground using a food-processing blender before being sieved to a particle size of 0.5 mm in diameter [2]. Then, it was soaked in 0.1 M sodium hydroxide (NaOH) solution for 24 hours and then thoroughly washed with distilled water several times to get a neutral pH of 7 [15]. The liquid portion was removed and the solid was dried again in an oven at 105°C for 24 hours [7] and again to get the particle size of 0.5 mm.

2.3. Batch Mode Adsorption Studies. The batch mode adsorption studies were carried out to find the adsorption capacity of coconut dregs as biosorbent. The experiments were conducted using 125 mL volumetric flasks filled with 100 mL dye [1] with various adsorbent dosages, initial dye concentration, and pH. The stock solutions of dyes were prepared by dissolving the dye powder in distilled water with a concentration of 1000 mg/L. The stock solutions then were diluted to the required initial concentration [1]. 1 M sodium hydroxide (NaOH) or 1 M hydrochloric acid (HCl) were used to adjust the pH of the solutions of dye and adsorbent to the required value and measured using a pH meter [2]. The volumetric flasks were agitated in a rotary shaker at various times at 25°C [13] and at a constant speed of 200 rpm [1]. The variables that were studied to identify the adsorption capacity were adsorbent dosage, initial dye concentration, pH, and adsorption time. Before the batch adsorption experiments were conducted, the experiments with these variables were designed first using Design of Expert Software (DOE).

2.3.1. Experimental Design. In this present study, the 2-Level Factorial Design of Design-Expert 7.1.5 was used to design the batch mode adsorption studies of MB dye and BRR dye. The experiments were carried out in a randomized complete block of 2^4 designs since there are four factors used. The factors that were used in this 2-Level Factorial Design are the effect of pH (2 to 7 for BRR dye) and (7 to 11 for MB dye); the effect of adsorbent dosage (0.25 to 1.5 g); the effect of adsorption time (30 to 180 min for BRR dye) and (30 to 240 min for MB dye); and the effect of dye initial concentration (20 to 50 mg/L). These resulted in 35 combinations of pH, adsorbent dosage, adsorption time, and dye initial concentration. These 35 combinations of runs included three center points and two replicates for each run.

2.3.2. Separation Techniques. For separation between the adsorbent and the dye solution, the sample was centrifuged at 5000 rpm for five minutes [3]. After centrifugation, the adsorbent was removed and the maximum wavelengths of 665 nm [16] and 541 nm [17] were used to measure the absorbance of MB and BRR using a UV Spectrophotometer.

2.4. Sample Analysis. Data were analyzed by calculating the amount of sorption at time t, q_t (mg/g), by using the following relationships:

$$q_t = \left(\frac{C_0 - C_t}{W}\right)V, \quad (1)$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of the dye at initial and at time t, respectively. W (g) is the mass of the adsorbent and V (L) is the volume of the dye solution used [2, 18]. The absorbance value obtained from the spectrophotometer was used to determine the final concentration of MB and BRR by plotting the standard calibration curve. The standard calibration data was prepared using several MB and BRR concentrations.

2.5. Adsorption Isotherm

2.5.1. Langmuir Isotherms. Langmuir isotherms were obtained by agitating the dye solution of different concentrations (20, 30, 40, and 50 mg/L) and the adsorbate of a fixed-dose, 0.25 g for 24 hours without changing the solution pH at a temperature of 25°C [10]. The Langmuir constants, K (related to the sorption energy between the adsorbate and the adsorbent) (L/mg) and $q_{\max,}$ the maximum adsorption capacity (mg/g) were calculated from the following equation [15]:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max}K} + \frac{c_e}{q_{\max}}, \quad (2)$$

where c_e is the equilibrium concentration (mg/L), and q_e is the amount adsorbed at the equilibrium time (mg/g) [15].

2.6. Freundlich Isotherm. Freundlich isotherms were obtained by agitating an adsorbent of different dosages (0.25, 0.5, 1, 1.5 g) and the dye solution of a fixed concentration, 20 mg/L for 24 hours without changing the solution pH at a temperature of 25°C [10]. The Freundlich constants, k_f (related to adsorption capacity) (L/mg) and 'n' (related to the intensity of adsorption) (dimensionless) were calculated from the following equation [10]:

$$\log_{10}\left(\frac{x}{m}\right) = \log_{10} k_f + \frac{1}{n}\log_{10} c_e, \quad (3)$$

where x is the amount adsorbed (mg) and m is the adsorbent dosage used (g) [10].

2.7. Adsorption Kinetics. The modelling of the kinetics of dye adsorption onto coconut dregs was investigated using two common models; the pseudo-first-order model and pseudo-second-order model. The pseudo-first-order and pseudo second-order equations are expressed as follows [8]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t,$$
$$\frac{t}{qt} = \frac{1}{K_2 \times qe^2} + \frac{t}{qe}, \quad (4)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g); K_1 is the rate constant of pseudo-first-order adsorption (L/min), K_2 is the rate constant of pseudo-second-order adsorption (g/mg.min) [8].

3. Results and Discussion

3.1. Screening by 2-Level Factorial Design

3.1.1. Adsorption Time and Dosage. Adsorption time is an incredibly important parameter to get relevant information about the ideal time required for the removal of dyes. Figure 1 and Figure 2 show the interaction between adsorption time and adsorbent dosage on the effect of adsorption capacity of MB dye and BRR dye, respectively. The interaction of two independent variables in the contour plot clearly illustrates that the adsorption process using a lower adsorbent dosage at a longer time yields the highest dye adsorption capacity. In Figure 1, as the contour line approached the longest adsorption time (240 min) and lowest adsorbent dosage (0.25 g), the adsorption capacity of MB dye increased from 2.1940 mg/g to 6.7144 mg/g. Meanwhile, In Figure 2, as the contour line approached the longest adsorption time (180 min) and the lowest adsorbent dosage (0.25 g), the adsorption capacity of BRR dye increased from 1.0485 mg/g to 3.7367 mg/g. The highest adsorption capacity was obtained when the longest adsorption time was used and it can be observed that the adsorption capacity is proportional to the adsorption time, which means that the longer time gives a higher adsorption capacity This finding is in agreement with the previous studies conducted by C. Namasivayam et al. [10], B.H. Hameed [19], and Despoina D. Asouhidou [20]. In fact, this result was predicted due to the findings reported by C. Namasivayam [10], B.H. Hameed [19], and Despoina D. Asouhidou [20]. Yunfei Hu [21] in his study found that the adsorption capacity between wasted tea powder and MB increases greatly at an optimum adsorption time of 120 min due to its strong chemical affinity between active sites. The longest time sometimes is required for the adsorption process because the adsorption process is carried out in dual phases starting with the sudden rise in the adsorption process because of the viability of binding sites and the process continues to the second phase where the decrease of adsorption process since the accumulated of active sites by the dye's molecules [22].

A longer time is required for higher adsorption capacity since the time needed to reach the equilibrium depends on the nature of the adsorbent and its available sorption sites [17]. In addition, during the adsorption process, the dye molecule has to first encounter the boundary layer effect, and then it has to diffuse from the boundary layer film onto the adsorbent surface and then finally it has to diffuse into the porous structure of the adsorbent [7]. Hence, the longer time will ensure that the equilibrium is reached and increases the adsorption capacity. Besides that, when the higher value of adsorbent dosage was used, the lower adsorption capacity for both dyes was obtained. This finding is in agreement with the previous study conducted by Najua Delaila which reported that the adsorption capacity decreased sharply with

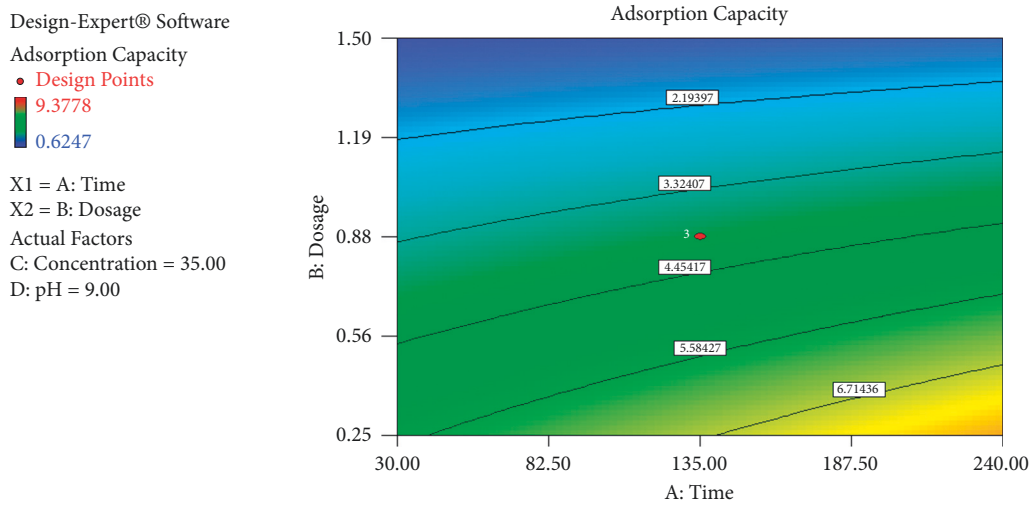

Figure 1: Contour plot for the interaction between time and dosage on adsorption capacity of MB dye.

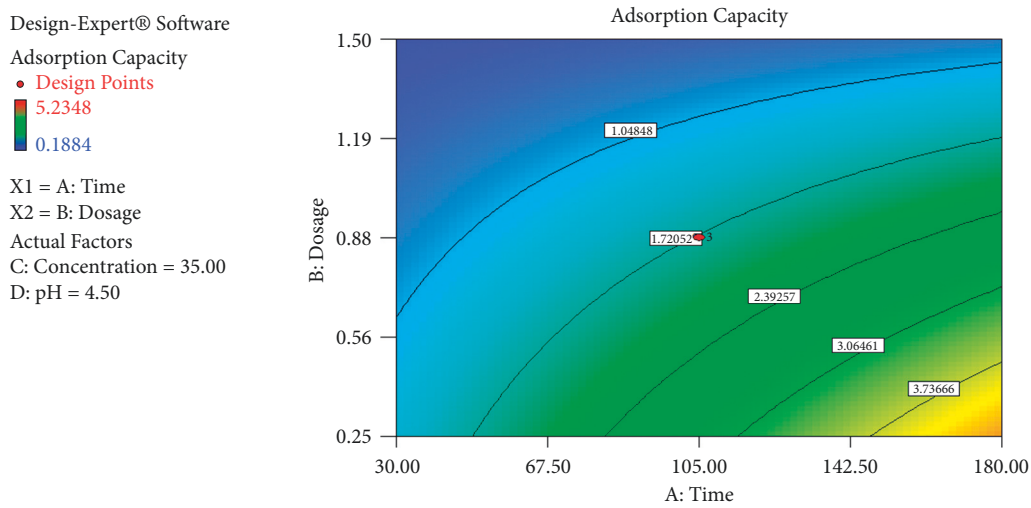

Figure 2: Contour plot for the interaction between time and dosage on adsorption capacity of BRR dye.

the increase of adsorbent dosage starting at 1.5 g [23]. The adsorption capacity was reduced when a higher adsorbent dosage was used. This is because the higher adsorbent dosage has overcrowding of adsorbent particles which then caused the adsorption sites to be overlapped [24]. In addition, the high adsorbent dosage could impose a screening effect on the dense outer layer of the cells, thereby shielding the binding sites of the dyes used [25].

3.1.2. Adsorbent Dosage and Initial Concentration of Dye. Adsorbent dosage is an important factor that affected adsorption efficiency. Figures 3 and 4 show the interaction between the adsorbent dosage and initial concentration of dye on the effect of the adsorption capacity of MB dye and BRR dye, respectively. In Figure 3, when the initial concentration of dye increased to 50 mg/L, the highest adsorption capacity of MB dye, which is nearing 5.0 mg/g, was obtained. In Figure 4, when the initial concentration of dye increased to 50 mg/L, the highest adsorption capacity of BRR dye, which is higher than 1.4 mg/g, was obtained. These phenomena occur due to the mass transfer driving force being stronger when the initial concentration of MB increases, therefore, resulting in more collisions between the active sites of biosorbent and MB, as well as enhancing the larger adsorption capacity [21]. The interaction of two independent variables in the contour plot clearly illustrates that the highest adsorption capacity for both dyes was obtained when the adsorbent dosage was reduced and the initial concentration of the dye was increased. This means, adsorption capacity is inversely proportional to the adsorbent dosage, which means that the lower dosage gives a higher adsorption capacity. In Figures 3 and 4, as the contour line approached the highest initial concentration of dye (50 mg/L) and the lowest adsorbent dosage (0.25 g), the adsorption capacity of MB dye and BRR dye increased from 2.0835 mg/g to 6.8582 mg/g and from 0.9952 mg/g to 2.8686 mg/g, respectively.

The split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration on the surface of the adsorbent has caused this

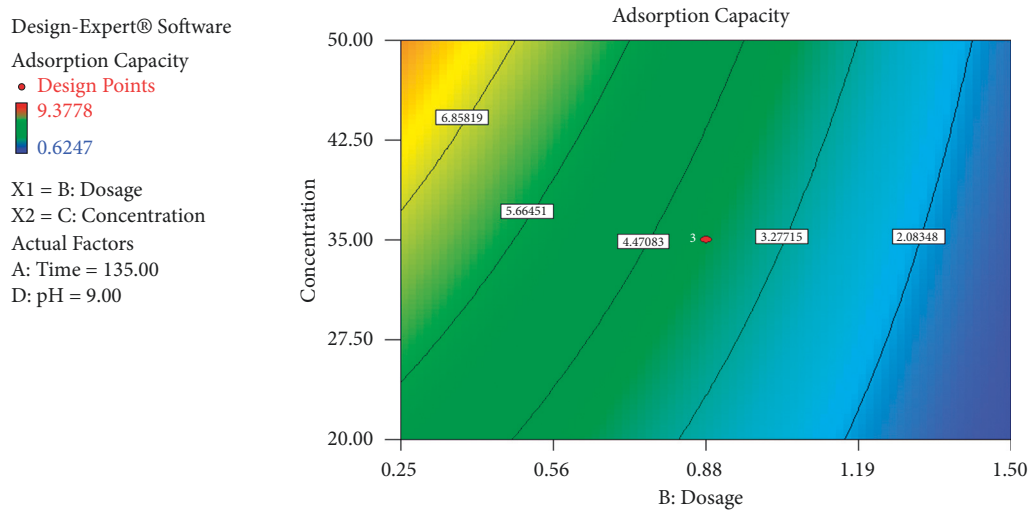

Figure 3: Contour plot for the interaction between adsorbent dosage and initial concentration on adsorption capacity of MB dye.

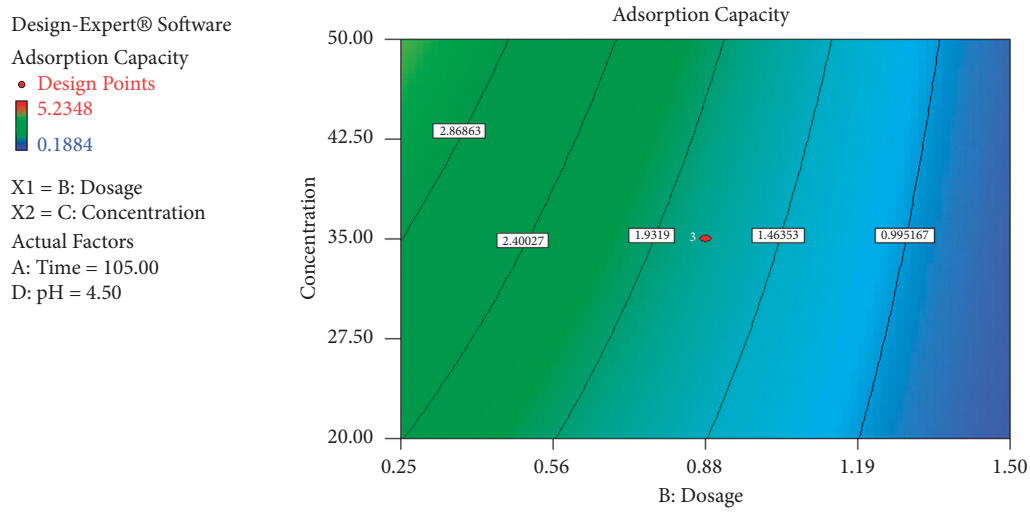

Figure 4: Contour plot for the interaction between adsorbent dosage and initial concentration on adsorption capacity of BRR dye.

happens when the dose of biosorbent dosage increases and this finding is in agreement with the previous study conducted by Najua Delaila [23]. The phenomenon can be clearly understood when the adsorbent dosage was reduced to 0.25 g, and the highest adsorption capacities of MB dye and BRR dye were obtained. The limited use of biosorption sites remaining, and unsaturated during the adsorption process will be one of the reasons for these phenomena [26].

Both graphs clearly illustrate that the highest adsorption capacities for both dyes were obtained when the initial concentration of dye was increased. As mentioned earlier, this result is similar to the previous studies conducted by Özlem Tunc et al., [3], N. Thinakaran et al., [24], Elass, K et al., [8], B.H. Hameed et al., [2] and Yingfei Hu et al. [2, 3, 8, 21, 24]. Previous work from Özlem Tunc, Hacer Tanaci, Zümriye Aksu [3], N. Thinakaran [24], Elass, K. [8], and B.H. Hameed [2] also found that higher dye concentration enhanced the adsorption capacity. Generally, dyes with higher concentrations possess a higher number of ions. These ions then will be competing for the available binding sites on the coconut dregs adsorbent, thus increasing the adsorption capacity [3]. Furthermore, since the initial concentration of dye provides an important driving force, all mass transfer resistances of the dye between the aqueous and solid phases can be overcome [2]. Therefore, a higher initial concentration of dye will enhance the adsorption process. Nevertheless, when the higher value of adsorbent dosage was used, it was observed that a lower adsorption capacity was obtained [22]. As stated earlier, this result is similar to the study conducted by Najua Delaila [23].

3.1.3. Adsorbent Dosage and pH. Another important factor that has been studied to govern the overall adsorption efficiency of coconut dregs with dye is the pH value. The pH values also play a significant impact on the adsorption capacity in the removal of dye molecules. From Figure 5, it can be observed that adsorption capacity is proportional to the

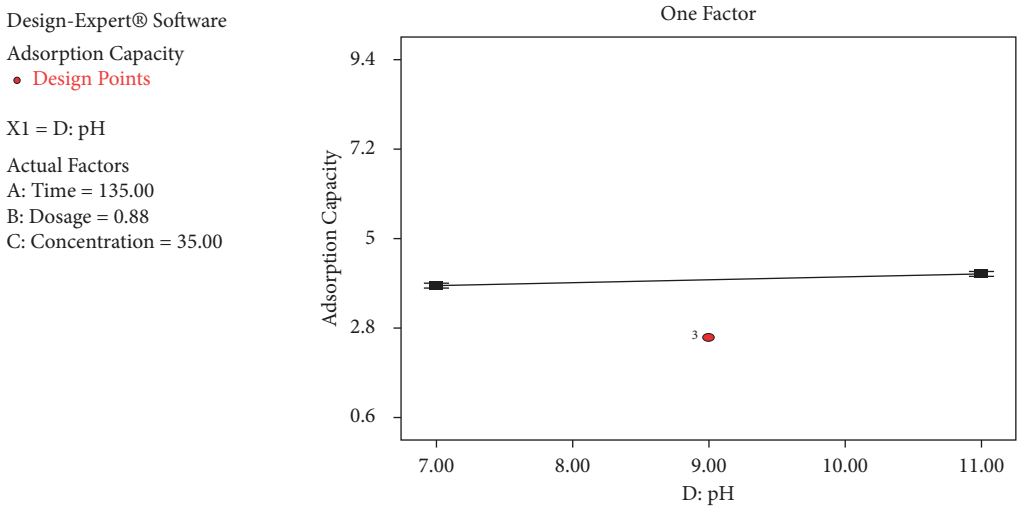

Figure 5: The Effect of pH on the Adsorption Capacity of MB.

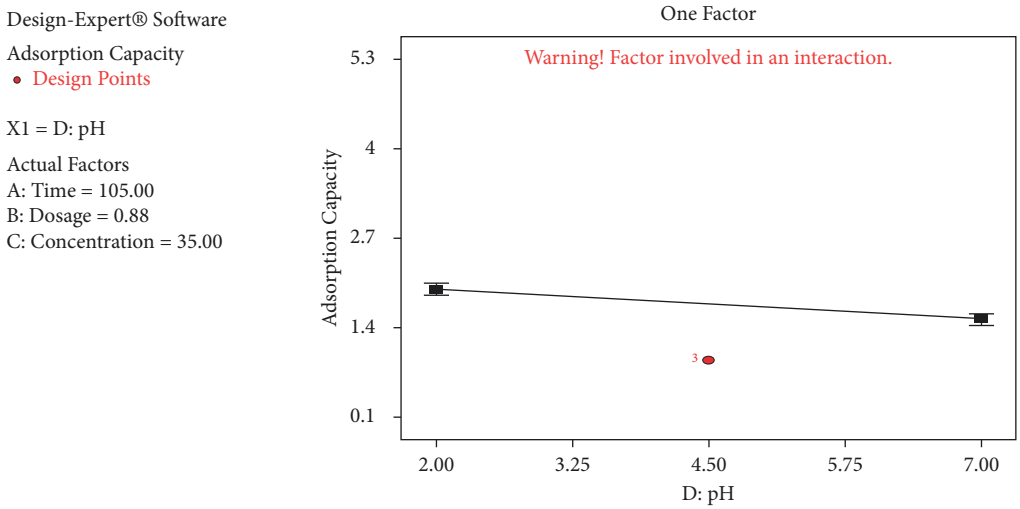

Figure 6: The Effect of pH on the Adsorption Capacity of BRR.

pH. This graph clearly illustrates that the highest adsorption capacity for MB dye was obtained when the pH was increased from 7 to 11. The same result was obtained with the previous studies of MB dye conducted by B.H. Hameed [2], C. Namasivayam [10], K.S. Low and C.K. Lee [16], and Elass, K. [8]. In Figure 5, when the pH increased to 11, the highest adsorption capacity of MB dye, which is nearing 5 mg/g, was obtained.

At higher pH, the adsorption of MB dye cations was very favourable due to the electrostatic attraction and solubilization of functional organic groups [27]. In other words, the increase in pH will increase the number of hydroxyl groups which increase the interaction between the dye and coconut dreg. As a result, the higher numbers of negatively charged surface sites on the adsorbent attract the cationic charge of MB dye, thereby increasing the binding strength between the adsorbate and the adsorbent. The good binding strength will ensure the good adsorption of dye onto the adsorbent. This result is in agreement with the study using dried ground seeds and peels of Nance (*Byrsonima crassifolia*) for the removal of MB from an aqueous solution [28]. However, when the pH decreases, the number of positively charged sites on the adsorbent increases while the number of negatively charged sites on the adsorbent decreases, which then decreases the electrostatic attraction between the adsorbent and the MB dye cations [27].

Figure 6 shows the graph of pH against the adsorption capacity of BRR dye. From the graph, it was observed that the adsorption capacity is inversely proportional to the pH. This graph clearly illustrates that the highest adsorption capacity for BRR dye was obtained when the pH is decreased from 7 to 2. As mentioned earlier, the same result was obtained in the previous study of acidic dye conducted by Despoina D. Asouhidou [17] shows the interaction between the adsorbent dosage and pH on the effect of the adsorption capacity of BRR dye. The interaction of two independent variables in the contour plot clearly illustrates that the highest adsorption capacity for BRR dye was obtained when

Table 1: Anova (analysis of variance) for 2-level factorial of MB adsorption capacity.

Source	Sum of squares	Df	Mean Square	F Value	p-value Prob > F	
Model	288.74	6	48.120	2191.82	<0.0001	Significant
A- contact time	15.76	1	15.760	717.79	<0.0001	Significant
B-adsorbent dosage	231.30	1	231.300	10534.57	<0.0001	Significant
C- initial Concentration	25.49	1	25.490	1160.99	<0.0001	Significant
D-pH	0.66	1	0.660	29.86	<0.0001	Significant
AB	7.51	1	7.510	341.90	<0.0001	Significant
BC	8.03	1	8.030	365.83	<0.0001	Significant
Curvature	5.51	1	5.510	251.00	<0.0001	Significant
Residual	0.59	27	0.022			
Lack of fit	0.31	9	0.035	2.26	0.0673	Not significant
Pure error	0.28	18	0.015			
Cor total	294.85	34				
Std. Dev.	0.1482		R-squared		0.9980	
Mean	3.8483		Adj R-Squared		0.9975	
C.V. %	3.8504		Pred R-Squared		0.9966	
PRESS	0.9714		Adeq precision		124.9529	

the adsorbent dosage and pH were reduced. Therefore, pH plays a significant part in the removal of dyes during the sorption process because the surface charge of dyes will change when the alteration of pH occurs [22].

The adsorption process of dye onto the adsorbent surface depends on the electrostatic attraction between them. Hence, the charge of the dye (basic or acidic dye) affects the adsorption process. Basically, a high electrostatic attraction or binding between dye and the adsorbent surface will ensure good adsorption. However, at higher pH, the adsorption of Brilliant Red Remazol dye anions was not favorable due to the electrostatic repulsion [27]. This is because as the pH of the system increases, the number of negatively charged sites on the adsorbent increases, and the number of positively charged sites on the adsorbent decreases [27]. As a result, a negatively charged surface site on the adsorbent does not attract the anionic charge of BRR dye due to the electrostatic repulsion, thereby decreasing the binding strength [27]. However, when the pH decreases, the number of positively charged sites on the adsorbent increases while the number of negatively charged sites on the adsorbent decreases. This will then ensure the good attraction between the anionic charge adsorbate (Brilliant Red Remazol) and the adsorbent. Moreover, when the lower value of adsorbent dosage was used, a higher adsorption capacity was obtained. As stated earlier, the same occurrence was found in the previous study conducted by Najua Delaila [23].

3.2. Factorial Design Analysis

3.2.1. Regression Analysis. Regression analysis was performed on the adsorption data obtained from the experiment. Regression analysis is the mathematical process of using observations to find relationships between variables for predicting future values. (5) and (6) were obtained through the batch mode adsorption analysis using a 2-Factorial Design for MB dye and BRR dye, respectively.

$$\begin{aligned}\text{Adsorption Capacity for MB} = {} & +1.59638 + 0.013142^{*}\text{Time} - 1.43483^{*}\text{Dosage} \\ & + 0.10626^{*}\text{Concentration} + 0.071566^{*}\text{pH} \\ & - 7.38048\text{E}-003^{*}\text{Time}^{*}\text{Dosage} - 0.053441^{*}\text{Dosage}^{*}\text{Concentration}\end{aligned} \tag{5}$$

$$\begin{aligned}\text{Adsorption Capacity for BRR} = {} & +0\cdot 35207 + 0\cdot 023960^{*}\text{Time} - 0\cdot 10271^{*}\text{Dosage} \\ & + 0\cdot 036067^{*}\text{Concentration} - 0\cdot 17869^{*}\text{pH} \\ & - 0\cdot 013926^{*}\text{Time}^{*}\text{Dosage} - 0\cdot 020494^{*}\text{Dosage}^{*}\text{Concentration} \\ & + 0\cdot 10430^{*}\text{Dosage}^{*}\text{pH}\end{aligned} \tag{6}$$

Table 1 shows the model "F-value" of 2191.82, which implies that the model is significant. There is only a 0.01% chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate the model terms are significant. In this case, A, B, C, D, AB, BC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The "Curvature F-value" of 251.00 implies there is significant curvature (as measured by the difference between the average of the center points and the average of the factorial points) in the design space. There is only a 0.01% chance that a "Curvature F-value" this large could occur due to noise. The "Lack of Fit

Table 2: Anova (analysis of variance) for 2-level factorial of BRR adsorption capacity.

Source	Sum of squares	Df	MeanSquare	F Value	p-value Prob > F	
Model	85.6013	7	12.2288	215.4148	<0.0001	Significant
A-time	24.9532	1	24.9532	439.5619	<0.0001	Significant
B-dosage	41.0835	1	41.0835	723.7029	<0.0001	Significant
C-concentration	2.36792	1	2.36792	41.7119	<0.0001	Significant
D-pH	1.52880	1	1.5288	26.9305	<0.0001	Significant
AB	13.6367	1	13.6367	240.2169	<0.0001	Significant
BC	1.18126	1	1.1813	20.8084	0.0001	Significant
BD	0.84988	1	0.8499	14.9711	0.0007	Significant
Curvature	1.83158	1	1.8316	32.2641	<0.0001	Significant
Residual	1.47598	26	0.0568			
Pure error	0.05767	18	0.0032			
Cor total	88.9089	34				
Std. Dev.	0.24		R-squared		0.9830	
Mean	1.67		Adj R-Squared		0.9785	
C.V. %	14.27		Pred R-Squared		0.9699	
PRESS	2.62		Adeq precision		41.4950	

F-value" of 2.26 implies there is a 6.73% chance that a "Lack of Fit F-value" this large could occur due to noise. This indicates that the model is fit. Meanwhile, the value of the determination coefficient (R^2) obtained is 0.9980. The "Pred R-Squared" of 0.9966 is in reasonable agreement with the "Adj R-Squared" of 0.9975. "Adeq Precision" measures signal-noiseless ratio. A ratio greater than 4 is desirable. The Adeq Precision of 124.9529 indicates an adequate signal. This model can be used to navigate the design space.

Table 2 shows the model "F-value" of 215.4148, which implies that the model is significant. There is only a 0.01% chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate the model terms are significant. In this case, A, B, C, D, AB, BC, and BD are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The "Curvature F-value" of 32.2641 implies there is significant curvature (as measured by the difference between the average of the center points and the average of the factorial points) in the design space. There is only a 0.01% chance that a "Curvature F-value" this large could occur due to noise. Meanwhile, the value of the determination coefficient (R^2) obtained is 0.9830. The "Pred R-Squared" of 0.9699 is in reasonable agreement with the "Adj R-Squared" of 0.9785. "Adeq Precision" measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The Adeq Precision of 41.4950 indicates an adequate signal. This model can be used to navigate the design space.

The numerical optimization was used to seek the point that maximizes the desirability function which ranges from zero (outside the limits) to one (goal). The highest adsorption capacity for MB dye is 9.378 mg/g. Through this optimal design, it provides a solution of 239.935 minutes of adsorption time, 0.250 g of adsorbent dosage, 49.990 mg/L of dye concentration, and a pH of 10.995 which will yield about 9.378 mg/g of MB adsorption capacity. However, the highest adsorption capacity for BRR dye is 5.235 mg/g. Through this optimal design, it provides a solution of 179.824 minutes of adsorption time, 0.254 g of adsorbent dosage, 49.952 mg/L of dye concentration, and a pH of 2.003 which will yield about 5.235 mg/g of BRR dye adsorption capacity.

Table 3: The Langmuir and freundlich parameters of adsorption isotherm at 25°C.

Dye	Langmuir model			Freundlich model		
	q_{max} (mg/g)	K (L/mg)	R^2	'n'	K_f (L/mg)	R^2
MB	5.7208	5.7666	0.9837	2.7285	0.9060	0.0924
BRR	3.7636	12.6364	0.9152	-0.9603	0.0934	0.0504

3.3. Isotherm Model. The Langmuir model assumes that the maximum adsorption corresponds to a saturated monolayer of dye molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of the adsorbate in the plane of the surface [8] The results obtained from the adsorption isotherm for both dyes have shown that MB dye and BRR dye were fitted well to the Langmuir Isotherm Model. The values of Langmuir and Freundlich Isotherm parameters for both dyes were summarized and compared in Table 3.

These results are well suited for MB dye study by Md. Nasir Udding et al., [29], Indrajit Ghosh et al., [30] and B. H. Hameed [31] whereby Langmuir Isotherm showed the goodness of- fit among the tested models using water hyacinth, husk of *Lathyrus sativus* and spent tea leave each. This is due to the R^2 values in the Isotherm Model graphs that are nearing the value of 1, which are 0.9837 and 0.9152 for MB dye and BRR dye, respectively. The R^2 value of 1 indicates that the respective equation better fitted the experimental data [32]. Meanwhile, the Freundlich Isotherm is based on the assumption that the adsorbent surface sites have a spectrum of different binding energies [8]. On the other hand, the R^2 values for Freundlich Isotherm Model graphs are far away from the value of 1 and lower than R^2 value in the Langmuir Isotherm Model graph, which are 0.0924 and 0.0504 for MB dye and BRR dye, respectively.

Table 4: Comparison of first-order and second-order adsorption rate constants.

Dye	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	First-order kinetic model			Second-order kinetic model		
			$q_{e,cal}$ (mg/g)	K_1 (L/min)	R^2	$q_{e,cal}$ (mg/g)	K_2 (g/mg.min)	R^2
MB	50	5.1259	4.3853	0.0219	0.9176	5.8445	173.0248	0.9509
BRR	50	3.0957	3.9564	0.0177	0.9742	-2.4969	391.6893	0.5636

3.4. Adsorption Kinetics. For the investigation of the pseudo-first-order model, the graph of log (q_e–q_t) against t [8] was plotted for both dyes. The values of adsorption capacity for q_e and q_t were taken at a constant dye initial concentration of dye, which is at 50 mg/L. The time used in these graphs varies from 20 minutes to 80 minutes. K_1 was determined from the slope and q_e was determined from the graph's intercept. The K_1 value obtained is 0.0219 L/min and the calculated q_e obtained is 4.3853 mg/g. Meanwhile, the K_1 value obtained is 0.0177 L/min and the calculated q_e obtained is 3.9564 mg/g.

The Pseudo-First-Order Equation for MB dye in this adsorption study is as follows.

$$\log(q_e - q_t) = \log 4 \cdot 3853 - \frac{0 \cdot 0219}{2 \cdot 303} t. \quad (7)$$

The Pseudo-First-Order Equation for BRR dye in this adsorption study is as follows:

$$\log(q_e - q_t) = \log 3 \cdot 9564 - \frac{0 \cdot 0177}{2 \cdot 303} t. \quad (8)$$

In the investigation of the pseudo-second-order model, the graph of (t/q_t) against t [8] was also plotted for both dyes. The value of adsorption capacity for q_t was taken at constant dye initial concentration, which is at 50 mg/L. The time used in these graphs varies from 20 minutes to 80 minutes. q_e was determined from the slope and k_2 was determined from the graph's intercept. The calculated q_e obtained is 5.8445 mg/g and the K_2 value obtained is 173.0248 g/mg.min. Meanwhile, the calculated q_e obtained is -2.4969 mg/g and the K_2 value obtained is 391.6893 g/mg.min.

The Pseudo-Second-Order Equation for MB dye in this adsorption study is as follows.

$$\frac{t}{qt} = \frac{1}{173 \cdot 0248 \times 5 \cdot 8445^2} + \frac{t}{5 \cdot 8445}. \quad (9)$$

The Pseudo-Second-Order Equation for BRR dye in this adsorption study is as follows:

$$\frac{t}{qt} = \frac{1}{391 \cdot 6893 \times (-2 \cdot 4969)^2} - \frac{t}{2 \cdot 4969}. \quad (10)$$

Table 4 lists the calculated adsorption constants at 50 mg/L initial dye concentrations by the pseudo-first-order and pseudo-second-order models. The correlation coefficients, R^2 of the pseudo-first-order model for MB dye is lower than the R^2 of the pseudo-second-order model. Hence, it can be concluded that the adsorption of MB follows the pseudo-second-order model. This result is in agreement with a previous study for adsorption of MB dye using waste tea powder [21], magnetic mesoporous silica [33] and MB adsorption using the ash of *C. polygonoides* (locally called balanza) where the boundary layer is not their rate-limiting step [21]. The same results were also found in H_2SO_4-treated eucalyptus leaves (SEUL) [34], and metal-organic framework [2] as adsorbents for the removal of methylene blue (MB).

This model is a widely used model for the adsorption process of solutes from liquid solution, whereby the rate of occupation of sorption sites is proportional to the number of unoccupied sites [30]. In the pseudo-Second-Order adsorption model, chemisorption involves sharing pr exchange of electrons of adsorbent and adsorbate and this model provides a more comprehensive and accurate description of the adsorption mechanism of MB using coconut dreg as a biosorbent. Meanwhile, the correlation coefficients, R^2 of the pseudo-first-order model for BRR dye is higher than the R^2 of the pseudo-second-order model. Hence, it can be concluded that the adsorption of BRR dye follows the pseudo-first-order model [33].

4. Conclusion

In this present study of the coconut dregs as the potential biosorbent for the treatment of dye, it can be concluded that the coconut dregs, an inexpensive and easily available material, were found to be very effective for the removal of MB dye and BRR dye from the aqueous solutions. The equilibrium data of dye adsorption were analyzed using the Langmuir and Freundlich isotherm models. The equilibrium data for both dyes fitted very well with the Langmuir Isotherm equation giving a maximum monolayer adsorption capacity as high as 5.7208 mg/g and 3.7636 mg/g for MB Dye and BRR dye, respectively. For the study of the adsorption kinetic, both dyes were fitted to different orders of adsorption. MB dye follows the first-order adsorption model while the BRR is suited to the second-order adsorption model. During the batch mode adsorption conducted on coconut dregs, the effect of various parameters has been studied and the results showed that; the higher adsorption capacity of dye was obtained with a lower adsorbent dosage (appropriate dosage of adsorbent, which is 0.25 g), a higher concentration of dye (50 mg/L), longer contact time (240 min for MB and 180 min for BRR), and appropriate pH (11 for MB and 2 for BRR). The appropriate pH depends on the type of dyes used. As shown in this study, the basic dye favours the higher pH and the acidic dye favours the lower pH to obtain higher adsorption capacity. In the future, treated coconut dregs with acids with a combination of MPR and ANN analysis should be considered in order to improve the adsorption capacity which is considered to be low in this study, and the prediction of dye removal in the biosorption process which has been successfully done by Indrajit Ghosh et al., 2021 [35] that used treated biosorbent for the

treatment of dye. In addition, ultrasound-assisted dye removal also can be added to improve dye removal efficiency [36, 37]. Regenerated biosorbent and their reuse of them could be one of the most important economic parameters to be considered in the future. The safe disposal method of dye after desorption also would be one of the crucial steps to be considered [34]. In principle, inappropriate handling of waste adsorbents containing heavy metals and non-biodegradable materials can result in major environmental issues. As a result, waste adsorbents must be safely disposed of in landfills, mixed with animal manure, and incorporated into construction materials. Stabilization/solidification is recognized as a good approach for processing waste adsorbents in this regard. As a result, practically all alternatives to dispose of toxic waste have adopted this option since it can change toxic waste into less toxic waste through chemical, physical, or thermal operations. Therefore, the use of readily available low-cost adsorbents, such as these natural waste materials from agriculture, to treat industrial wastewater containing a significant number of organic dyes by adsorption is an attractive alternative to the typical aqueous waste processing approaches. Low-cost biosorbents of coconut dregs, without a doubt, have a lot of potential for future commercial applications with many advantages like a low-cost being , easily available, and save to the environment.

Data Availability

All the data are provided in the manuscript.

Conflicts of Interest

The authors declare no conflicts of interest.

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Supplementary Materials

Experimental Results for Batch Mode Adsorption Studies of MB Dye. Experimental Result for Batch Mode Adsorption Studies of BRR Dye. Optimal Design for Highest MB Adsorption Capacity. Optimal Design for Highest BRR Adsorption Capacity. (*Supplementary Materials*)

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