Optimization of operating parameters on the activated carbon from Pinang frond for adsorption of remazol brilliant blue R

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Abstract. Activated carbons are frequently utilized for waste water treatment especially in dye removal in textile industries. With high level of carbon content, various organic materials have been chosen as based materials for activated carbon. In this study, activated carbon from pinang frond (PFAC) was created by using a physical activation and optimized the operating parameters such as activation temperature (°C), activation time (hour) and, CO₂ flow rate (mL/min). Experimental design (DoE) for PFAC preparation was developed and optimized using response surface methodology (RSM). It was found that the optimum PFAC preparation conditions was at the activation temperature of 867°C, activation time of 6.0 hour and CO₂ flow rate of 476 mL/min. By verification with experimental values, the predicted values from the model was only less than 2% of errors for RBBR removal onto PFAC. This can be pointed out that the model is sufficient and suitable to predict the operating parameters fixed responses.

1. Introduction

Activated carbon is broadly treated as an adsorbent for elimination pollutants of inorganic and organic matter effectively in aqueous solution [1], or from a gaseous environment [2]. Activated carbons have a comparatively high total pore volume and surface area. The activated carbons commercially available made from petroleum coke, lignite, and bituminous coal are expensive, which limits to use and application [3]. Therefore, due to economic reasons that are the most important factor about the research nowadays, other alternative precursors, which are inexpensive and abundantly available, have been investigated for activated carbon production. Nevertheless, some of these alternative precursors had higher capability than commercials activated carbon [4]. From the literature, cocoa bean husk [5], pinang frond [6], kenaf core fibres [7], palm kernel shell [8], waste polystyrene foams [9], coconut shells [10], oil palm shell [11,12], and tobacco waste [13], have all been used to prepare activated carbon.

To produce activated carbon, chemical and physical activation treatments are needed. The advantages of physical activation are the possibility of developing a structure with more pores and large active area [10] and having less effect in terms of the secondary pollution problem during the disposal stage [14]. The activated carbon preparation conditions are the most important operating parameters due to its adsorption capacity or uptake, such as CO₂ flow rate, activation time and activation temperature [6,15].

About 0.7 million tons of 10,000 different dyes are produced annually. They are coming from the processes of variety in the textile industry [16]. Numerous dyes varieties are used, for instance; basic dyes, acid dyes, direct dyes, dispersed dyes, and reactive dyes. Based on [17], reactive dyes were used worldwide in almost 45% for producing textiles. One of reactive dyes is Remazol Brilliant Blue R.
(RBBR), which has the favourable characteristics of high solubility in water, bright colour, and a low energy consumption dyeing process. This kind of dyes is toxic and highly carcinogenic to organisms when discharged in stream of waste water [18]. RBBR has a toxic effect cause by mycelia growth of fungus [18]. Since dyes toxicity and crucial to the ecosystem impact, many studies focused on this topic [19]. Therefore, it is very interesting to study on removal of Remazol Brilliant Blue R (RBBR) dyes from wastewater.

Pinang (Areca catechu), which under the Arecaceae family is a tropical tree that mainly grows across tropical Asia to the central Pacific in a region from East Africa [20]. Traditionally, the main part used from this tree is the nut (or seed endosperm) as a stimulant masticatory for chewing purposes. This habit can be originated usually in some parts of Asia and India. The pinang frond as a waste material is typically being disposed without any utilization of it [21]. In fact, there is few research work on the utilization of pinang frond as activated carbon adsorbent in the previous literature. Therefore, the aim of this study is preparing activated carbon from pinang frond and to observe the prospective in aqueous solution for RBBR dye elimination by optimising the operating parameters in terms of CO2 flow rate, activation time, and activation temperature.

The experimental design (DoE) is a structured and ordered method that is used to define the relationships between the different variables that affect the process and the result of the process. The experimental design is the strategy for collecting empirical knowledge based on the analysis of experimental data. DoE generates a set of experiments design by varying systematically all relevant variables and it helped to identify (i) factors that most influence the results and (ii) optimal conditions. The most common DoE used is response surface methodology (RSM). RSM is a collection of mathematical statistics techniques that useful for modelling and analysis problems. The aim of RSM is to optimize the response where is subjected by several variables [22]. There were several design classified in RSM including Box-Behnken design, 3-Level Factorial, face centered composite design (FCCD), and hybrid design. Nevertheless, amongst RSM designs, FCCD turn into most appropriate design in activated carbon production due to its robustness and flexibility.

FCCD allows estimation of curvature by fractional factorial design with a central point plus a bunch of star points (axial point). Stabilize the variance of the predicted response and provide a measure of pure error can be achieved by the replicates at the center point [23]. The more replicates can generate more precise estimation error. Commonly, FCCD contains of a \(2^n\) axial or star points, \(n_c\) center run, and \(2^n\) factorial points, where \(n\) represents the variables number implemented in the study. Two parameters are needed to be defined; number of center points \(n_c\) and distance \(\alpha\) of the axial points from the design center [24]. Where \(\alpha\) is equal to 1 for face centered and \(n\) in the design based on the number of factors.

2. Materials and methods

2.1. Pinang frond activated carbon (PFAC) preparation
Pinang frond was taken from Sungai Petani, Kedah, Malaysia. It was cleaned and then dried at 110°C for 24 hours due to the moisture content removal. Next, by using a stainless steel vertical tubular reactor blanketed with a tube furnace, the sample was ground and placed into it and heated by 20°C/min up to an activation temperature between 600 – 900°C under a 150 ml/min flow rate of purified nitrogen (99.99%). Once the activation temperature was reached, the activation agent of CO2 was introduced at flow rates between 150 – 600 ml/min for 1 – 7 hours. After the process is done, the reactor was needed to be cooled down by flowing nitrogen up to room temperature. The samples were placed in an airtight container for further study on adsorption of RBBR to determine the optimization of operating parameters. The characterization of PFAC can be found detail in [6,15].

2.2. Experimental design for preparation of PFAC
DoE for PFAC preparation was developed and optimized using RSM in Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA). A standard FCCD under RSM design has been selected on study for preparation of PFAC in terms of operating parameters. Activation temperature
(x1, °C), activation time (x2, hour) and, CO2 flow rate (x3, mL/min) have been chosen for independent variables on this study.

Table 1 shows the variables investigated in terms of ranges and levels. Meanwhile, table 2 summaries a complete design matrix of the experiments conducted based on the ranges and the levels given. 8 factorial points, 6 axial points and 6 replicates at the center points were implemented for those three variables using FCCD, indicating that altogether 20 experiments for this procedure, as calculated from Equation 1:

\[
N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20
\]

Where \( N \) is the total experiments needed number and \( n \) is the factors number.

**Table 1. Coded variable levels for independent variables using FCCD**

| Variables (factors) | Coded variable levels |
|---------------------|-----------------------|
| Activation temperature (°C) | -1 600 0 750 +1 900 |
| Activation time (hour) | -1 1.0 0 4.0 +1 7.0 |
| CO2 flow rate (mL/min) | -1 150 0 375 +1 600 |

The center points which are the 6 replicate points (Run 15-20) in design matrix is used to verify data reproducibility and experimental error. Variables are encoded into (-1.1) intervals where low and high levels are encoded as -1 and +1, respectively. The response was RBBR removal (Y) and determined based on batch adsorption studies. In the adsorption test, a 0.2 g of PFAC was introduced into flask containing 200 mL of RBBR solution with initial concentration of 200 mg/L and was stored in water bath shaker at 30°C (120 rpm) until equilibrium was achieved. The RBBR concentrations before and after adsorption were analysed using Double-beam UV-Visible spectrometer (Model Shimadzu UV-1800, Japan). Equation 2 shows the percentage RBBR removal at equilibrium.

\[
RBBR \text{ Removal} (\%) = \left( \frac{C_o - C_e}{C_o} \right) \times 100
\]

Where \( C_o \) is the liquid-phase concentrations of the adsorbate at initial (mg/L) and \( C_e \) is at equilibrium concentration (mg/L).

3. Results and Discussion

3.1. Pinang frond activated carbon characterization

Pinang frond activated carbons have BET surface area in the range of 576.89 up to 958.23 m²/g with total pore volume in the range of 0.3449 up to 0.5469 mL/g and average pore diameter of 2.32 nm [15]. The increment of activation temperature, activation time, and CO2 flow rate can increase BET surface are and total pore volume. However, these characterizations would be decreased when each parameter pass the certain value as an optimum condition. The detail of the characterization of pinang frond activated carbon including the SEM analysis can be found in [15].

3.2. Experimental design

In this study, FCCD was used on design the experiment of preparing PFAC. One response of RBBR removal, \( Y (\%) \), with variables of activation temperature (x1), activation time (x2) and CO2 flow rate (x3) were studied. Design Expert Software version 6.0.6 (STAT-EASE Inc., Minneapolis, US) was
used to analyse the experimental data. Table 3 summaries the response for preparation of PFAC based on table 2.

The highest order polynomials become the model chosen due to the significant effect with the additional terms. Based on table 3, RBBR removal (Y) response was generated from quadratic model, which generated by FCCD consists of coded factors which reveals the variables significance and interaction concerning response. The one factor of coefficient stands for the only certain factor effect, while the two factors of coefficients correspond to the interaction between two factors. The coefficients with second-order term stand for quadratic effect. Equation 3 represents the final empirical model with coded factors for the response.

\[ Y = 70.89 + 5.95 x_1 + 3.19 x_2 + 2.26 x_3 - 3.25 x_1^2 - 2.05 x_2^2 - 0.2 x_3^2 - 0.21 x_1 x_2 - 1.81 x_1 x_3 - 0.29 x_2 x_3 \] (3)

The adequacy and significance of the models were verified by analysis of variance (ANOVA). By dividing the sum of the squares of each of the variation sources, the means squares were obtained, while by the respective degree of freedom is meant for the model and the error variance. If Prob > F value less than 0.05, then it points out that the model has a significant effect on the response and the result is not random [25]. Table 4 shows the RBBR removal by PFAC model from the ANOVA. The F-value is 7.36 and Prob > F is 0.0022 for RBBR removal indicates that RBBR removal model was significant. In this case, activation temperature (x_1), activation time (x_2) and CO2 flow rate (x_3) were significant model terms.

Figure 1 illustrates the three-dimensional response surface which the RBBR removal was reached at the CO2 flow rate of 300 to 550 mL/min, time 3.0 to 6.0 h, and activation temperature of 800 to 870°C. The RBBR removal was better with the increased of CO2 flow rate, time, and activation temperature, which is due to the increment of surface area which caused by the internal porous cavities development at these operating parameters. As the more pore on the sample has been developed, the percentage of dyes removal were also increased, which is good agreement with Bello et al. [26] that used banana stalk to preparation of activated carbon and found that the significant effect on malachite green removal due to the time and activation temperature. The increment of temperature stimulates devolatilization rate, hence effects significantly on the activated carbon pore structure [27]. In fact, at higher CO2 flow rate, activation time, and temperature ought to be enough to remove the volatile components and moisture for developing the pores.

However, the RBBR removal decreased after exceeded activation temperature 870°C, time 6.0 h and CO2 flow rate 550 mL/min. The possible reason was that beyond optimum values of activation conditions, some pores start to collapse, which leads to decrease in surface area and percentage dyes removal. According to Ahmad and Alrozi [28], they found that too long for both activation temperature and time might be shrunk the adsorption capacity and surface area of the activated carbon from mangosteen peel.

According to Lua and Yang [29] increasing the CO2 flow rate, activation time, and activation temperature can enhance the adsorption capacity caused by more pore to be enlarged and developed. However, if it over exceeds beyond optimum value, the activated carbon undesirable characteristics can be created such as decline in surface area and pore volume.
Table 2. Experimental design matrix

| Run | PFAC preparation variable |       |       |       |
|-----|---------------------------|-------|-------|-------|
|     | Activation temperature, $x_1$ (°C) | Activation time, $x_2$ (hour) | CO$_2$ flow rate, $x_3$ (mL/min) |
| 1   | 600                        | 1.0   | 150   |
| 2   | 900                        | 1.0   | 150   |
| 3   | 600                        | 7.0   | 150   |
| 4   | 900                        | 7.0   | 150   |
| 5   | 600                        | 1.0   | 600   |
| 6   | 900                        | 1.0   | 600   |
| 7   | 600                        | 7.0   | 600   |
| 8   | 900                        | 7.0   | 600   |
| 9   | 600                        | 4.0   | 375   |
| 10  | 900                        | 4.0   | 375   |
| 11  | 750                        | 1.0   | 375   |
| 12  | 750                        | 7.0   | 375   |
| 13  | 750                        | 4.0   | 150   |
| 14  | 750                        | 4.0   | 600   |
| 15  | 750                        | 4.0   | 375   |
| 16  | 750                        | 4.0   | 375   |
| 17  | 750                        | 4.0   | 375   |
| 18  | 750                        | 4.0   | 375   |
| 19  | 750                        | 4.0   | 375   |
| 20  | 750                        | 4.0   | 375   |
Table 3. Matrix for PFAC preparation variables and response

| Run | RBBR removal, Y (%) |
|-----|---------------------|
| 1   | 52.8                |
| 2   | 69.1                |
| 3   | 61.9                |
| 4   | 72.8                |
| 5   | 62.8                |
| 6   | 67.3                |
| 7   | 66.2                |
| 8   | 74.4                |
| 9   | 55.8                |
| 10  | 75.4                |
| 11  | 62.5                |
| 12  | 71.1                |
| 13  | 64.4                |
| 14  | 72.9                |
| 15  | 72.2                |
| 16  | 72.2                |
| 17  | 72.4                |
| 18  | 72.1                |
| 19  | 72.3                |
| 20  | 72.3                |

3.3. Operating parameters optimization

The aim of the experimental design is to determine the optimum operating parameters on activated carbon preparation with regards to high RBBR removal. Table 5 shows the model validation for PFAC in RBBR dyes removal. Based on the higher desirability, the optimized parameters were chosen and verified by experiments. By targeting at the maximum value within range value of parameters studied, the operating parameters optimization was achieved by using Design Expert Software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA). The activation temperature of 867°C, activation time of 6.0 hour and CO₂ flow rate of 476 mL/min were found as the RBBR removal optimum conditions on PFAC. From the table, it shows that the predicted values were in good agreement with the experimental values. Only less than 2% of errors can be clearly seen between the predicted and the actual values for RBBR removal onto PFAC. This can be pointed out that the model is sufficient and suitable to predict the operating parameters fixed responses.
Table 4. RBBR removal by ANOVA analysis for PFAC

| Source | Sum of Squares | Degree of Freedom | Mean Square | F-Value | Prob > F |
|--------|----------------|-------------------|-------------|---------|----------|
| Model  | 653.98         | 9                 | 72.66       | 7.360   | 0.0022   |
| $x_1$  | 354.03         | 1                 | 354.03      | 35.87   | 0.0001   |
| $x_2$  | 101.76         | 1                 | 101.76      | 10.31   | 0.0093   |
| $x_3$  | 51.08          | 1                 | 51.08       | 5.180   | 0.0462   |
| $x_1^2$| 28.97          | 1                 | 28.97       | 2.930   | 0.1175   |
| $x_2^2$| 11.51          | 1                 | 11.51       | 1.170   | 0.3056   |
| $x_3^2$| 0.11           | 1                 | 0.11        | 0.011   | 0.9199   |
| $x_1x_2$| 0.36           | 1                 | 0.36        | 0.037   | 0.8521   |
| $x_1x_3$| 26.28          | 1                 | 26.28       | 2.660   | 0.1338   |
| $x_2x_3$| 0.66           | 1                 | 0.66        | 0.067   | 0.8010   |

Table 5. PFAC Model validation for RBBR removal

| Dye | Model desirability | Activation temperature | Activation time | CO$_2$ flow rate | RBBR removal % | Error (%) |
|-----|-------------------|------------------------|-----------------|------------------|----------------|-----------|
|     |                    |                        |                 |                  | Predicted      | Experimental|          |
| RBBR| 0.989             | 867 ºC                 | 6.0 h           | 476 mL/min       | 74.91          | 76.4      | 1.98     |

4. Conclusions
Based on the results obtained within the framework of this study, it has been shown that pinang frond based activation carbon (PFAC) can be successfully prepared by using pinang frond (PF). The optimum PFAC preparation conditions obtained from face centered composite design were found at the activation temperature, activation time and CO$_2$ flow rate of 867ºC, 6.0 hour and 476 mL/min, respectively. The optimization model was suitable and sufficient to predict the response from the operating parameters fixed.
Figure 1. Response surface plot of RBBR removal of PFAC: (a) Effect of activation temperature and time, CO₂ flow rate = 375 mL/min; (b) Effect of activation temperature and CO₂ flow rate, t = 4h; (c) Effect of activation time and CO₂ flow rate, temperature = 750°C.

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