Optimization of Preparation Conditions for Acid Red 88 Dye Removal using Rubber Seed Coat Based Activated Carbon

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Abstract. This study investigates the optimal conditions for preparation of activated carbon from rubber seed coat (RSC) for removal of Acid Red 88 (AR88) dye from aqueous solution. The RSC activated carbon was prepared using physiochemical activation method which consisted of sodium hydroxide (NaOH) treatment and carbon dioxide (CO₂) gasification. Central composite design (CCD) was used to determine the effects of the three preparation variables; CO₂ activation temperature, CO₂ activation time and NaOH impregnation ratio (IR) on AR88 percentage removal and RSC activated carbon yield. Based on the CCD, a quadratic model and a linear model were respectively developed for AR88 percentage removal and RSC activated carbon yield. The optimum conditions for activated carbon preparation were obtained by using activation temperature of 775°C, activation time of 2 h and IR of 2.25, which resulted in 38.29 % of AR88 removal and 33.26 % of activated carbon yield.

1. Introduction

Synthetic dyestuff is extensively used in textile, paper, printing industries and dye houses due to their ease of production, fastness and variety of colors compared to natural dyes [1]. More than 100,000 commercially available dyes are known and approximately one million tons of these dyes are produced annually worldwide [2]. Azo dyes, one of the major classes of synthetic dyes used in textile industries are characterized by presence of one or more azo bonds (-N=N-) in association with one or more aromatic systems. They are known to be toxic and carcinogenic [3]. As one of the azo dyes group, therefore, the removal of Acid Red 88 (AR88) is necessary and very important.

There are several methods are available for removing dyes from wastewater such as membrane separation, aerobic and anaerobic degradation, chemical oxidation, coagulation and flocculation, adsorption and reverse osmosis. Among them, adsorption process is widely used and most efficient method especially if the adsorbent can be produced from low cost or waste materials [4]. Activated carbon is the most employed adsorbent for dye removal from aqueous solution because of its excellent adsorption properties [5]. Based on the literature, many researchers have tried to produce more...
economical activated carbons for removal of various pollutants using alternative cheap and renewable materials such as rambutan peel [6], corn cob [7], orange peel [8], bamboo [9], ginger waste [10], oil palm empty fruit bunch [11], and banana pseudostem fibers [12]. In this work, rubber seed coat based activated carbon (RSCAC) was prepared as an adsorbent to remove AR88 from aqueous solution. The aim of this study was to optimize the physicochemical activation conditions of RSCAC using central composite design (CCD) that involves sodium hydroxide (NaOH) and carbon dioxide (CO₂) as activation agents throughout this study.

2. Experimental study

Acid Red 88 (AR88), 4-(2-Hydroxy-1-naphthylazo)-1-naphthalenesulfonic acid sodium salt supplied by Sigma Aldrich (M) Sdn. Bhd. was used as an adsorbate. AR88 has an empirical formula of HOC₁₀H₆N=NC₁₀H₆SO₃Na with molecular weight of 400.38 g/mol. Rubber seed coat (RSC) used for preparation of activated carbon was obtained locally in the area of Selama, Perak, Malaysia. The RSC was firstly washed thoroughly to remove dirt and inorganic matters prior to dried in oven at 100°C for 24 h. The dried precursor was ground into small pieces and was sieved to the size of 1-2 mm. Carbonization step was carried out at 500°C and held for 2 h under nitrogen gas using the furnace. The flow rate of nitrogen gas and the heating rate were held constant at 150 cm³/min and 10°C/min, respectively. The char produced was mixed with NaOH pellets with different impregnation ratio (IR).

The activation step was done using similar reactor as in carbonization step but at final temperature of 775°C. Once the desired activation temperature was reached, the gas flow was switched to carbon dioxide (CO₂) at the same flow rate for different period of time. The activated carbon was cooled to room temperature under nitrogen flow and washed with hot deionized water to recover the remaining NaOH. The washing process was continued using 0.1M HCl, then washed several times with hot deionized water until the pH of the washing solutions reached 6-7.

Adsorption studies were performed using Erlenmeyer flasks where 300 mg of adsorbent were mixed with 200 mL aqueous dye solutions of 100 mg/L initial concentration in 20 sets of these flasks. The mixture was agitated at 120 rpm at 30 °C until equilibrium was attained. The pH of the solution was natural without any pH adjustment. The concentration of adsorbate was determined using a double UV-Vis spectrophotometer (UV1800 Shimadzu, Japan) at maximum wavelength of 535.5 nm. The percentage removal at equilibrium was calculated by Equation (1).

$$\text{Removal} \, (\%) = 100 \times \frac{(C_o - C_e)}{C_o}$$  \hspace{1cm} (1)

where $C_o$ and $C_e$ are the liquid-phase dye concentrations at initial state and at equilibrium (mg/L), respectively. The RSCAC yield was calculated as the dry weight of final activated carbons, $w_c$, to the dry weight of precursors, $w_o$, as expected by Equation (2):

$$\text{Yield} \, (\%) = 100 \times \frac{w_c}{w_o}$$  \hspace{1cm} (2)

In this work, a standard response surface methodology (RSM) design called central composite design (CCD) was used to study the parameter of preparing RSCAC [13]. There are three independent variables studied for the preparation of RSCAC which were activation temperature ($x_1$), activation time ($x_2$) and NaOH:char IR ($x_3$). These three variables together with their respective ranges were chosen based on the literature and preliminary studies [6]. The two responses; AR88 removal ($Y_1$) and RSCAC yield ($Y_2$) were used to develop an empirical model which correlated the response to the three activated carbon preparation variables. Scanning electron microscopy was used to study the surface morphology of the precursors, chars and the activated carbon prepared including the pore structure, surface structure and pore arrangement. The analysis was carried out using a scanning electron microscope (Model LEO SUPRA 55VP, Germany). 

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3. Results and discussion

3.1 Development of regression model equation

The correlation analysis between RSCAC preparation variables and response, AR88 removal and RSCAC yield, were developed using CCD. According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased. The complete design matrixes together with both response values obtained from the experimental work is shown in Table 1.

Run 15-20 at the center point were conducted to determine the experimental error and the reproducibility of the data. AR88 removal and RSCAC yield were found to range from 25.98 to 42.18% and 27.02 to 38.46%, respectively. The test carried out by Fit Summary suggested that quadratic model was statistically significant for AR88 removal ($Y_1$) and RSCAC yield ($Y_2$), where the models were not aliased. The final empirical formula models for both responses in terms of coded factors after excluding the insignificant terms are represented as follows:

$$Y_1 = 38.34 + 4.55 x_1 - 0.30 x_2 + 1.32 x_3 - 1.68 x_1^2 - 1.08 x_2^2 + 0.16 x_3^2$$
$$- 0.26 x_1 x_2 - 0.73 x_1 x_3 - 0.071 x_2 x_3$$

(3)

$$Y_2 = 33.16 - 3.58 x_1 - 1.10 x_2 - 1.34 x_3 - 0.79 x_1^2 + 0.097 x_2^2 + 0.15 x_3^2$$
$$+ 0.055 x_1 x_2 - 0.10 x_1 x_3 - 0.13 x_2 x_3$$

(4)

The effect of the particular factor represented by the coefficient with one factor, while interaction between two factors and quadratic effect represented by the coefficient with two factors and those with second order terms, respectively. The positive and negative sign in front of the coefficient from empirical formula models for both responses shows the synergistic and antagonistic effect. The correlation coefficients, $R^2$ value evaluates the quality of the developed models. In fact, high value for $R^2$ and low standard deviation was the best indicator in order to develop a good model which is closer to unity as it will give predicted value closer to the actual value for the responses [11].

| Run | Level | RSCAC preparation variable | AR88 removal, $Y_1$ (%) | RSCAC yield, $Y_2$ (%) |
|-----|-------|----------------------------|-------------------------|------------------------|
| 1   | -1    | Activation temp, $x_1$ (°C) | 700                     | 28.53                  |
| 2   | +1    | Activation time, $x_2$ (h) | 1.00                    | 39.03                  |
| 3   | -1    | IR, $x_3$                  | 1.00                    | 28.75                  |
| 4   | +1    | -1                         | 850                     | 39.75                  |
| 5   | -1    | +1                         | 700                     | 33.08                  |
| 6   | +1    | -1                         | 850                     | 42.18                  |
| 7   | -1    | +1                         | 700                     | 34.54                  |
| 8   | +1    | +1                         | 850                     | 41.09                  |
| 9   | -1.682| 0                          | 649                     | 25.98                  |
| 10  | +1.682| 0                          | 901                     | 40.85                  |
| 11  | 0     | -1.682                     | 775                     | 36.73                  |
| 12  | 0     | +1.682                     | 775                     | 33.49                  |
| 13  | 0     | 0                          | 775                     | 37.64                  |
| 14  | 0     | 0                          | 775                     | 39.57                  |
| 15  | 0     | 0                          | 775                     | 38.06                  |
| 16  | 0     | 0                          | 775                     | 38.48                  |
| 17  | 0     | 0                          | 775                     | 38.29                  |
| 18  | 0     | 0                          | 775                     | 38.80                  |
| 19  | 0     | 0                          | 775                     | 33.19                  |
| 20  | 0     | 0                          | 775                     | 33.19                  |

Table 1. Experimental design matrix for preparation of RSC activated carbon.
From the experimental data, the $R^2$ values for Equation (3) and (4) were 0.9689 and 0.8122, respectively. The standard deviations for the two models were 1.09 and 2.29 for Equation (3) and (4), respectively. The $R^2$ values for AR88 removal was considered relatively high, indicating that the predicted values for AR88 removal of the RSCAC would be more accurate and closer to its actual value. The $R^2$ for RSCAC yield was considered as moderate to validate the fit, which might lead to larger variation in the RSCAC yield predicted from the model. Although the value for standard deviation slightly high, the predicted values for this model is still considered as suitable to correlate the experimental data. AR88 removal model shows much more accurate prediction and closer to its actual values, compared to RSCAC yield models.

### 3.2 AR88 removal

Based on analysis of variant (data not shown), both the activation temperature and IR variables were found to have significant effects, meanwhile activation time showed the least significant effect on this response. Figure 1a shows the three-dimensional response surfaces that illustrates the interaction effects of the activation temperature and IR on the AR88 removal. For this plot, the activation time was fixed at zero level ($t = 2$ h).

Figure 1(a) shows AR88 removal generally increased with increase in activation temperature and IR. The result obtained were in agreement with effect of activation temperature an IR for production of activated carbon from cassava peel and apricot stones [2, 13]. Activation time was not as significant as activation temperature and IR in preparation of activated carbon. Increasing activation temperature and activation time would increase reaction rates, promote enlargement opening of pores, thus increase adsorption uptake of dye onto the activated carbon [14]. However, prolong the activation time might lead to undesirable effect depending on requirement of specific activated carbon application, in term of pores enlargement [15]. IR ratio played critical role in formation of pores and increasing surface area of activated carbon. At high IR, pores development was due to intercalation of sodium metal in the carbon structure. New pores created was due to catalytic oxidation of carbon surface by sodium metallic salt [16, 17].

### 3.3 RSCAC yield

Figure 1b shows three-dimensional response surface which illustrates the effects of RSCAC preparation variables on the RSCAC yield by plot the effect of activation temperature and activation time on the RSCAC yield, with IR fixed at zero level ($IR = 2.25$). The RSCAC yield was found decreased with increasing activation temperature and activation time. However, activation time is not really significant for this response.

![Figure 1](image_url)

**Figure 1.** Three-dimensional response surface plot of (a) AR88 removal (Effect of activation temperature and IR, $t = 2h$) of RSCAC and (b) RSCAC yield (Effect of activation temperature and activation time, $IR = 2.25$).
This result shown were in agreement with the experimental data by Ahmad et al. [18] which found that activation temperature plays an important role on the yield of activated carbon prepared by rattan sawdust whereas activation time did not show much effect on the carbon yield. In addition, the overall weight loss was found to increase with IR, whereas in decreasing yield of activated carbon at high temperature. The weight loss was due to devolatilization of the precursors, primary to increase of the pore development and create new pores, as a result of intensifying dehydration and elimination reactions. When temperature increasing, C-NaOH and C-CO\textsubscript{2} reaction rate is increased as well, leading towards decreasing of carbon yield [19]. Thus, increasing of IR cause decreasing of RSCAC yield due to oxidation process on the surface of carbon atoms.

### 3.4 Process optimization

Optimization of process parameters to obtain high carbon yield and high AR88 removal was one of the main objectives of this study. However, it is difficult to optimize both these responses under the same condition because the interest region of factors is different. Since high adsorption capacity always comes with low activated carbon yield, the function of desirability was applied using Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) in order to compromise between these two responses. In optimization analysis, target criteria was set as maximum values for two response, AR88 removal and RSCAC yield, while the three particular variable (activation temperature, activation time and IR) were set in range being studied. The experimental conditions with the highest desirability were selected to be verified. The predicted and experimental results of AR88 removal and RSCAC yield obtained at optimum conditions are listed in Table 2. The optimum RSCAC was obtained by using activation temperature, activation time and IR of 775\textdegreeC, 2h and 2.25, respectively. The optimum RSCAC showed AR88 removal of 38.29\% and RSCAC yield of 33.26\%. It was observed that the experimental values obtained were in good agreement with the values predicted from the models, with relatively small errors between the predicted and the actual values, which was only 0.13\% and 0.30\%, for AR88 removal and RSCAC yield, respectively.

| Table 2. Model validation. |
|-----------------------------|
| Model desirability | Activation temperature, $x_1$ (oC) | Activation time, $x_2$ (h) | IR, $x_3$ | AR88 removal (%) | RSCAC yield (%) |
|-----------------------------|---------------------------------|-----------------|--------|----------------|-----------------|
| Pred. | Exp. | Error (%) | Pred. | Exp. | Error (%) |
| 0.886 | 775 | 2.0 | 2.25 | 38.34 | 38.3 | 0.13 | 33.16 | 33.3 | 0.30 |

### 3.5 Surface morphology

The surface morphology of samples was examined using scanning electron microscopy (SEM). Figure 2 shows the SEM micrographs of the samples. RSC surface textures were observed as rough, uneven, undulating and very little pores were presence as observed in other biomass [20]. After carbonization and activation processes, irregular holes and pores were developed and found on the surfaces of the sample. This is probably due to effect of the diffusion of NaOH and CO\textsubscript{2} molecules onto the sample, which create more pores on the sample’s surface [21, 22].
4. Conclusion

The response surface methodology (RSM) technique was successfully utilized in optimizing the process condition for the preparation of activated carbon from rubber seed coat. The optimum conditions obtained for preparing the activated carbon were 775°C, 2h and 2.25 for activation temperature, activation time and impregnation ratio, respectively, and resulting in maximum AR88 removal of 38.29% and 33.26% carbon yield. The result of study indicates the potential of rubber seed coat to be a potential feedstock for production of activated carbon by using physiochemical activation method. Thus, indicates the advantages of RSM method by reducing trial numbers, time and cost of formulation development.

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