Adsorption of Quinoline from Aqueous Solution by NaOH-treated Biochar derived from Orange Peel: Response Surface Methodology Optimization

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Abstract: During this research project, response surface methodology (RSM) was used to optimise the adsorption of quinoline on modified orange peel biochar (MOPBC). The RSM was laid out using a design of experiments CCD (central composite design) with three experimental factors: initial concentration, temperature, and adsorbent dosage as the main variables. The F-value of the model was 97.16 with a p-value less than 0.0001. Indicated that the experimental data does not deviate from the model. The maximum quinoline removal of 98.01% when initial concentration dsorbent dosage and temperature were 50 mg/L, 0.02g and 40 °C.

Keywords: Response surface methodology, Quinoline, Biochar, Adsorption.

1. Introduction

The substantial progress of coking industry has produced a large amount of coking wastewater while driving the world economy. Coking wastewater contains a large number of non-biodegradable organic pollutants, such as phenol, quinoline and pyridine [1,2]. The release of untreated coking wastewater can lead to severe pollution of natural water sources and have lasting environmental consequences [3]. Quinoline is a nitrogen-containing, difficult-to-biodegrade organic matter and one of the major components in coking wastewater [4,5]. In addition, quinoline is often utilized as a raw ingredient in the production of chemicals, pesticides and pharmaceuticals. Treatment technologies for quinoline-containing wastewater will be developed.

Adsorption is extensively adopted to decontaminate diverse organic pollutants from water [6,7]. As the most attractive adsorbent, activated carbon demonstrates excellent adsorption capacity. Recently, the use of bio-waste materials for biochar production, categorized as a renewable and cost-effective alternative to activated carbon, has been of interest in numerous studies [8,9].

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2. Materials and Methods

2.1 Preparation of Biochar Samples

Orange peels were washed repeatedly with distilled water and were torn into thin slices and dried at 90 °C. Then, they were ground and passed through 80 mesh sieves. 5 g of orange peel powder was kept at 900 °C for 1 h in a nitrogen atmosphere. The resulting carbon was then stirred in 0.1 M sodium hydroxide. After modification, it was washed with hydrochloric acid and distilled water to obtain a neutral pH. Ultimately, it was dried at 100°C. The biochar prepared from orange peels was named as MOPBC.

2.2 Batch adsorption study

A quantity of MOPBC was added to 50 ml of quinoline solution of a certain concentration and pH 7 and maintained in a 100 mL glass bottle which was placed in a constant temperature hydrothermal magnetic stirrer. After 60 minutes of adsorption, the samples were drawn and the adsorbents were separated for obtaining the remaining concentration of quinoline. The remaining concentrations of quinoline were determined by a UV752 UV-Visible Spectrophotometer (Yoke) at the wavelength of 280 nm using a calibration curve.

The quinoline removal (%) is calculated as follows:

$$R\ (\%) = (C_0 - C_e) / C_0 \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium quinoline concentrations (mg/L), respectively, and R (%) is quinoline removal.

2.3 Levels of Research Study

We employed RSM with CCD to determine the effect of three independent variables: initial quinoline concentration (A), temperature (B) and adsorbent dosage (C) on adsorption of quinoline by MOPBC. The levels of variables are provided in Table 1.

Table 1. Levels of variables used in CCD.

Codes	Variables	Ranges and levels				
		-2	-1	0	+1	+2
A	Initial concentration (mg/L)	25	50	75	100	125
B	Temperature (ºC)	25	40	55	70	85
C	Adsorbent dosage (g)	0.005	0.01	0.015	0.02	0.025

3. Results and discussion

3.1 Model development and analysis

The responses of 20 experiments, including the removal of quinoline and the predicted values, are given in Table 2.

Table 2. CCD matrix responses.

Run	A	B	C	C_e (mg/L)	Actual value (%)	Predicted value (%)
1	75	55	0.005	40.35	46.20	47.54
2	75	85	0.015	4.05	94.60	95.09
3	75	25	0.015	13.28	82.29	82.82
4	75	55	0.015	16.39	78.15	76.44
5	75	55	0.015	18.61	75.19	76.44
6	50	40	0.010	15.49	69.03	69.28
7	50	70	0.010	9.79	80.43	79.84
8	100	40	0.010	44.32	55.68	53.56
9	75	55	0.015	18.23	75.69	76.44
10	25	55	0.015	1.25	95.00	94.00
11	75	55	0.015	20.37	72.84	76.44
12	75	55	0.025	4.80	93.60	93.28
13	75	55	0.015	16.21	78.39	76.44
14	100	40	0.020	16.74	83.26	82.83
15	75	55	0.015	17.00	77.34	76.44
16	50	70	0.020	2.40	95.21	96.31
17	100	70	0.010	31.13	68.87	67.63
18	100	70	0.020	14.19	85.81	84.54
19	125	55	0.015	44.39	64.49	66.51
20	50	40	0.020	1.07	97.87	98.10

According to the analysis of variance (ANOVA) results (Table 3), the model has an F-value of 97.16 and a p-value less than 0.0001, indicating the significance of the model and a good correlation between variables and response. The high correlation coefficient (R^2 = 0.9887) suggests that only 1.13% of the variability cannot be explained by the regression model. Additionally, the adjusted coefficient (Adj-R^2) of 0.9785 is very close to R^2, revealing the best fitness of the model for the empirical data. The C.V. value of 2.54 %, much less than 10 %, indicates that the experiment had strong stability and good precision and credibility. The adequate precision (the ratio of effective signal to noise) is 35.9264, significantly higher than 4.0, indicating an adequate response signal [10,11].

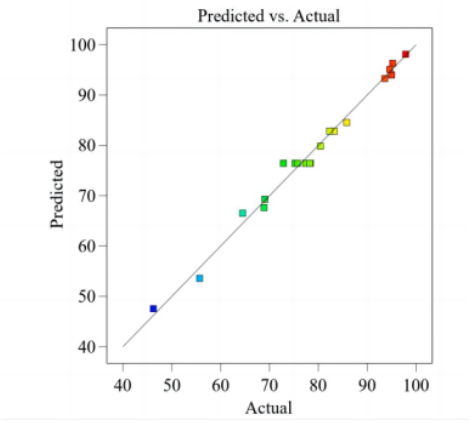
Based on the p-values of the independent variables, A, B, C, BC, A^2, B^2 and C^2 are significant ($p<0.05$). The model terms with a p-value > 0.05, including AB and AC, were insignificant and thus excluded from the model. Therefore, the empirical model equation was developed as follows:

$$Y = 76.44 - 6.87A + 3.07B + 11.43C + 0.8750AB + 0.1125AC - 3.09BC + 0.9542A^2 + 3.13B^2 - 1.51C^2 \quad (2)$$

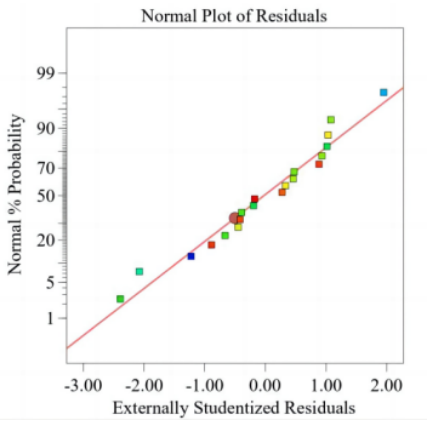
Table 3. ANOVA results for quinoline adsorption on MOPBC.

Source	Sum of squares	DF	Mean square	F-value	p-value
Model	3463.57	9	384.84	97.16	<0.0001
A	755.43	1	755.43	190.72	<0.0001
B	150.68	1	150.68	38.04	0.0001
C	2091.69	1	2091.69	528.09	<0.0001
AB	6.13	1	6.13	1.55	0.242
AC	0.1013	1	0.1013	0.0256	0.8762
BC	76.26	1	76.26	19.25	0.0014
A^2	22.89	1	22.89	5.78	0.0371
B^2	246.2	1	246.2	62.16	<0.0001
C^2	57.1	1	57.1	14.42	0.0035
Residual	39.61	10	3.96		
Lack of Fit	17.17	5	3.43	0.765	0.612
Pure Error	22.44	5	4.49		
Cor Total	3503.18	19			
R^2	0.9887				
R^2_{Adj}	0.9785				
C.V.	2.54%				
Adequate Precision	35.9264				

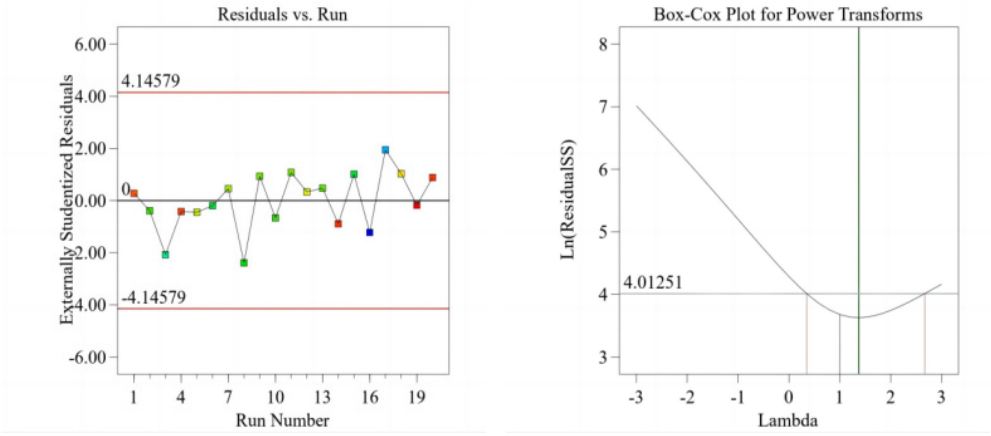
Figure 1a shows the predicted and actual values calculated from the quadratic polynomial model. As shown, the predicted values agree well with the actual values. Figure 1b displays that the points are closely aligned to a straight line, revealing a perfect normal distribution and independence of the residuals. As shown in Figure 1c, the residuals were scattered randomly around ±4.1, which shows the high efficiency of the model for well presentation and explanation of actual data. Figure 1d demonstrates that the standard transformation with all variables and responses fell closest to the best λ value within the confidence interval.



(a)



(b)



(c) (d)

Figure 1 Linear regression modelling of quinoline adsorption on MOPBC.

3.2 Effect of process parameters on adsorption of quinoline by MOPBC

Figure 2 shows their 3D response surfaces and corresponding contour plots for the adsorption of quinoline onto MOPBC. The shape of the contour lines reflects the magnitude of the interaction, and the response surface plots can be used to interpret the interrelationships between variables and to determine the optimal level of each variable when the maximum response value is achieved. In the 3D response surface plots, the darker the surface colour (red), the higher the quinoline removal rate. As shown in Figure 2a, the temperature exhibited a marked effect on the response. The quinoline removal experienced a reduction with the increasing temperature from 25 to 45 °C and then an increase with further temperature increases. The quinoline removal is reduced with the initial quinoline concentration and increased with the adsorbent dosage (Figure 2a-c). In Figure 2c, the contours line are the densest, which indicats that the interaction of adsorbent dosing and temperature has the greatest effect on quinoline removal. On the other hand, the sparser contour lines in Figure 2b suggest that the influence of the interaction between initial solution concentration and adsorbent dosage on quinoline removal is not as pronounced as that of other factors.

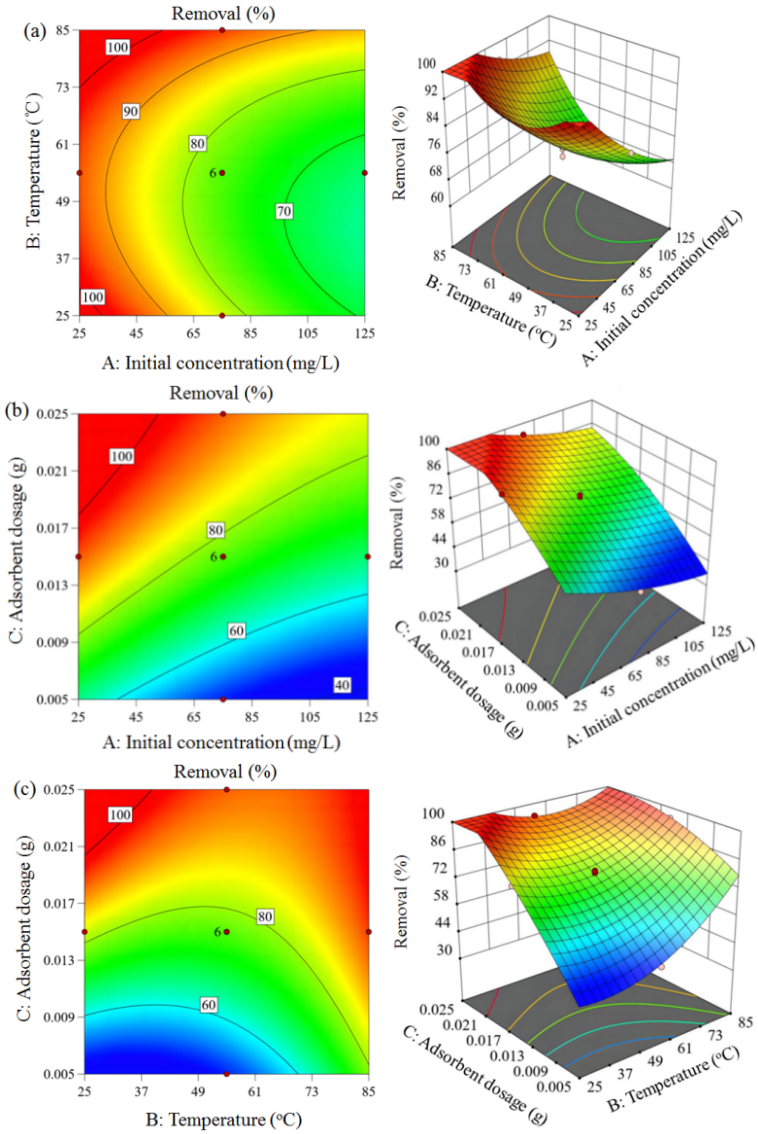


Figure 2 3D surface and contour plots on quinoline removal.

Figure 3 illustrates the desirability values of the three variables and the generated response values. The optimal conditions can meet an overall agreeability of 97.89 %, which is high according to the desired objectives. The optimal experimental conditions obtained through response surface methodology optimization were: initial concentration of 50 mg/L, 40 °C, and adsorbent dosage of 0.02 g. At this point, the quinoline removal rate was 98.01 %. Three groups of parallel tests were conducted under the best conditions, and the mean quinoline removal rate was 97.87 %, which was approaching the model prediction with an error of 0.14%. Therefore, the experiments to validate the model showed that the model was precise.

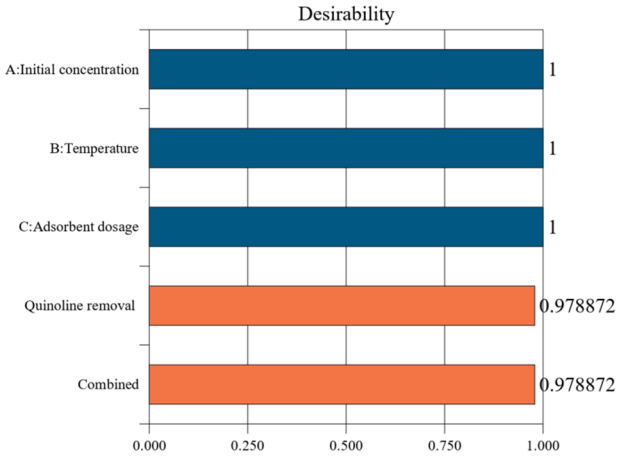


Figure 3 Desirability for each factor along with generated response.

4. Conclusion

Response surface methodology was used to optimise the adsorption of quinoline on MOPBC, and the effects of initial concentration of quinoline, temperature and adsorbent dosage as well as their interactions were investigated. The results showed that all three factors had a significant effect on the adsorption of quinoline by MOPBC. The best conditions for MOPBC to absorb the quinoline was initial concentration of 50 mg/L, 40 °C, and adsorbent dosage of 0.02 g. The predicted removal rate at this point was 98.01 %.

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