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Process Optimization for the Preparation of Activated Coke from Industrial Waste Using Response Surface Methodology

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ABSTRACT

Fine blue-coke and direct liquefaction residue of coal are byproducts in the process of coal chemical production. They were taken as raw materials for the preparation of activated coke by the activation of carbon dioxide. The conditions (activation temperature, activation time and carbon dioxide flow rate) for activated coke preparation were optimized by response surface methodology (RSM). Results showed that activation temperature and activation time had a significant effect on the activated coke iodine adsorption value. The synergistic effect of activation time and carbon dioxide flow had a great influence on iodine adsorption value of activated coke. RSM optimization experiment obtained the optimum activation conditions were activation temperature of 850°C, activation time of 90min and carbon dioxide flow rate of 60 mL/min. Under these conditions, the obtained activated coke iodine adsorption value can reach 401 mg/g, which could meet the needs of industrial desulphurization.

INTRODUCTION

The flue gas produced from non-ferrous metal smelting processes has become the top priority in air pollution control. Low concentration sulphur dioxide treatment methods include wet, semi-dry, dry, etc. (Bashkova et al. 2001, Siyi 2015). The traditional wet and semi-dry processing technologies have high cost, the products resulting from the treatment process are wet, and produce secondary pollution such as wastewater slag, plugging and corrosion of equipment (Gong & Yang 2018). Activated coke flue gas desulphurization technology is a resource-based dry process technology, and can also remove nitrogen oxides, dioxins, heavy metals and HCl from the flue gas, has the advantage that the product is dry and does not produce secondary pollution such as waste residue (Yan et al. 2013, Yang et al. 2017). Activated coke is desulphurizer of flue gas desulphurization technology by activated coke and is the key material to the performance and efficiency of desulphurization. The traditional preparation of activated coke is based on coal as raw material and coal tar as binder (Li 2008), so the production cost is high. Fine blue-coke and direct liquefaction residue of coal are byproducts in the process of coal chemical production (Tian et al. 2015, Zhang et al. 2012). The production cost is low using fine blue-coke and coal direct liquefaction residue as raw materials to prepare activated coke without adding adhesive. The preparation of high-quality activated coke is affected by the ratio of raw materials, carbonization temperature, carbonization time, activation temperature, activation time, activation atmosphere and other conditions, it is therefore necessary to optimize the selection of suitable preparation conditions (Gao et al. 2016, Li 2008, Zhao et al. 2016). However, the traditional test method requires a large number of experiments, and the experimental data are difficult to analyse and heavy workload.

The response surface method is often used to explore, improve, and optimize various process conditions. It can easily optimize the synergistic effects of multiple factors and facilitate the management and analysis of experimental data. Cheng et al. (2015) used Hawaiian nutshells as raw materials, using response surface methodology to optimize CO_2 physical activation of activated carbon. Di et al. (2017) used response surface methodology to optimize the enhanced coagulation process to treat micro-polluted water and optimize the optimal process conditions for coagulation treatment of micro-polluted water. Finally, it was verified by the model that the response surface method was used to optimize the feasibility and effectiveness of the enhanced coagulation process for the treatment of micro-polluted water. Theydan & Ahmed (2012) used the date kernel as the raw material and optimized the activation condition

of the activated carbon using the Box-Wilson centre composite design in response surface methodology. The results showed that the optimal conditions for $FeCl_3$ activation were activation temperature of 707°C and activation time of 76 min. The optimal conditions for $ZnCl_2$ activation are activation temperature of 717°C and activation time of 30min.

Response surface methodology is applied to the analysis of experimental data and optimization of experimental conditions. The effect of different activation conditions on the iodine adsorption value of activated coke is studied in this paper.

MATERIALS AND METHODS

Experimental raw materials: The raw materials used in the experiment were fine blue-coke and coal liquefaction residue. The fine blue-coke was from Shenmu Blue Coke Group and the direct coal liquefaction residue came from a direct liquefaction plant. Due to the fact that ash may be transferred into the activated coke during the preparation of activated coke, and high ash content is not good for activated coke. DCLR deashing is performed before the experiment. The specific method is: Take 100 g DCLR, add 25 mL HF and 175 mL H_2O in order. Stir well and put it in a fume hood for 4 hours, and then filter by suction, wash it with distilled water until it is nearly neutral, and finally dry it at 120°C. The proximate analysis and elements analysis of fine blue-coke, coal direct liquefaction residue (DCLR) and de-liquefaction residue (D-DCLR) are given in Table 1.

Preparation of activated coke: The D-DCLR was blended into a selected amount of fine blue-coke according to a certain ratio, and the mixture was evenly mixed at room temperature, some water was added to the mixture and stirred well. Under 5 MPa, it was pressed and formed into columnar strips (5 mm×10 mm), then they were dried at room temperature.

The pressed and formed columnar strips were carbonized and activated in the tube furnace under nitrogen protection. When the carbonization process was completed, the temperature was further increased to the activation final temperature, and the CO_2 gas cylinder was opened to adjust the gas flow. After the activation was completed, the entire system was cooled to room temperature under nitrogen protection.

Experimental design: Data analysis software (JMP10, Cary, NC, USA) was used for experimental design and data analysis. Three-factor and three-level response surface experiments were designed to study the synergistic effect of activation temperature, activation time, and carbon dioxide flow rate on the iodine adsorption value of activated coke. The respective ranges of the three factors are provided in Table 2, and the experimental design and experimental results are given in Table 3.

SEM characterization: The SEM analysis of activated coke was performed using a JSM-6390A scanning electron microscope to characterize the morphology of the carbonized material and the activated material. The scan voltage was 10 kV and the scan magnification was 1000x.

DATA ANALYSIS AND DISCUSSION

Analysis of variance: The variance analysis was used to evaluate the effect of each factor on the activated coke iodine adsorption value. The results are given in Table 4. The experimental design default P value of less than 0.05 has significant statistical significance (Hesas et al. 2013, Salman 2014, Sulaiman et al. 2018). Table 4 shows the activation temperature ($P = 0.0028 < 0.05$) and activation time ($P = 0.0062 < 0.05$), carbon dioxide flow ($P = 0.4308 > 0.05$), indicating that the effect of activation temperature and ac-

Table 1: Proximate analysis and elements analysis of raw material.

Sample	Proximate analysis (%)				Elements analysis (%)				
	M_t	A_{ad}	V_{ad}	FC_{ad}	C_{ad}	O_{ad}	H_{ad}	N_{ad}	$S_{t,\ ad}$
Fine blue-coke	2.15	16.77	12.07	69.01	72.88	0.3	1.06	0.88	0.6
DCLR	0.14	17.74	33.75	48.37	75.64	17.91	3.573	0.9	1.978
D-DCLR	0.26	10.62	33.19	55.93	78.24	15.4	3.733	0.96	1.667

Table 2: Parameters and their levels used for response surface design.

Factor level	Activation temperature (°C)	Activation time (min)	CO_2 flow ($mL \cdot min^{-1}$)
1	700	30	60
2	800	60	80
3	900	90	100

Table 3: The experimental conditions and results of iodine adsorption value.

Experiment sequence	Activation temperature (°C)	Activation time (min)	CO_2 flow ($mL \cdot min^{-1}$)	Iodine value ($mg \cdot g^{-1}$)
1	900	60	60	279.4
2	700	30	80	218.44
3	800	90	100	325.12
4	800	90	60	386.08
5	800	60	80	246.92
6	800	30	100	312.05
7	700	60	100	237.68
8	800	30	60	245.35
9	700	60	60	233.68
10	900	90	80	309.88
11	800	60	80	248.92
12	700	90	80	243.2
13	900	30	80	279.4
14	900	60	100	312.05
15	800	60	80	248.92

Table 4: Variance analysis of different factors

Factor	Degree of freedom	Sum of square	Mean square	F ratio	P value
Activation temperature (°C)	1	7671.2691	7671.2691	29.8813	0.0028
Error	14	21207.4029	1514.8145		
Sum	15	28878.672			
Activation time/min	1	5277.2401	5277.2401	20.5561	0.0062
Error	14	23601.4319	1685.8166		
Sum	15	28878.672			
CO_2 flow ($mL \cdot min^{-1}$)	1	188.3741	188.3741	0.7338	0.4308
Error	14	28690.2979	2049.3069		
Sum	15	28878.672			

tivation time on the iodine adsorption value are significant, while the CO_2 flow alone has no significant effect on the activated coke iodine adsorption value.

Mean value analysis: The average value of iodine adsorption values at different levels for each factor were calculated. The results are shown in Fig. 1. From the figure, it can be seen that as the activation temperature increases, the iodine adsorption value shows a trend of increasing; at the range of 700°C to 800°C the iodine adsorption value is more affected by the activation temperature. The activation process causes the activator to react with the disordered carbon in the coke and the tar and other substances present in the original pore to cause it to burn out and open the closed pore. As the activation temperature rises, the activator reacts more strongly with the coke, and an excessively high activation temperature to burn out the exposed carbon. Loss of carbon causes the pores to collapse, generating more mesopores and macropores, which reduce their adsorption capacity. The iodine adsorption value shows a tendency of decreasing first and then increasing with the prolonging of the activation time. The initial activation stage was the opening of closed pores. With the increase of activation time, the burning loss rate of carbon increases, and the decrease of micropores volume leads to the decrease of adsorption capacity of activated coke. Continue to increase activation time, so that the exposed carbon is further burned out and the new pores are formed, and the iodine adsorption value of activated coke shows an increasing trend.

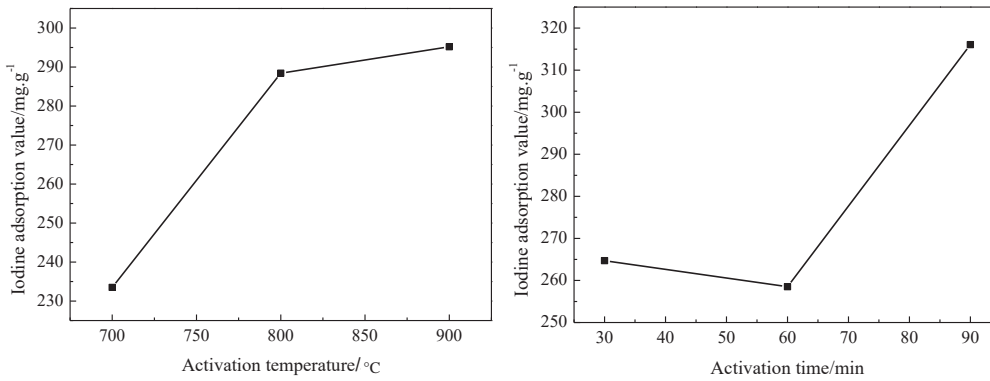

Fig. 1: The iodine adsorption value of activated coke.

Effect of activation conditions on activated coke strength and yield: Fig. 2(a) shows the effect of activation temperature on compressive strength and yield of activated coke. The results show that the compressive strength and yield of activated coke decrease with increasing activation temperature. When the activation temperature is 850°C, the compressive strength and yield of activated coke is 513.8 N and 81.03%, respectively. This is because when the activation temperature is lower, the activator reacts less with the surface of the activated coke material, the reaction is slower and the reaction depth is shallower, so the yield and the compressive strength of the activated coke are higher. When the activation temperature rises to 850°C, the reaction between the activator and the carbon material is intensified and the depth of the reaction is further deepened, resulting in serious loss of carbon material, and a large amount of hydrogen in the coal liquefaction residue is released at higher temperature, and organic components are generated more frequently. The volatiles escaped, resulting in a decrease on the yield and compressive strength. It can be seen that the higher the activation temperature, the more severe the loss of carbon material, and the lower the yield and compressive strength of activated coke.

Fig. 2(b) shows the effect of activation time on the activated coke yield and compressive strength. The results show that the compressive strength and yield of activated coke have a similar trend with the activation temperature as the activation time increases. When the activation time is 90 min, the compressive strength of the activated coke is 573.2 N and the yield is 82.26%. The activation time is continuously prolonged, and the amount of activator continuously increases, making the activator sufficiently enter the pores of the carbon material, fully reacting with the surface and interior of the carbon material, generating a large amount of volatiles to escape, and making the activated coke pores further developed. The compressive strength and yield of activated coke continue to decrease with the increased activation time.

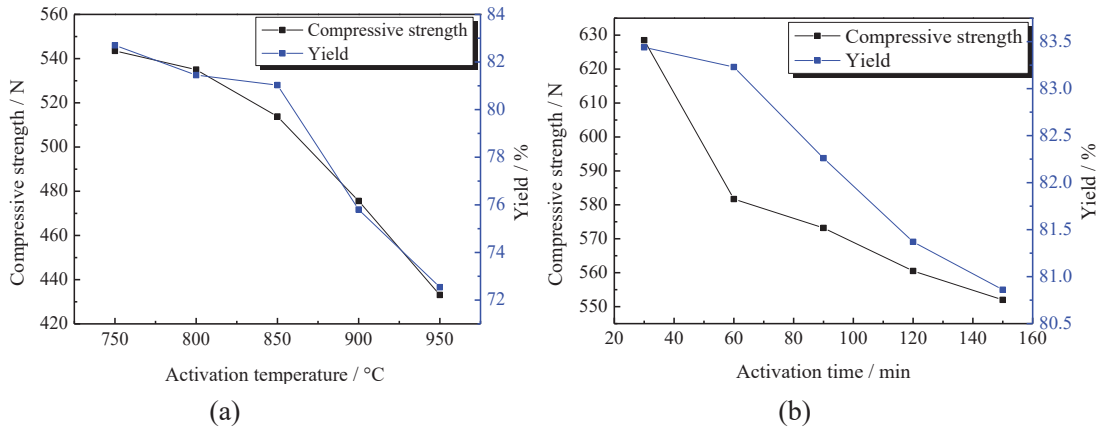

Fig. 2: The yield and strength of activated coke.

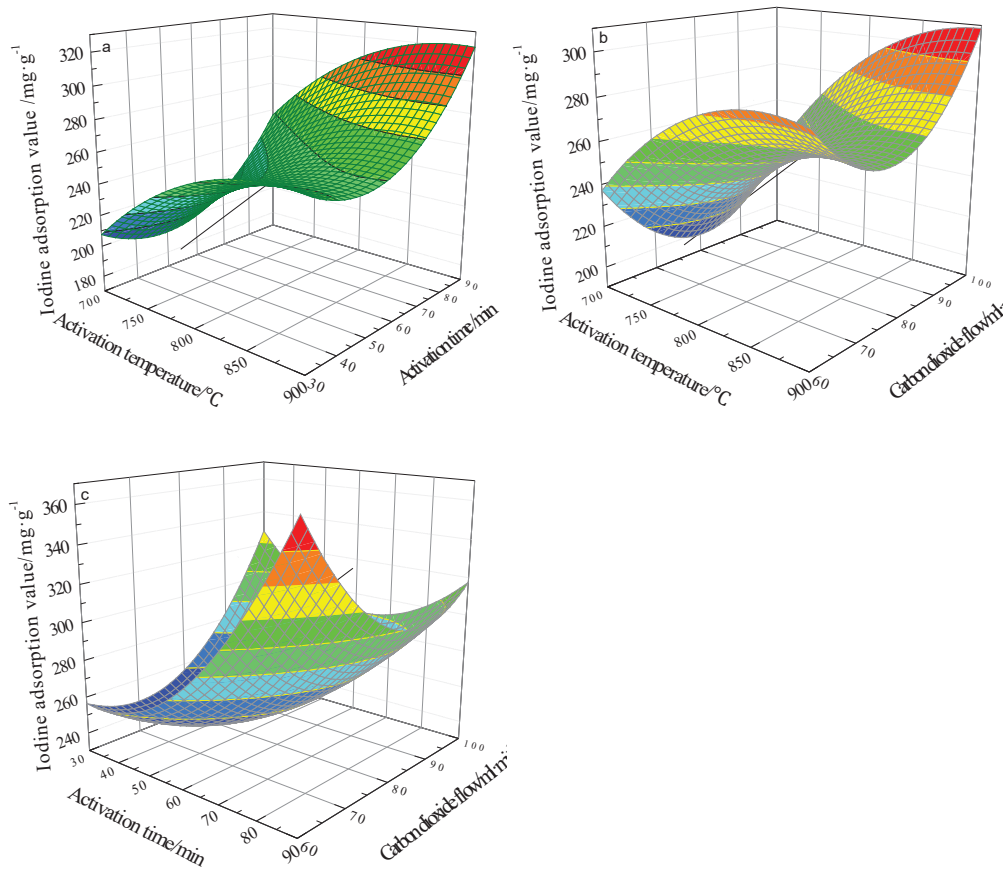

Fig. 3: Response surface map.

Parameters optimization: Response surface methodology was used to explore the optimal synergy of the three activation factors and the effect on the activated coke iodine adsorption value. The relative relationship between the dependent variable and the independent variable is calculated by the following second-order polynomial:

$$Y = 248.92 + 30.96625X_1 + 25.68375X_2 + 4.8525X_3 + 1.43X_1X_2 + 7.1625X_1X_3 - 31.0225X_2X_3 - 19.265X_1^2 + 33.075X_2^2 + 36.0745X_3^2$$

Where, X_1, X_2, X_3 are equal to

$$\frac{\text{activation temperature (°C)} - 800}{100},$$

$$\frac{\text{activation time(min)} - 60}{30} \text{ and } \frac{CO_2 \text{ flow (mL/min)} - 80}{20}$$

respectively.

The calculated values of R^2 and response surface model variance analysis are given in Table 5 and Table 6. R^2=0.96 and P=0.0069 indicate that this model is suitable for predicting the effect of various factors on the adsorption of activated coke at various levels (Ab Ghani et al. 2017, Zheng et al. 2017). The 3-D response surface plot was used to study the synergistic effect of different factors on the activated coke iodine adsorption value. The results are shown in Fig. 3.

Table 5: Summary of model data.

R^2	Adjust R^2	RMSE
0.96	0.88	16.023

Table 6: Analysis of variance of response surface quadratic model.

Source	Degree of freedom	Sum of square	Mean square	F ratio	P value
Model	9	27595.051	3066.12	11.9432	0.0069
Error	5	1283.622	256.72		
Correction sum	14	28878.672			

In Fig. 3(a), the iodine adsorption value of the activated coke as a function of activation temperature and activation time, the CO_2 flow rate is 80 mL/min. It can be seen from the figure, when the activation temperature is 900°C and the

activation time is 90 min, the iodine adsorption value of the activated coke is higher and can reach 309.88 mg/g.

In Fig. 3(b), the iodine adsorption value of the activated coke is a function of activation temperature and CO_2 flow rate, with activation time of 60 min. The figure shows that when the activation temperature is 900°C, CO_2 flow rate of 100 mL/min, the iodine adsorption value of activated coke is 312.05 mg/g.

In Fig. 3(c), the iodide adsorption value of activated coke is a function of activation time and CO_2 flow rate, with activation temperature of 800°C. The figure shows that when activation time is 90 min, CO_2 flow rate of 60 mL/min, the iodine adsorption value is 386.08 mg/g.

In summary, the synergistic effect of CO_2 flow and activation time during the activation process has a great influence on the iodine adsorption value. By optimizing the experimental conditions, the optimal experimental conditions are as follows: activation temperature 850°C, activation time 90 min, carbon dioxide flow rate 60 mL/min. The iodine adsorption value was 401 mg/g, which could meet the needs of industrial desulphurization.

SEM characterization: Fig. 4(a) is SEM photograph of sample carbonized at 600°C for 60 min. Fig. 4(b) is SEM photograph of sample activated by carbon dioxide at 900°C for 90 min. Fig. 4(a) shows that the surface of sample is dense, irregular in shape and with slits. This is due to the large amount of water and volatile matter escaping during carbonization process, which results in slit structure in the carbonized sample. Activator enters into the charcoal material in activation process and provides favourable conditions so that the activation process can be fully carried out and more pore structure can be formed. Fig. 4(b) shows that the sample after activation has rich pore structure and a relatively uniform pore distribution. This is due to the activator reacts with the carbon on the surface and inside of the carbon material under high temperature conditions, the activator continuously etched the surface and inside of the carbon material.

Desulphurization performance: At room temperature, the inlet air amount was controlled at 1300 mg/m^3, the bed height at 13 cm, and the desulphurization performance of activated coke prepared under the optimal conditions was examined. The desulphurization rate for the first 120 minutes is shown in Fig. 5.

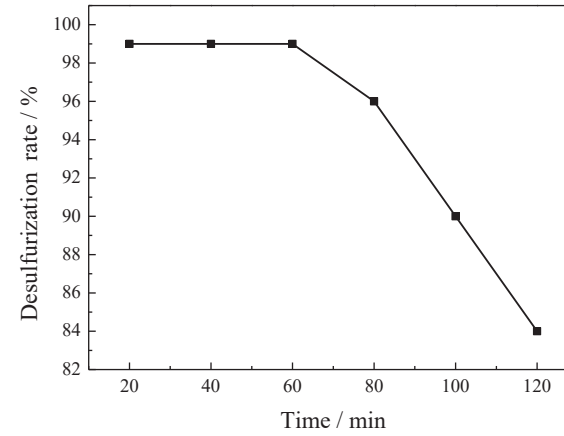

Fig. 5: The desulphurization rate of activated coke (%).

As can be seen from Fig. 5, the desulphurization rate in the first 60 minutes remains stable at 99%, and then it decreased but remained above 80%, indicating that the activated coke has a high removal rate for low concentrations of sulphur dioxide. With the extension of desulphurization time, the main reason for the decrease in desulphurization rate is that the activated sites on activated coke surface are

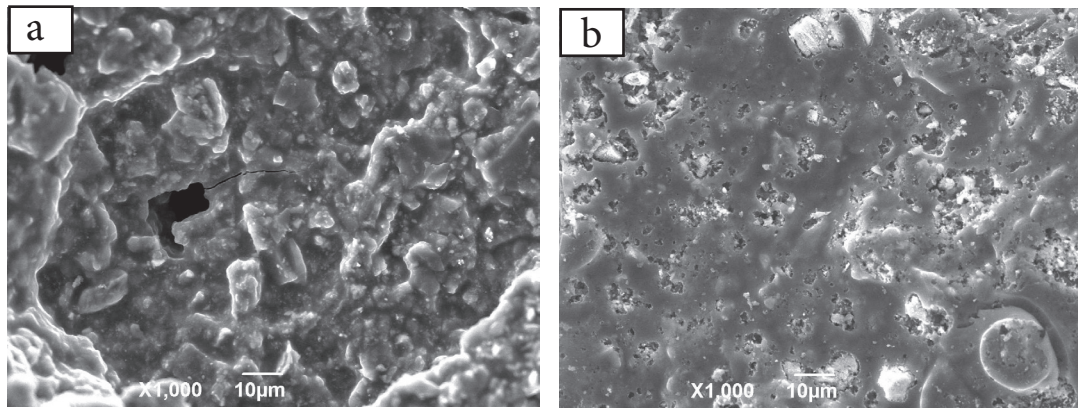

Fig. 4: The SEM analysis of activated coke.

occupied by the adsorbed gas, resulting in a reduction in the activated sites and a decrease in the desulphurization rate.

CONCLUSIONS

The activation temperature and activation time had a more significant effect on the activated coke iodine adsorption value than the carbon dioxide flow using the method of variance analysis. The synergistic effect of activation time and carbon dioxide flow had a great influence on iodine adsorption value of activated coke. RSM optimization experiment obtained better conditions: activation temperature 850°C, activation time 90 min, carbon dioxide flow rate 60 mL/min. The adsorption value of activated coke iodine prepared under these conditions was 401 mg/g. With the increase of activation temperature and activation time, the compressive strength and yield of activated coke are reduced. The carbonization process provides favourable conditions for activator to enter into the carbon material and react with it adequately. The desulphurization rate in the first 60 minutes remains stable nearly 99%.

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