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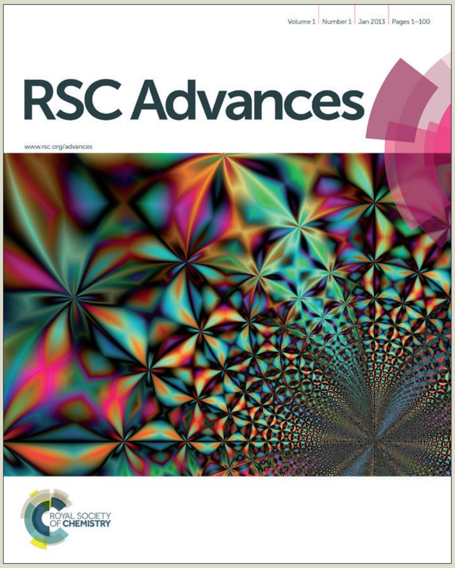

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Modification of abandoned fine blue-coke: optimization study on removal of *p*-nitrophenol using response surface methodology

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Abstract

The abandoned fine blue-coke was modified with the physiochemical method including of nitric acid (HNO_3) treatment and nitrogen gas (N_2) calcination, and used as an adsorbent for *p*-nitrophenol (PNP) removal. The preparation process was optimized to improve the adsorption ability based on the 2_{IV}^{6-2} Fractional factorial design, steepest ascending method and Box-Behnken design (BBD) of Response Surface Methodology (RSM) technique. The significant factors on each experimental design response were identified by means of the analysis of variance (ANOVA). The predicted adsorption capacity of PNP on MFBC was found to agree with the experimental values. The optimum experimental conditions were found as follows: HNO_3 concentration: 4.46 mol/L, modification temperature: 87.8 ℃, modification time: 20.3 h, impregnation ratio of HNO_3 to MFBC:10 ml/1g, calcination time: 2 h, and calcination temperature: 716 ℃. More, surface roughness of the MFBC increased obviously after the modification by FESEM and HRTEM analysis, and the total pore volume and specific surface area increased by 0.8 and 1.2 times, respectively. PNP equilibrium adsorption capacity on MFBC was found to be 156.9 mg/g at 328 K, which highlights its potential application in waste water treatment.

Keywords: Abandoned fine blue-coke; Adsorption; *P*-nitrophenol; Modified process; Response surface methodology

1. Introduction

P-nitrophenol (PNP) as a toxic substance, is widely present in the wastewater of chemical, medicine, pesticide, dye and washing industry.[1] It has strong stimulation to the skin and can be absorbed through skin and digestive tract.[2, 3] The adsorption method has been widely adopted to treat phenolic wastewater due to its good treatment effect.[4] Among the adsorbents, activated carbons are widely used because of its high adsorption capacity.[5] However, its high-cost limits the wide application in the field of wastewater treatment.[6] Recently, many researchers have tried to prepare low-cost adsorbents using the industrial and agricultural byproducts, such as abandoned tea,[1] coconut husk,[7] bagasse,[8] etc. However, these raw materials are hard to collect and carbonization process is necessary in the preparation, resulting in the low yield, which is not suitable for industrial production. Therefore, the cheap, high-yield, and efficient adsorbents are developed for the treatment of phenolic wastewater.

The fine blue-coke with a particle size less than 6 mm is a byproduct of coal pyrolysis, produced at the relatively low temperature (600-700 ℃).[9, 10] It is mostly disposed as low-grade fuel materials or abandoned in the rivers and fields since it cannot meet the iron alloy, ferrosilicon, silicon carbide, calcium carbide production requirement.[10, 11] The investigation revealed that millions of tons of fine blue-coke are abandoned annually in China, which accounts for about 10% of the total blue-coke.[12] This not only causes the waste of large amounts of energy, but also heavy contamination of the environment. On account of their high carbon content and certain pore size distributions, if modified moderately, fine blue-coke will possess relatively large specific surface area and thus can be recognized as a potential adsorption material.

Currently, many physical and chemical activation methods were employed to modify blue-coke, which specially used as the catalyst carrier for desulfurization and denitrification.[13-15] However, it is not reported in the literature that the modified fine blue-coke was directly used for the wastewater treatment.[9] In our previous work, it was found that fine blue-coke can adsorb phenol and p-nitrophenol and the adsorption capacity was increased significantly after nitric acid treatment and subsequent high temperature modification.[16] The objectives of this research is to use abandoned fine blue-coke as raw materials to produce adsorbents for the treatment of PNP in the wastewater. The operating conditions of the modification process are determined, which influence the type and distribution of the surface functional groups and the adsorption capacity of fine blue-coke for various substances. The response surface methodology (RSM) was adopted to optimize the modification process for abandoned fine blue-coke in this work, as it is a useful experimental design method to study two or more variables including the effect of their interaction on response value.[17]. This research provides an environmental friendly method to remove PNP using abandoned fine blue-coke as an adsorbent, which has a potential application in other phenolic wastewater treatment.

2. Materials and methods

2.1 Preparation of modified fine blue-coke

Shenmu fine blue-coke (FBC) was selected as raw material and obtained from Yulin City, Shanxi Province, China. The FBC was firstly washed with warm water and subsequently dried at 105 ℃ for 24h to remove surface dirt and other impurities. The dried FBC was crushed and sieved to less than 100 meshes. The samples obtained were then mixed and reacted with nitric acid aqueous solution at a certain ratio of HNO_3 to FBC. The mixture was filtered. The solid was dried at 105 ℃ and heated at different temperatures for different time under the protection of nitrogen in a tube furnace, then cooled to room temperature. The modified fine blue-coke (MFBC) was thus obtained and kept in a hermetic bottle for subsequent uses.

2.2 Adsorption studies

For batch adsorption studies, 250 mg of MFBC were mixed with 50 ml PNP aqueous solutions of 400 mg/L initial concentration in a set of 100 ml Erlenmeyer flasks. The pH of the solution was natural without any pH adjustment. The mixture was agitated at 200 rpm/min at 25 ℃ for 4h until equilibrium was reached. The concentrations of PNP in the supernatant solutions before and after adsorption were determined using a double beam UV–Vis spectrophotometer (722S, China) at its maximum adsorption wavelength of 400 nm. The PNP uptake at equilibrium, q_e (mg/g), was calculated by Eq. (1):

$$q_e = \frac{(C_0 - C_e)\times V}{W} \tag{1}$$

where C_o and C_e (mg/L) are the concentrations of PNP before adsorption and when the adsorption reached equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry modified fine blue-coke used (g).

2.3 Design of experiments

2.3.1 Fractional factorial design

As a multifactor statistical experimental design method, fractional factorial design can reduce a fraction of or even several tenths of the experimental number to quantify the effects of factors and their interactions on the indexes.[18] In this work, the methodology of 2_{IV}^{6-2}Fractional factorial design was applied to screen out the factors which have significant influence on PNP uptake. Six independent variables including nitric acid concentration (C_{HNO3}, mol/L), modification temperature (T_m, ℃), modification time (t_m, h), impregnation ratio of HNO_3 to FBC (IR, ml/mg), calcination temperature (T_C, ℃) and calcination time (t_c, h) were chosen to be screened by 2_{IV}^{6-2}Fractional factorial design experiment in 16 runs. The low and high factor settings were coded as −1 and +1, the mid-point was coded as 0. Both independent variables and their coded levels were shown in Table 1. The conversion between coded and natural values was shown in Eq. (2). All experiments were carried out in duplicate, and average of PNP uptake (q_e) was taken as the response.

$$X_i = \frac{x_i - x_{i0}}{\delta_i} \tag{2}$$

where X_i is the coded value, x_i is the corresponding natural value, x_{i0} is the natural value in the center of the domain and δ_i is the increment of x_i corresponding to one unit of X_i.

The experimental design, data analysis and modeling were performed by Design-Expert 8.0.6. Its statistical significance was determined by an F-test and the significance of the regression coefficients was analyzed by a t-test. The model obtained was expressed as Eq. (3).[18] From the regression analysis, the significant variables ($p<0.05$) were considered to have greater impact on the PNP uptake and were screened out to conduct the next experiments.

$$Y = \alpha_0 + \sum_{i=1}^{k} \alpha_i X_i + \sum_{i=1}^{j-1} \sum_{j=2}^{k} \alpha_{ij} X_i X_j \tag{3}$$

where Y is the response variable(PNP uptake , q_e), $\alpha_0$is a constant, $\alpha_i$is the linear coefficient, $\alpha_{ij}$is the interaction coefficients, X_i and X_j are the coded values of the independent variables.

Table 1

Independent variables and their coded levels for the 2_{IV}^{6-2}Fractional factorial Design

Factor	Code	Units	Coded variable levels		
			－1	0	＋1
C_{HNO3}	x_1	mol/L	0.1	1.55	3
T_m	x_2	℃	25	57.5	90
t_m	x_3	h	3	13.5	24
IR	x_4	ml/g	5:1	12.5:1	20:1
T_C	x_5	℃	400	550	700
t_c	x_6	h	0.5	2.25	4

2.3.2 The steepest ascending method

The direction of steepest ascent was parallel to the normal of contour line of the response curve of model (2) and passed through the center point of the factorial design. Increment was direct ratio to regression coefficients α_i. Experiments were performed along the path of steepest ascent until no further increase in the response was observed. This point would be near the optimal point and could be used as the center point for optimization.[19]

2.3.3 The Box-Behnken design

Box-Behnken design (BBD) is one of response surface designs which are adequate for fitting a quadratic surface and usually good for the process optimization.[20] Once critical factors were identified via screening and significant gross curvature had been detected in the design space, the BBD was proceeded to obtain a quadratic model. Four factors which have significant influence on PNP uptake (q_e) were selected out according to the results of the 2_{IV}^{6-2}Fractional factorial experiment. The high and low levels of the Box-Behnken experiment variables were determined by the results of the steepest ascending experiment which were shown in

Table 2. For each independent variable, a BBD for the four variables, consisting of 16 factorial points, 8 axial points and 3 replicates at the center points were employed, indicating that altogether 27 experiments were required, as calculated from Eq. (4).[20] All experiments were carried out in duplicate and the average of PNP uptake (q_e) was taken as the response. An empirical second-order polynomial model relating the four process variables to response variables as Eq. (5)[21] represented was utilized. The statistical software Design-Expert version 8.0.6 (STAT-EASE Inc., Minneapolis, USA) was used for regression analysis of the experimental data to fit the equations developed and also for the evaluation of the statistical significance of the equations.

$$\mathrm{N} = 2^{\mathrm{n}} + 2\mathrm{n} + \mathrm{cp} = 2^4 + 2 \times 4 + 3 = 27 \qquad (4)$$

where n is the factor number and cp is the replicate number of the central point.

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{j-1} \sum_{j=2}^{n} \beta_{ij} X_i X_j + \sum_{i=1}^{n} \beta_{ii} X_i^2 \qquad (5)$$

where Y is the predicted response (PNP uptake , q_e), β_0 is a constant, β_i is the linear coefficient, β_{ij} is the interaction coefficients, β_{ii} is the quadratic coefficients.

Table 2

Independent variables and their coded levels for the BBD

Factor	Code	Units	Coded variable levels		
			-1	0	+1
C_{HNO3}	x_1	mol/L	3	3.73	4.46
T_m	x_2	℃	72.6	80.2	87.8
t_m	x_3	h	18.1	20.5	22.8
T_C	x_5	℃	692	763	834

2.4 Characteristics

A field emission scanning electron microscopy (FESEM) instrument (SU8020, Japan) was employed to estimate the surface morphology of the raw material and MFBC at an accumulation voltage of 5KV with 20K and 100K magnification. A high-resolution transmission electron microscope (HRTEM) unit (JEM-2100F, Japan) was employed to intuitively depict the microstructure and morphology of the raw material and MFBC. A specific surface area and porosity analyzer (Coulter SA3100, America) was employed to determine the surface area, pore volume and pore size distribution of the raw material and MFBC. Prior to analysis, the sample was degassed at 200 ℃ in a vacuum condition for a period of at least 2 h. The nitrogen adsorption isotherm was measured over a relative pressure (P/P_0) range from approximately 10^{-7} to 1. The BET surface area was calculated from the isotherms by using the Brunauer-Emmett-Teller (BET) equation. The total pore volume was calculated from nitrogen adsorption data as the volume of liquid nitrogen at a relative pressure of approximately 0.99 to 1.[22]

3. Results and discussion

3.1 2_{IV}^{6-2} Fractional factorial design

According to the preliminary single-factor investigation results of nitric acid concentration (C_{HNO3}, mg/L), modification temperature (T_m, ℃), modification time (t_m, h), impregnation ratio of HNO_3 to FBC (IR, ml/mg), calcination temperature (T_C, ℃) and calcination time (t_c, h), the independent variables and their coded levels were shown in Table 1. The 16 experimental runs and results of the 2_{IV}^{6-2} Fractional factorial design were shown in Table 3.

According to the data listed in table 3, the statistical software Design-Expert version 8.0.6 was used to get the significance of each factor analysis and regression model analysis of variance. Results were shown in table 4.

Table 3

2_{IV}^{6-2} Fractional factorial design matrix and results

Run	Modification variables						PNP uptake
	C_{HNO3} (mol/L)	T_m (℃)	t_m (h)	IR (ml/g)	T_C (℃)	t_c (h)	q_e (mg/g)
1	3(+1)	90(+1)	3(-1)	5(-1)	400(-1)	4(+1)	15.3
2	3(+1)	25(-1)	24(+1)	5(-1)	400(-1)	4(+1)	13.5
3	0.1(-1)	25(-1)	24(+1)	5(-1)	700(+1)	4(+1)	14
4	0.1(-1)	25(-1)	24(+1)	20(+1)	700(+1)	0.5(-1)	15.4
5	3(+1)	25(-1)	3(-1)	20(+1)	700(+1)	4(+1)	33.2
6	3(+1)	90(+1)	24(+1)	5(-1)	700(+1)	0.5(-1)	63.2
7	3(+1)	25(-1)	24(+1)	20(+1)	400(-1)	0.5(-1)	15.1
8	3(+1)	90(+1)	24(+1)	20(+1)	700(+1)	4(+1)	70.9
9	3(+1)	90(+1)	3(-1)	20(+1)	400(-1)	0.5(-1)	17.2
10	3(+1)	25(-1)	3(-1)	5(-1)	700(+1)	0.5(-1)	30.2
11	0.1(-1)	90(+1)	24(+1)	5(-1)	400(-1)	0.5(-1)	11.3
12	0.1(-1)	90(+1)	3(-1)	5(-1)	700(+1)	4(+1)	14.1
13	0.1(-1)	25(-1)	3(-1)	5(-1)	400(-1)	0.5(-1)	10.7
14	0.1(-1)	90(+1)	3(-1)	20(+1)	700(+1)	0.5(-1)	13.3
15	0.1(-1)	25(-1)	3(-1)	20(+1)	400(-1)	4(+1)	10.7
16	0.1(-1)	90(+1)	24(+1)	20(+1)	400(-1)	4(+1)	11.2

Table 4

ANOVA for response of dependent variable q_e for 2^{6-2}_{IV} Fractional factorial design

Source	Sum of Squares	Degree of freedom	Mean Square	F Value	p-value[a] Prob> F
Model	5194.30	13	399.56	218.27	0.0046
X_1	1558.28	1	1558.28	851.23	0.0012
X_2	339.4806	1	339.4806	185.4452	0.0053
X_3	305.3756	1	305.3756	166.815	0.0059
X_4	13.50563	1	13.50563	7.377603	0.1130
X_5	1393.156	1	1393.156	761.0273	0.0013
X_6	2.640625	1	2.640625	1.442472	0.3527
X_1X_2	356.2656	1	356.2656	194.6142	0.0051
X_1X_3	253.6056	1	253.6056	138.535	0.0071
X_1X_4	11.73063	1	11.73063	6.407989	0.1270
X_1X_5	953.2656	1	953.2656	520.7323	0.0019
X_1X_6	3.900625	1	3.900625	2.130761	0.2818
X_2X_4	0.455625	1	0.455625	0.24889	0.6673
X_2X_6	2.640625	1	2.640625	1.442472	0.3527
Residual	3.66	2	1.83		
Cor Total	5197.96	15			

R-square = 0.9947.

[a] Significant at the 5% level.

As can be seen from the table 4, the fitting regression of the model was significant ($P < 0.05$). The determination coefficient of the model R^2 was 0.9947, which means that the regression model and the actual values were fit well. According to the P-value of each independent variable, nitric acid concentration x_1, modification temperature x_2, modification time x_3 and calcination temperature x_5 were most significant factors for the response value ($P < 0.05$). The remaining main factors, impregnation ratio of HNO_3 to MBC x_4 and calcination time x_6 were not significant

(P > 0.05). On this basis, nitric acid concentration, modification temperature, modification time and calcination temperature were picked out to conduct further investigation in the next step. The simplified model fitting equation after removal of insignificant factors was obtained as follows:

$$Y = 22.456 + 9.869X_1 + 4.606X_2 + 4.369X_3 + 9.331X_5 + 4.719X_1X_2 + 3.981X_1X_3 + 7.719X_1X_5 \quad (6)$$

3.2 The steepest ascending method

According to the regression equation (6) of 2_{IV}^{6-2} Fractional factorial design model, the fastest rising route direction was obtained as follows:

$$\nabla f = \left(\frac{\partial f}{\partial X_1}, \frac{\partial f}{\partial X_2}, \frac{\partial f}{\partial X_3}, \frac{\partial f}{\partial X_5}\right) = (9.869 + 4.719X_2 + 3.981X_3 + 7.719X_5, 4.606 + 4.719X_1, 4.369 + 3.981X_3, 9.331 + 7.719X_5) \quad (7)$$

Set the center (0, 0, 0, 0) of 2_{IV}^{6-2} Fractional factorial design as a starting point, and it can gotten that the $\nabla f = (9.869, 4.606, 4.369, 9.331)$. X_1 was chosen as the standard because its coefficient was bigger. One basal increment (Δ) of C_{HNO3} (x_1) was defined as 0.73 mol/L. The X_2, X_3, X_5 also increased as the following proportion:

$$\frac{\Delta X_1}{9.869} = \frac{\Delta X_2}{4.606} = \frac{\Delta X_3}{4.369} = \frac{\Delta X_5}{9.331} \quad (8)$$

Design of the steepest ascent path experiment and corresponding results were listed in Table 5. It can be seen from Table 5 that the response value exhibited an increasing tendency from the center to the step 3, but all steps beyond this point resulted in a decrease. Therefore, the optimal region of the response value q_e was near at this point. And the next BBD should select this point as the central level(x_1=3.73, x_2=80.2, x_3=20.5, x_4=763).

Table 5

Results of the steepest ascent path experiments

Steps	Coded variables				Natural variables				Response
	X_1	X_2	X_3	X_5	x_1	x_2	x_3	x_5	q_e(mg/g)
Δ	0.5	0.233	0.221	0.473	0.73	7.6	2.3	71	
Center	0	0	0	0	1.55	57.5	13.5	550	24.2
Center+ Δ	0.5	0.233	0.221	0.473	2.28	65.1	15.8	621	40.4
Center+2Δ	1	0.466	0.442	0.946	3	72.6	18.1	692	57.6
Center+3Δ	1.5	0.699	0.663	1.419	3.73	80.2	20.5	763	70.2
Center+4Δ	2	0.922	0.884	1.892	4.46	87.8	22.8	834	69.3
Center+5Δ	2.5	1.155	1.105	2.365	5.19	95.4	25.1	905	60.4

In this experiment, the response value q_e was remarkably improved, implying that the steepest ascending method was an efficient and effective technique to approximate the optimal conditions.[19]

3.3 The Box-Behnken design

3.3.1 Development of regression model equation and statistical analysis

Based on the results of 2_{IV}^{6-2} Fractional factorial design, nitric acid concentration (X_1), modification temperature (X_2), modification time (X_3) and calcination temperature (X_5) were chosen to be optimized by Box–Behnken design (BBD) in order to obtain the maximum PNP uptake. The high and low levels of the Box-Behnken experiment were determined by the results of the steepest ascent path experiment, which were shown in Table 2. The BBD matrixes together with both the response values obtained from the experimental work were shown in Table 6. Run 10, 16, 27 have been performed with the tested variable parameters at the middle level (center point runs). The response values q_e were found to range from 45.4 to 78.8

mg/L. The quadratic model equation for predicting the optimum point was achieved through the BBD and input variables, and then empirical relationship between the response (*Y*) and the independent variables in the coded levels (X_1, X_2, $X_3$and X_5) was indicated on the basis of the experimental results for PNP uptake as follows:

$$Y = 71.80 + 5.13X_1 + 9.17X_2 - 0.57X_3 - 7.38X_5 + 0.55X_1^2 - 2.53X_2^2 - 4.31X_3^2 - 6.14X_5^2 - 3.67X_1X_2 - 1.35X_1X_3 + 0.55X_1X_5 + 2.30X_2X_3 + 3.40X_2X_5 + 3.20X_3X_5 \quad (9)$$

Coefficients with one factor represent the effect of the particular factor, while coefficients with two factors and those with second-order terms represent the interaction between two factors and quadratic effect, respectively. The positive sign in front of the terms indicates a synergistic effect, whereas a negative sign indicates an antagonistic effect.[6]

The adequacy of the models was further justified by the analysis of variance (ANOVA). The results of the ANOVA for the quadratic model were listed in Table 7. The model *F*-value of 14.44 and low p-value < 0.0001 indicate that the model was significant.[23] The small F-values of 9.70 and high P-values of 0.0970 obtained for the lack-of-fit for q_e were found to be non-significant which further verifies that the quadratic model is statistically valid.

Table 6

Box-Behnken Design matrix and results

Run	Modification variables				PNP uptake
	C_{HNO3}(mol/L)	T_m (℃)	t_m(h)	T_C (℃)	q_e(mg/g)
1	4.46(+1)	72.6(-1)	20.45(0)	763(0)	69.6
2	3.73(0)	72.6(-1)	20.45(0)	692(-1)	68.6
3	3(-1)	80.2(0)	22.8(+1)	763(0)	66.5
4	3.73(0)	87.8(+1)	22.8(+1)	763(0)	76.9
5	3.73(0)	72.6(-1)	22.8(+1)	763(0)	47.7
6	3.73(0)	87.8(+1)	20.45(0)	692(-1)	77.6
7	3.73(0)	80.2(0)	22.8(+1)	834(+1)	57.4
8	4.46(+1)	80.2(0)	20.45(0)	692(-1)	78.8
9	3.73(0)	72.6(-1)	20.45(0)	834(+1)	45.4
10	3.73(0)	80.2(0)	20.45(0)	763(0)	72
11	3.73(0)	72.6(-1)	18.1(-1)	763(0)	56.2
12	3.73(0)	87.8(+1)	20.45(0)	834(+1)	68
13	4.46(+1)	87.8(+1)	20.45(0)	763(0)	76.9
14	3.73(0)	80.2(0)	18.1(-1)	692(-1)	69.6
15	3.73(0)	80.2(0)	22.8(+1)	692(-1)	61.7
16	3.73(0)	80.2(0)	20.45(0)	763(0)	72.9
17	3(-1)	80.2(0)	20.45(0)	834(+1)	51.1
18	4.46(+1)	80.2(0)	18.1(-1)	763(0)	75.8
19	3(-1)	87.8(+1)	20.45(0)	763(0)	75.3
20	3(-1)	72.6(-1)	20.45(0)	763(0)	53.3
21	3.73(0)	80.2(0)	18.1(-1)	834(+1)	52.5
22	3(-1)	80.2(0)	20.45(0)	692(-1)	69.4
23	4.46(+1)	80.2(0)	20.45(0)	834(+1)	62.7
24	3(-1)	80.2(0)	18.1(-1)	763(0)	61.8
25	4.46(+1)	80.2(0)	22.8(+1)	763(0)	75.1
26	3.73(0)	87.8(+1)	18.1(-1)	763(0)	76.2
27	3.73(0)	80.2(0)	20.45(0)	763(0)	70.5

Table 7

ANOVA for response of dependent variable q_e for BBD

Source	Sum of Squares	Degree of freedom	Mean Square	F Value	p-value[a] Prob> F
Model	2451.97	14	175.14	14.44	< 0.0001
X_1	315.19	1	315.19	25.99	0.0003
X_2	1010.17	1	1010.17	83.30	< 0.0001
X_3	3.85	1	3.85	0.32	0.5833
X_5	654.16	1	654.16	53.95	< 0.0001
X_1X_2	54.02	1	54.02	4.45	0.0565
X_1X_3	7.29	1	7.29	0.60	0.4531
X_1X_4	1.21	1	1.21	0.100	0.7575
X_2X_3	21.16	1	21.16	1.74	0.2111
X_2X_4	46.24	1	46.24	3.81	0.0746
X_3X_4	40.96	1	40.96	3.38	0.0910
X_1^2	1.61	1	1.61	0.13	0.7216
X_2^2	34.00	1	34.00	2.80	0.1199
X_3^2	99.19	1	99.19	8.18	0.0144
X_4^2	200.90	1	200.90	16.57	0.0016
Residual	145.52	12	12.13		
Lack of Fit	142.58	10	14.26	9.70	0.0970
Pure Error	2.94	2	1.47		
Cor Total	2597.49	26			

R-square = 0.9440, Adj R-Squared=0.8786, Pred R-Squared=0.6813.

[a] Significant at the 5% level.

The quality of the model developed was evaluated based on the correlation coefficients, R^2 value. In fact, the developed model seems to be the best at low standard deviation and high R^2 statistics (closer to 1) as it will give the predicted value closer to the actual value for the responses.[24] Fig. 1 showed the correlation of experimental and predicted values of PNP uptake (q_e). Good agreement between the actual and predicted values of PNP uptake was confirmed by high values of coefficient of determination R^2 (0.9440) and the adjusted R^2 (0.8786). Value of adjusted R^2 suggested that the total variation of 87.86% q_e was attributed to the independent variables and only about 12.14% of the total variation cannot be explained by the model. On the basis of mentioned findings, it can be concluded that the model can be applied for further analysis of effect of process variables. [23]

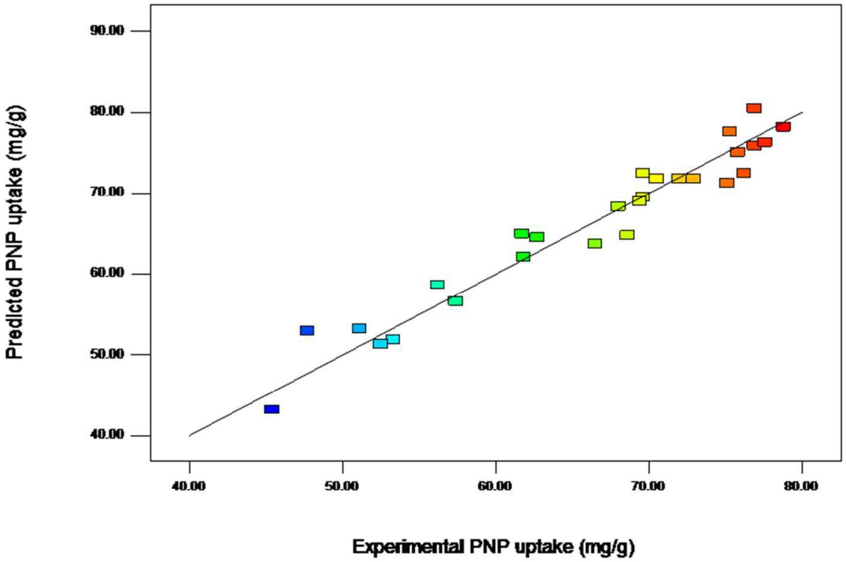
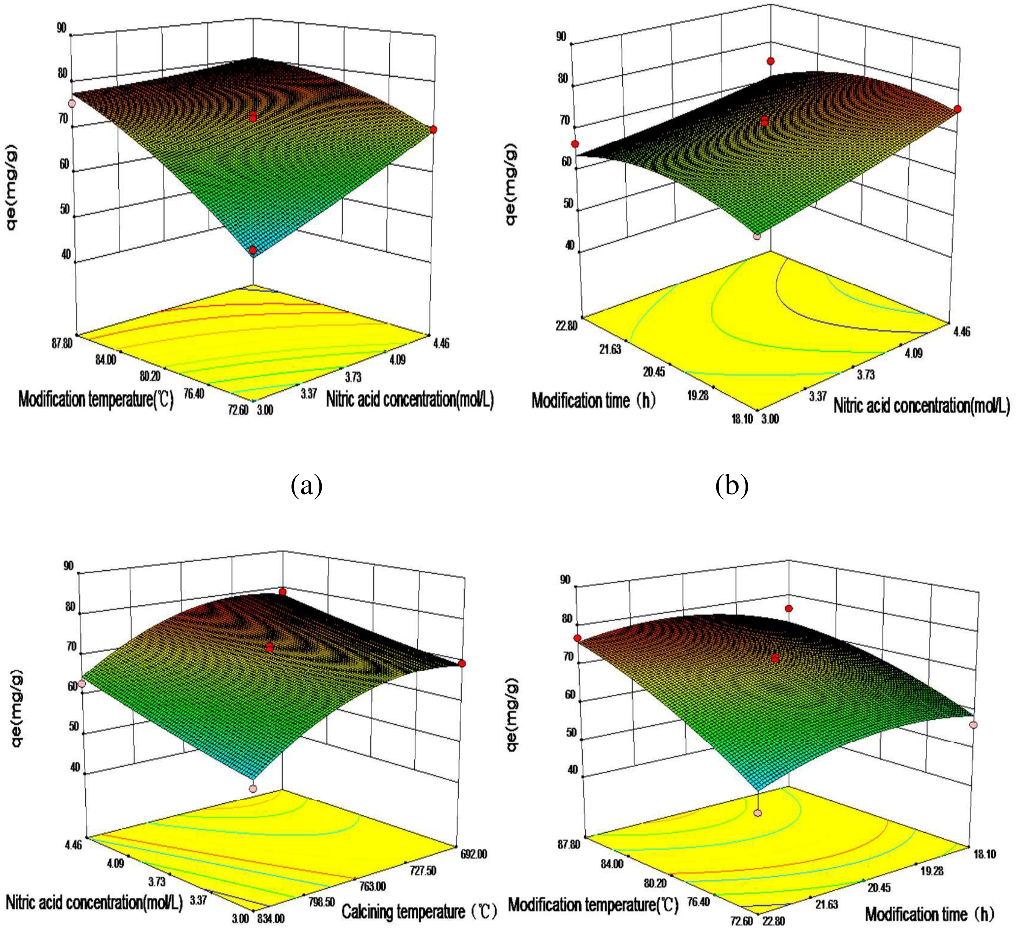


Fig. 1. The correlation of experimental and predicted values of PNP uptake (q_e) in Box-Behnken Design.

3.3.2 Effects of process variables

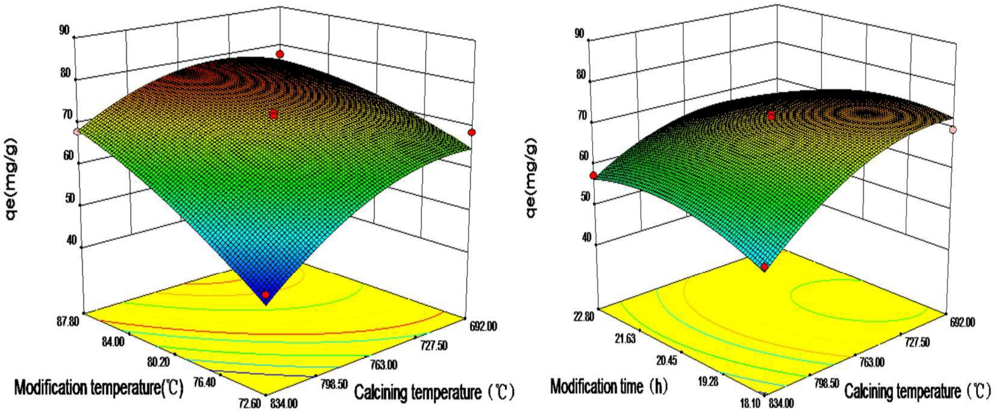
Based on the P-value of each variable as shown in Table 7, the nitric acid concentration, modification temperature and calcination temperature were found to have significant effects ($P<0.001$) on the PNP uptake for the modification of fine blue-coke, whereas modification time showed the least significant effect ($P>0.05$).

Among all the factors being considered, modification temperature and calcination temperature were found to impose the greater effect on the PNP uptake, as they showed the higher F-value compared to nitric acid concentration and modification time. Besides, the quadratic effect of modification time on PNP uptake was significant as well, indicating that all these four factors had certain effects on the PNP uptake. Fig. 2 showed the three-dimensional response surfaces which were constructed to show the interaction effects of these factors on the PNP uptake.



(a) (b)

(c) (d)



(e) (f)

Fig.2. Three-dimensional response surface plot of PNP uptake; effect of modification temperature and nitric acid concentration (a), effect of modification time and nitric acid concentration (b), effect of nitric acid concentration and calcination temperature (c), effect of modification temperature and modification time (d), effect of modification temperature and calcination temperature (e), effect of calcination temperature and modification time (f).

The effect of nitric acid concentration on PNP uptake of MBFC was shown in Fig. 2 (a-c). When modification temperature, modification time and calcination temperature were fixed at the zero level, the PNP uptake generally increased with nitric acid concentration increasing from 3 mol/L to 4.46 mol/L. The results were in agreement with the Qiu et al.’s[25] works which reported that the adsorption amount of the MCs toward BT and DBT increased obviously by increasing of the concentration of nitric acid from 35% to 85%. Nitric acid is a typical modifier used for the surface modification of coal-based adsorbents. Shim et al.[26] found that the nitric acid oxidation treatment gives rise to a large increase in the amount of carbon surface oxide groups such as carboxyl, lactone and anhydride. Most of these acidic groups would be decomposed into basic groups such as hydroxyl, carbonyl, and quinone during the calcination step.[27] Haydar et al.[28] suggested that an adsorption mechanism of carbon toward PNP was involving an interaction between some basic groups located in graphene layers and the aromatic ring of PNP. Based on these literatures, the increase of PNP uptake with nitric acid concentration in our work might be due to the increase of oxygen-containing groups after the oxidative modification, which could be beneficial to the PNP uptake.

As shown in Figs 2 (a) (d) (e), when nitric acid concentration, modification time and calcination temperature were fixed at the zero level, the PNP uptake increased with increasing of modification temperature from 72.6 ℃ to 87.8 ℃. As the modification temperature increased to about 80 ℃, a deal of bubbles appeared in the experiment. This phenomenon might be ascribed to the fact that with increasing modification temperature, the reaction between nitric acid and ash impurities such as calcium carbonate in the pores of FBC was accelerated. The impurities inside the pores of FBC were effectively removed, which was beneficial to the PNP uptake of MFBC. Additionally, the increment in temperature might be conducive to the formation of oxygen-containing groups on MFBC surface, which contribute to a significant increase in the PNP uptake of MFBC after further calcination step. Qiu et al.[25] found that the densities of the oxygen-containing groups on the MCs and the adsorption desulfurization rate increased when the nitric acid oxidation temperature increased from 60 ℃ to 80 ℃.

The effect of modification time on PNP uptake of MBFC was shown in Figs. 2 (b) (d) (f). As shown in Figs 2 (b) (d) (f), when nitric acid concentration, modification temperature and calcination temperature were fixed at the zero level, the PNP uptake firstly increased with modification time increasing from 18.1 h to 20 h, and then an invariant tendency appeared after 20 h. The modification time was analyzed to be a significant factor in 2_{IV}^{6-2} Fractional factorial experiment, however, this variable became an insignificant factor in BBD experiment. This was because in the 2_{IV}^{6-2} Fractional factorial experiment, the large span of modification time ranged from 3h to 24h, which had a greater influence on PNP uptake. On the other hand, in the BBD experiment, the modification time changed from 18.1 h to 22.8 h and the variation range was relatively narrow, resulting in a slighter effect on PNP uptake compared to other factors. The modification time was thus determined as an insignificant factor in the BBD experiment. However, considering its significant quadratic term examination, it cannot be ignored in equation fitting. The effect of modification time on PNP uptake was also attributed to the increase in the densities of oxygen-containing groups on MFBC with the increase of modification time.[25]

As can be seen from Figs 2 (c) (e) (f), when nitric acid concentration, modification temperature and modification time were fixed at the zero level, the PNP uptake firstly increased with calcination temperature increasing from 692 ℃ to 720 ℃, and then exhibited an obviously decreasing tendency above 720 ℃. Aber et al.’ s[29] work also reported that the adsorption ability of the ACF samples increases when activation temperature increases until 700 ℃ and then decreases after further increase in activation temperature. This was perhaps due to the opening of pores of MFBC and the increasing of number of micropores with calcination temperature increasing, but the micropores widen to become mesopores when the temperature continued to increase as Sudaryanto et al.[30] reported, which might lead to decrease of the PNP uptake when calcination temperature was above 720 □ in this work. On the other hand, Liu et al.[26] found that calcination process resulted in the destruction of most of the acidic groups to form basic groups, which was also beneficial to the PNP uptake. Nian et al.[31] reported that oxygen functional groups on activation carbon surface such as carboxyl, anhydride and lactone groups would be desorbed as CO_2 while hydroxyl, carbonyl and quinone groups would be desorbed as CO during thermal treatment process in an inert environment. The increase in temperature also caused the CO_2 and CO to further gasify the carbon, leading to widening of the pores. However, when the calcination temperature was above 750 ℃, the majority of oxygen functional groups including these basic groups would be desorbed as CO_2 and CO,[31] which leaded to decrease of PNP uptake when the calcination temperature was above 720 ℃ in this work.

3.3.3 Process Optimization

Based on the results of a fractional factorial experiment, the effects of impregnation ratio of HNO_3 to FBC and calcination time were not significant. However, the modification reaction might be unable to proceed normally if the ratio was too small and the nitric acid would be wasted if the ratio was too large, an appropriate impregnation ratio of HNO_3 to FBC was thus set as 10:1. The calcination time was determined as 2 h because too long or too short calcination time could reduce the surface area and the adsorption capacity of MFBC prepared, as longer activation time might destroy the pore structure formed previously whereas shorter calcination time could not enrich the formation of porosity.[5] According to the BBD experiment, together with the quadratic equation fitting of these four variables: nitric acid concentration, modification time, modification temperature and calcination temperature, the expected response value was set as 80 mg/g, the optimal combination of each factor determined by Design-Expert version 8.0.6 (STAT-EASE Inc., Minneapolis, USA) and the experimental verification values were as follows (Table 8).

Table 8

The optimal conditions and the experimental verification value

C_{HNO3} (mol/L)	T_m (℃)	t_m (h)	IR (ml/g)	T_C (℃)	t_c (h)	PNP uptake, q_e (mg/g)	
						Predicted	Experimental
4.46	20.3	87.8	10/1	716	2	80	79.6

The adsorption isotherms of PNP onto MFBC obtained under optimum conditions at different temperatures were depicted. The maximum equilibrium adsorption capacity of p-nitrophenol onto MFBC was 156.9 mg/g at 328 K. The comparison of PNP uptake between MFBC via the above-mentioned optimized process and the materials used in the literatures can be seen in Table 9. The comparative data showed that MFBC has quite high PNP uptake compared to other adsorbent materials, and may be used effectively for the removal of PNP from aqueous streams.

Table 9

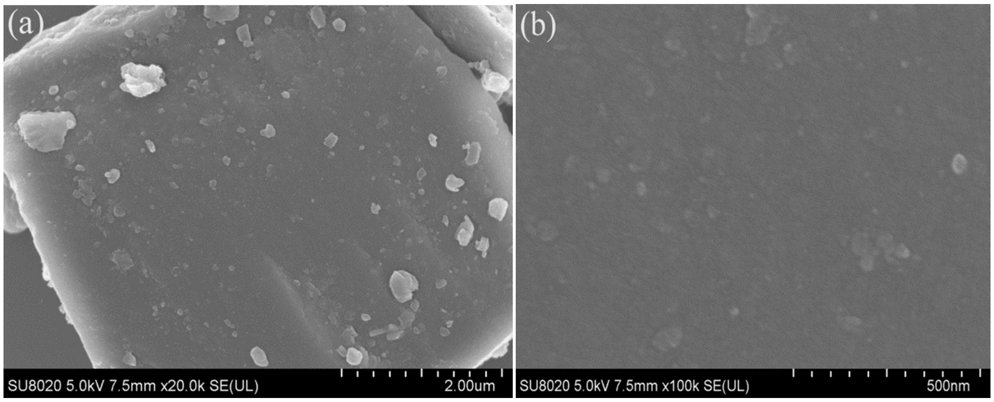
Comparison of PNP uptake of modified fine blue-coke with other materials

Materials	The maximum adsorption capacity on PNP(mg/g)
MFBC(in this work)	156.9
ATW[1]	142.85
Modified pyrophyllite[32]	0.268
Bagasse fly ash[8]	0.77-1.16
Wood fly ash[33]	134.9
Fly ash[34]	7.80-9.61
Micro porous cyclodextrin[35]	167.0
Charred saw dust[36]	147.0
Modified Bentonite[37]	107.27
Modified starch[38]	131.5
Rice husk[39]	15.31
Rice husk char[39]	39.21

Petroleum coke[39]	11.06
Coke breeze[39]	4.64
Silica beads[40]	116
Pyrolyzed residue from animal bones[41]	111.0
Pyrolyzed oil shale[41]	4.895
$ZnCl_2$ pyrolyzed oil shale[41]	6.026
KOH pyrolyzed oil shale[41]	0.895

3.4 Characterization of fine blue-coke modified under optimum conditions

Fig. 3 (a-b) and (c-d) exhibited FESEM images of the precursor (FBC) and the fine blue-coke modified under optimum conditions (MFBC), respectively. As can be seen from Fig. 3 (a-b), there were very few pores available on the surface of the precursor. However, after HNO_3 treatment and high temperature activation under the optimum modification conditions, the surface roughness of fine blue-coke increased obviously and many pores were developed on the surface of MFBC, as clearly shown in Fig. 3 (c-d). The HRTEM images (Fig. 3 (e-f)) further exhibited the more rough surface of MFBC than that of FBC. This showed that HNO_3 and high temperature were effective in creating well-developed pores on the surfaces of the precursor, hence leading to the fine blue-coke with large surface area and porous structure which had high PNP uptake. Similar observations were reported by other researchers in their works of preparing activated carbons from mangosteen peel[6] and coconut husk[7].



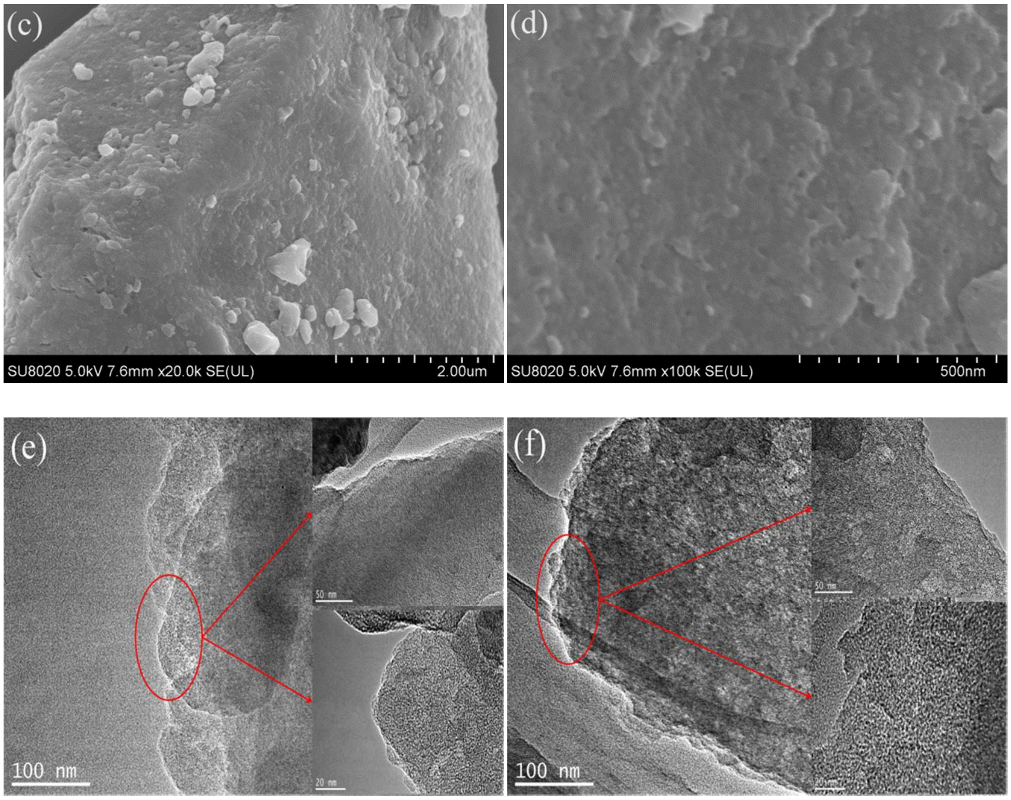


Fig.3. FESEM images of FBC (a-b) and MFBC (c-d); HRTEM images of FBC (e) and MFBC (f).

As presented in Fig. 4(a), the N_2 adsorption-desorption isotherms exhibit characteristics of type IV curves (according to the IUPAC classification) with a sharp capillary condensation step in the relative pressure range of 0.4–0.7 and H4-type hysteresis loop. In detail, a increase is shown at low relative pressure, and the next slow rise of isotherms appear at medium relative pressure, while the isotherms rise at the relative pressure are close to 1.0 points, indicating the co-existence of micropores, mesopores, and macropores in the FBC and MFBC[43]. Furthermore, the total pore volume and specific surface area of fine blue-coke were increased by 0.8 and 1.2 times after modified, respectively. Fig. 4(b) showed the pore size distribution of FBC and MFBC estimated using the BJH method, which revealed the FBC and MFBC almost have the same pore size distribution in the range of 0 ~ 5 nm. And the most of pores were in the micropores and mesopores region according to the IUPAC classification.[42] This demonstrates that the physiochemical activation process has contributed to the high surface area and total pore volume of the fine blue-coke, but could not change the pore diameter distribution of fine blue-coke. This is perhaps due to some new pores were created and some blocked pores were opened under the physiochemical activation process, which make the surface area and total pore volume of MFBC increased obviously. However, the activation temperature of the fine blue-coke is almost the same as the formation temperature of the fine blue-coke at about 700□, and it isn't high to make the pores continue to widen, which result in the pore diameter distribution of modified blue-coke remain almost the same as that of the raw fine blue coke. Similar phenomenon has been reported by Qiu et al. [25] and Chingombe et al. [44]. They also found that the specific surface area of activated carbon increased but the pore diameter distribution had not obviously changed after nitric acid oxidation and the high temperature activation process.

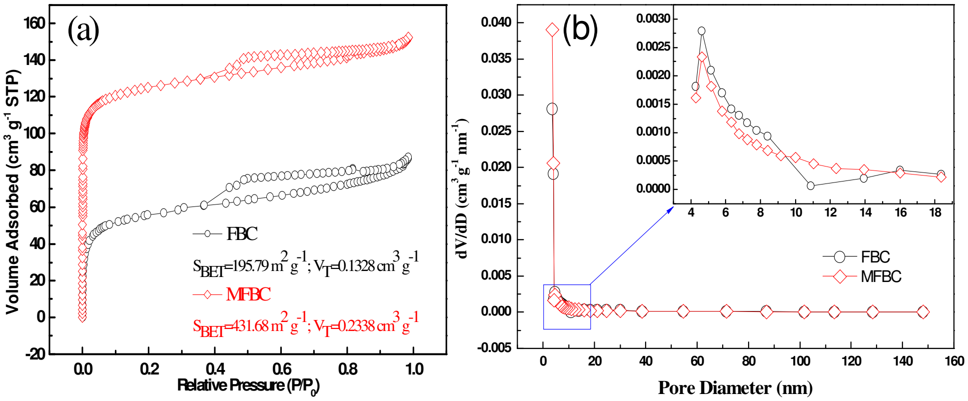


Fig.4. N_2 adsorption-desorption isotherm (a) and pore size distribution curves (b) of samples

4.Conclusion

Based on the application of three types of experimental designs, that was, a fraction factorial design (2_{IV}^{6-2}), a steepest ascent method and a Box-Behnken design, the effects of the modified processes on PNP uptake of the modified fine blue-coke, such as nitric acid concentration, modification temperature, modification time, impregnation ratio of HNO_3 to FBC, calcination temperature and calcination time were systematically investigated. This study clearly demonstrated that impregnation ratio of HNO_3 to FBC and calcination time had no significant effect on the PNP uptake of the modified fine blue-coke. However, the nitric acid concentration, modification time and temperature, calcination temperature exhibited a distinctive effect on the PNP uptake. The first and second order models fitting were well good. No obvious lack-of-fit phenomenon occurred, and the experimental values were close to fitting ones. The optimized process for modification was as follows: nitric acid concentration was 4.46 mol/L, modification temperature was 87.8 ℃, modification time was 20.3 h, impregnation ratio of HNO_3 to FBC was 10 ml/g, calcination time was 2 h and calcination temperature was 716 ℃. As can be seen from FESEM and HRTEM results, the surface roughness of MFBC increased obviously. The total pore volume and specific surface area increased by 0.8 and 1.2 times, respectively. PNP equilibrium adsorption capacity was found to be 156.9 mg/g at 328 K. Compared with previous literatures, the fine blue-coke modified by optimized process in this work had excellent adsorption property on PNP and may have a potential application in waste water treatment.

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