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Orthogonal Experiment was Designed based on Discrete Element Method to Optimize the Parameters of Mercury Ion Adsorption Process in Water

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Abstract

In view of the influence of many factors on the removal of mercury ions in water, the adsorption efficiency of self-developed cobalt ferrite/SBA15 adsorbent was studied. The temperature, PH, adsorption time and the amount of adsorbent were analyzed. The Multi-factor discrete element simulation experiments of variable temperature, pH and adsorption time were carried out by using design-Expert software. The results show that ambient temperature, PH and adsorption time have significant effects on the adsorption efficiency, among which adsorption time has the most obvious effect, and there is also a significant interaction between the factors. The optimized parameters were temperature =36.43℃, PH=4.88, time =70min, and the adsorption efficiency can reached 86.82%.

Keywords

Mercury Ion Adsorption; Orthogonal Test; Parameter Optimization.

1. Introduction

Mercury is an important toxic metal element that can be found in water, suspended matter, aquatic life and underwater sediments [1]. Among them, chlor-alkali industry and battery industry will produce a large number of mercury-containing wastewater. Therefore, appropriate and economic methods to remove mercury ions from water bodies are the focus of research. The adsorption method is favored because of its fast rate, large processing capacity and no secondary pollution. However, in the process of adsorption, there are many factors affecting the removal efficiency and removal rate. Obviously, the traditional single factor experiment has been unable to meet the requirements, the number of orthogonal experiments, can be based on a large number of experiments to get the optimal solution. Response surface method (RSM) has the advantages of fewer experiments, high efficiency in establishing suitable model fitting and evaluating the relationship between factors. In this study, the effects of temperature, pH and time on the adsorption efficiency of mercury ion adsorbents in the process of removing bivalent mercury from water were studied by response surface methodology. The optimal solution was found by model fitting with design-Expert software, and the interaction among influencing factors was analyzed.

2. Experiments

2.1. Methods

With potassium dichromate acidified by nitrate as the fixed solution, mercury solution concentration of 100mL was prepared by dissolving mercury chloride, PH of the solution was adjusted to an appropriate value, a certain amount of mercury ion adsorbent (cobalt ferrite /SBA15-SH adsorbent) was weighed, and the adsorption was carried out by shock under a given adsorption temperature. After a certain experimental time was reached, 0.1 mL of the

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adsorption solution was diluted 1000 times and the fluorescence value of the solution was measured. After the reaction, the fluorescence value of the solution was compared with that of the original solution diluted 1000 times to calculate the adsorption efficiency. The adsorption efficiency was calculated by the equation.

$$\eta = (1 - C_{ab}/C_{ori}) \times 100\%$$

where, η is the removal efficiency of mecurcy, %; C_{ab} and C_{ori} are the concentration of mecury ion at the absorbed and original solution respectively, mg/m^3.

2.2. One-factor Control Experiment Scheme

In the experiment of cobalt ferrite /SBA15-SH adsorption of mercury, the effects of PH, temperature and the amount of adsorbent on the adsorption effect were studied by keeping other conditions unchanged. One-factor control experimental scheme is shown in Table.1.

Table 1. One-factor control experimental scheme

factors	factor levels	reaction condition
PH	0.86, 3, 5, 7	The initial adsorption concentration was 7mg/L; the temperature was 35℃; and the amount of adsorbent was 0.200g
temperature(℃)	22, 25, 35, 45	The initial adsorption concentration was 7mg/L; the PH was 5; and the amount of adsorbent was 0.200g
time(min)	20, 40, 60, 90	The initial adsorption concentration was 7mg/L; the PH was 5; he temperature was 35℃; and the amount of adsorbent was 0.200g
Amount (g/L)	0.033, 0.05, 0.1, 0.165, 0.2, 0.33	The initial adsorption concentration was 7mg/L; the PH was 5; he temperature was 35℃;

2.3. Optimization of Influencing Factors of Mercury Adsorption based on RSM

Based on the initial optimization of the parameters of PH, temperature and adsorption time in the single factor experiment, in order to better find the optimal value of the adsorption effect, the software design-Expert 8.0 was used to Design the Multi-factor orthogonal experiment according to the surrounding range values obtained from the single factor optimization results, and the PH, temperature and adsorption time were taken as three independent variables. A, B, C, each variable was set at the low, medium, and high levels, and encoded with -1, 0, and 1 respectively. The adsorption efficiency was taken as the response value for the study. The adsorption conditions were as follows: mercury concentration to be adsorbed 20mg/L, adsorbent dosage 0.2g/L. See Table .2 . for specific design.

Table 2. Factors and level of orthogonal experiment

codes	factors	code levels		
		-1	0	1
A	PH	4	5	6
B	temperature	30	35	40
C	adsorption time	50	60	70

3. Results and Discussion

3.1. Analysis of One-factor Control Experiment Results

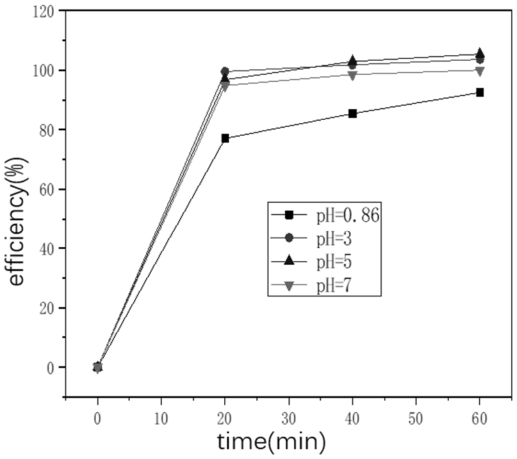

Fig 1. The effects of PH

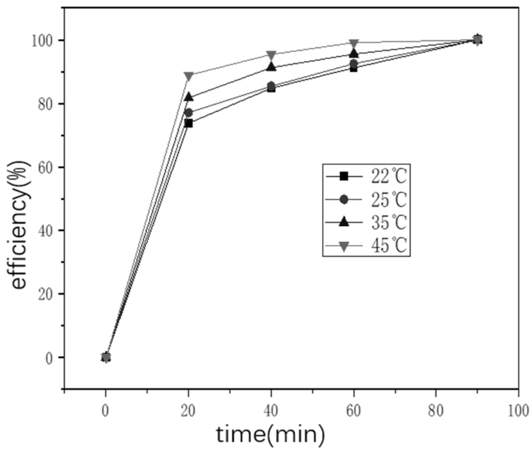

Fig 2. The effects of temperature

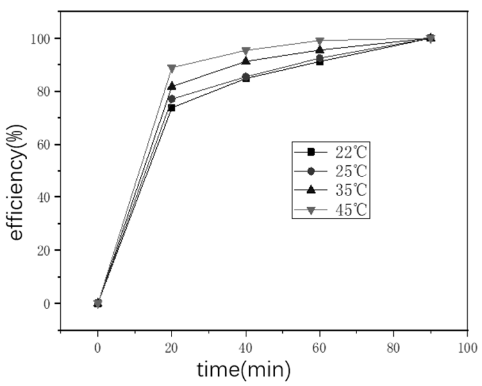

Fig 3. The effects of time

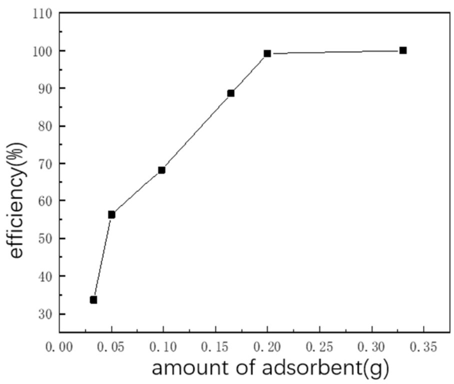

Fig 4. The effects of amounts

It can be seen from Fig.1. that when the adsorption PH is 0.86 of the original fixed solution, the adsorption performance is poor. When the PH of the solution is adjusted to 3, 5 and 7, the adsorption performance is improved. The adsorption effect is the best when PH=5. When the PH is low, the concentration of H+ in the solution is high, and the mercury ion will compete with H+. When the PH is increased, the competition effect of H+ decreases, and the adsorption efficiency of mercury ion is improved. However, when PH continues to rise, mercury ions will exist in the form of hydroxide, resulting in a decrease in adsorption efficiency.

Fig.2. shows that temperature has a significant effect on the adsorption effect, but when the adsorption time is 90min, the adsorption effect is almost the same, proving that the adsorption effect of this adsorbent on mercury ion is mainly chemical adsorption. The adsorption process is that mercury ions in water complexed with sulfhydryl groups on the surface of adsorbent through chelating coordination. The adsorption rate increases with the increase of temperature, but after the equilibrium time, the adsorption capacity is saturated and the adsorption efficiency is the same.

In Fig.3., the adsorption efficiency keeps improving as time goes by. In the first 20min, the adsorption efficiency quickly reaches 80%, and in 40min, it reaches 85%. Then, the adsorption gradually slows down and basically reaches equilibrium after 1h. The rapid adsorption rate is caused by the grafting of -SH and the strong affinity between its sulfhydryl group and mercury ion. Therefore, 1h was chosen as the best reaction time.

The influence of the amount of adsorbent on the adsorption efficiency can be seen from Fig.4. When the concentration of mercury remains unchanged, the adsorption efficiency increases with the increase of the amount of adsorbent. When the amount of adsorbent reaches 0.2g/L, the adsorption efficiency almost reaches a balance. Therefore, in the Multi-factor orthogonal experiment, 0.2g/L was selected as the adsorption amount.

3.2. Analysis of Multi-factor Orthogonal Experiment Results

BBD response surface in the software of Design-Expert 8.0 was used for the experiment. There were 17 test points in this Design experiment, which were divided into two categories: one was the factorial point, and the independent variable was the three-dimensional vertex formed by three factors, with a total of 12 factorial points; The other is zero, which is the central point of the region, that is, the optimal reaction condition point determined in the single factor. The zero point is repeated for five times. The adsorption efficiency was taken as the response value. Experimental design scheme and results are shown in Table 3.

Table 3. Orthogonal experiment and results

number	levels and results			
	PH	temperature	time	efficiency
1	0	0	0	82.69
2	0	1	-1	71.13
3	-1	-1	0	72.07
4	0	1	1	87.08
5	1	0	-1	61.28
6	0	0	0	81.45
7	0	0	0	82.07
8	-1	0	1	82.02
9	0	-1	1	78.69
10	-1	0	-1	74.88
11	-1	1	0	76.68
12	0	-1	-1	59.61
13	0	0	0	82.07
14	1	0	1	77.46
15	1	-1	0	67.53
16	1	1	0	71.68
17	0	0	0	82.07

3.3. Establish Model Equation and Regression Analysis

Design-expert 8.0 software was used to analyze the values in the table, and quadratic regression model was used to fit, and the quadratic multiple regression equation between the adsorption efficiency (Y) was obtained with PH(A), temperature (B) and adsorption time (C) as independent variables.

$$Y=-4.17+0.35A+0.156B+0.0376C-0.00023AB+0.0026AC-0.0001565BC$$
$$-0.051487A^2-0.00197B^2-0.00030C^2$$

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Table 4. Model analysis of quadratic polynomial

sources of variance	sum of squares	degrees of freedom	the mean square	value of F	value of P
A	95.91	1	95.91	15.71	0.0054
B	102.75	1	102.75	16.83	0.0046
C	425.59	1	425.59	69.71	< 0.0001
AB	0.05	1	0.05	0.01	0.9284
AC	20.43	1	20.43	3.35	0.1101
BC	2.45	1	2.45	0.40	0.5466
A^2	111.62	1	111.62	18.28	0.0037
B^2	102.39	1	102.39	16.77	0.0046
C^2	38.18	1	38.18	6.25	0.0410
residual	42.74	7	6.11		
lack of fit	41.97	3	13.99	72.79	0.0006
pure error	0.77	4	0.19		
summation	969.82	16			
standard deviation	2.47		R2	0.9559	
average		75.91	R2 adjusted value	0.8993	
variable coefficient, %	3.26		R2 predicted value	0.3064	
press		672.70	adequate prediction		12.31

The results of variance analysis of the regression model are shown in Table.4.. The value of 0.0006 (p valued <0.01 means statistically significant; P valued < 0.05 means statistically significant), indicates that the regression fitting model was highly significant. According to the P value of PH, temperature and adsorption time, it can be judged that the three experimental factors have significant effects on the adsorption efficiency, among which the effect of adsorption time is extremely significant, and the effect of experimental factors on the adsorption efficiency is in the order of adsorption time, temperature and PH from large to small. The coefficient of determination (R2) of the model fitting was 0.9559, indicating that the adsorption efficiency had a good correlation and credibility with the predicted value of the model fitting.

3.4. Diagnosis of Regression Models

The diagnosis of the regression model is shown in Fig.5. .Fig.5.(a) shows that each handicap is normally distributed on a straight line. The predicted value and residual distribution in Fig.5.(b) indicate that the residual is scattered and irregular, indicating that the fitting degree of the regression equation and the experimental data is high. In Fig.5.(c), the residual distribution under each experimental condition is represented as a scattered random distribution, indicating that the assumptions established according to the experimental conditions are independent. Fig.5.(d) shows that there is a good linear correlation between the experimental value and the predicted value under each experimental condition. It shows that the regression model is correct.

The above analysis proves that the regression model established under the selected experimental conditions is effective and can be used to optimize the independent variables.

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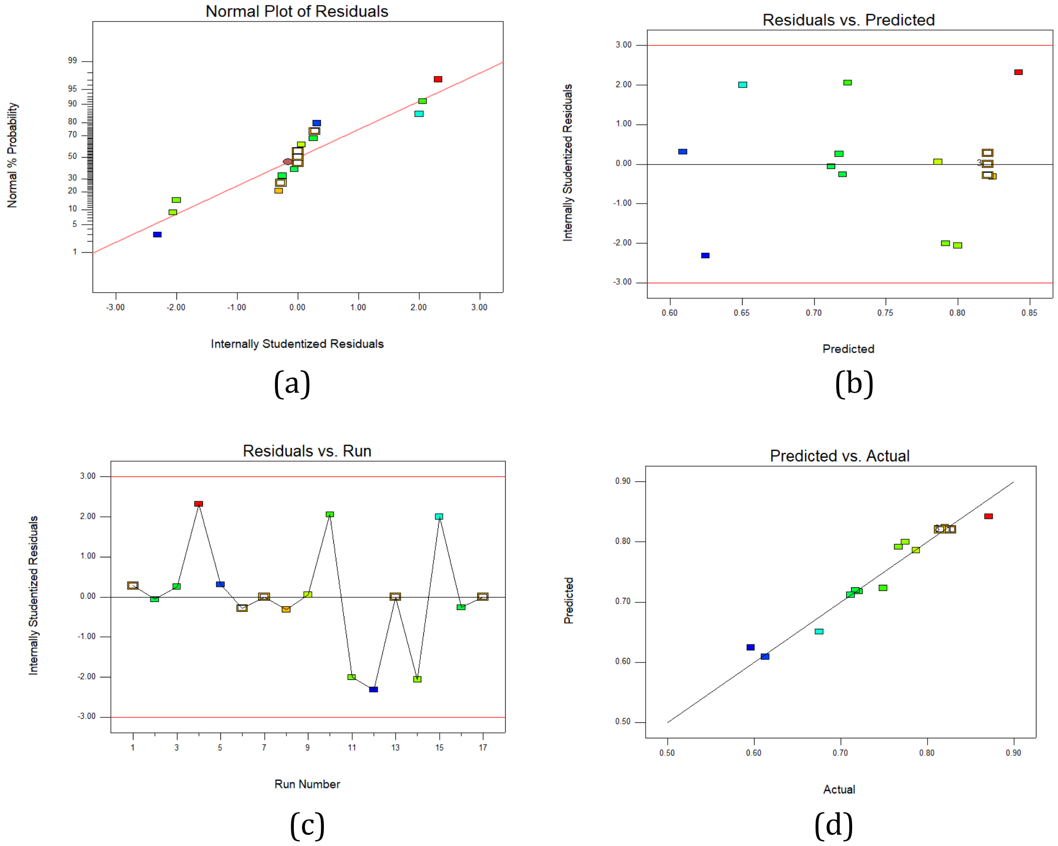


Fig 5. (a)Normal distribution of residual; (b)Residual of predicted value; (c)The residual under the number of runs; (d)Predicted value and Actual Value.

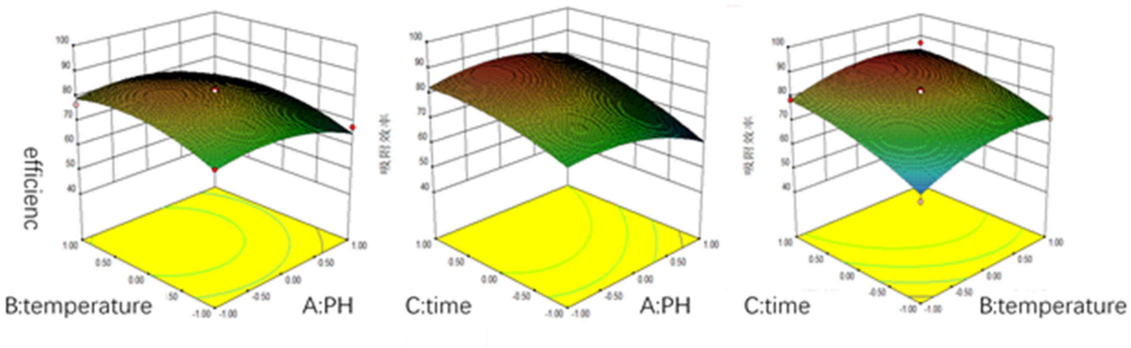
3.5. Response Surface Analysis

For the regression model of the adsorption efficiency, the 3D response surface of the interaction between independent variables on the adsorption efficiency was drawn by using design-Expert 8.0 software, as shown in Figure 8. It can be seen that the change of the adsorption efficiency is not monotonous in the range of PH 4-6, temperature 30-40℃ and adsorption time 50-70min. However, it basically showed a trend of first increasing and then decreasing, which was consistent with the results of single factor experiments.

The response surface of temperature and PH is shown in Fig.6.(a). When the temperature is between 30-40℃, the adsorption efficiency first increases and then decreases with the increase of PH. At low temperature and low PH and high temperature and high PH, the curve is steeper, and the influence of PH is greater. The response surface of PH and adsorption time is shown in Fig.6.(b). When the PH is between 4-6, the adsorption efficiency increases rapidly with the adsorption time and then slowly decreases. The response surface of temperature and adsorption time is shown in Fig.6.(c). When the temperature is between 30-40℃, the adsorption efficiency increases first and then decreases with the increase of temperature.

3.6. Parameter Optimization Analysis

The Optimization function in design-Expert 8.0 was used to optimize the adsorption efficiency under the condition that the maximum adsorption efficiency was obtained by solving the regression model, and the optimal parameters were PH=4.88, temperature =36.43℃, and adsorption time was 70min. At this time, the adsorption efficiency could reach the maximum 86.82%. The optimum reaction conditions determined by this method are in good agreement with those determined by the previous single factor experiment.



(a) (b) (c)

Fig 6. (a)Response surface of the interaction: temperature and PH; (b)adsorption time and PH; (C)adsorption time and temperature

4. Conclusion

The response surface was used to optimize the adsorption conditions of mercury ions, and the following conclusions were drawn.

(1) The optimal adsorption parameters were: temperature =36.43℃, PH=4.88, time =70min. Through parameter optimization, the removal efficiency of mercury ions can reach 86%.

(2) In contrast, the influence of influencing factor C (adsorption time) is very significant, and that of influencing factors A (PH) and B(temperature) is significant. The significance of p-value analysis of each fitting term is: C>B>A>AC>BC>AB. The analysis of residual error, variance and other parameters shows that the fitting effect is good.

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