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Study on Key Factors of Adsorption of Phosphorus by Steel Slag Filter Based on Response Surface Method

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Abstract. Excessive phosphorus emission is one of the important reasons for the eutrophication of water. At the same time, phosphorus is a significant mineral resource. In this paper, the response surface method is used to study the key influencing factors of phosphorus removal by steel slag filter and its action. Four factors affecting the dosage, initial pH, reaction time and calcium-phosphorus molar ratio were selected. The phosphorus removal was used as the response value. The interaction between various factors was established by Box-Behnken response surface analysis. The optimal conditions were determined by equation regression analysis: dosage = 2 cm^3; initial pH = 7; molar ratio of calcium to phosphorus was 2:1; reaction time = 2 h.

1 Introduction

In recent years, the phenomenon of eutrophication of water bodies in China has become more and more serious. The excessive emission of phosphorus is one of the main factors causing eutrophication of water bodies. The traditional methods of phosphorus removal include chemical methods and biological methods. Phosphorus recovery is difficult, and the adsorption method is receiving increasing attention due to its advantages in phosphorus recovery.

Studies have shown that the adsorption method of phosphorus removal is the use of porous or large specific surface area of solid matter on the phosphate ion in water, through physical adsorption, ion exchange, chemical reaction or surface precipitation and other processes to achieve phosphorus separation [1]. Our previous studies have found that, in order to produce raw materials for steel plant waste slag unburned slag type filter having good adsorption phosphorus removal [2-6], the present study is to response surface method, is used to screen unburned slag the key adsorption filter phosphorus removal by impact factor, to explore its regular pattern, to explore the optimum operating parameters of slag adsorption filter phosphorus removal.

2 Materials and methods

2.1. Test Material

In this experiment, the steel slag of a steelmaking plant in Jinan City is selected as the raw material, and the XRD test results of the steel slag are shown in Figure1 below. Its main component is CaO accounted for 57.78% of the steel slag composition, followed by SiO_2 accounted for 19.90% of the total composition, and then Al_2O_3 accounted for 7.45% of the total composition, Fe_2O_3 accounted for 5.78% of the total composition, and MgO accounted for 4.03% of the total composition. SO_3 accounted for 2.81% of total composition, MnO accounted for 0.52%, TiO_2 accounted for 0.52%, K_2O accounted for 0.52%, P_2O_5 accounted for 0.24%, Na_2O accounted for 0.20%, Cl accounted for 0.06%, V_2O_5 accounted for 0.05%, SrO accounted for 0.05%, and Cr_2O_3 accounted for 0.04%. ZrO_2 accounts for 0.03%.

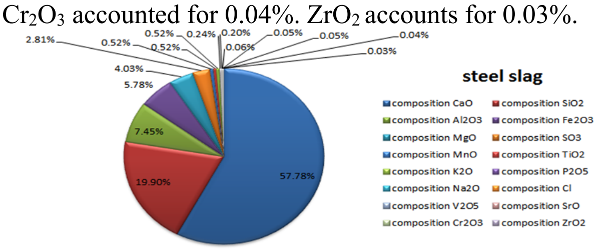

Fig.1 Composition of steel slag

2.2. Experiment method

2.2.1Test plan

In this experiment, artificial phosphorus was used to simulate phosphorus-containing wastewater. The water-dispensing drug was 0.2769 g $CaCl_2$ after drying, and 0.4394 g of KH_2PO_4. The concentration of calcium and phosphorus in the solution was 100 mg/l. In the experiment, 200 ml of phosphorus-containing wastewater was taken in an Erlenmeyer flask, and the pH was adjusted to 7.00, T=20 °C. Referring to the steel slag (bulk density = 0.8037 g/cm^3), each group is weighed into 1.0, 2.0, 3.0, 4.0, 5.0 cm^3 and placed in 5 conical flasks, and shaken in a constant temperature shaking box for 3 h. After taking out, the concentration of phosphorus

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in the water sample and the pH value of the effluent were measured by filtration through a membrane to analyze the phosphorus removal efficiency.

2.2.2 Response surface test

Minyu Zuo, et.al and Jianguo Li, et.al [10-11] used the response surface method to study the influence factors affecting the adsorption and dephosphorization performance of steel slag filter materials, and obtained the calcium content and initial pH value of the filter material. Both factors have a significant effect on phosphorus removal performance. Jibing Xiong, et.al [12] used a single factor variable experimental method to study the effect of steel slag on the removal of phosphate from wastewater, and obtained the pH value affecting the removal efficiency of phosphate. Li Yanbo , et.al [13] designed a single factor experiment to study the main influencing factors of phosphorus removal efficiency of steel slag. The conclusion is that the initial pH, the dosage of filter material, the reaction time and the initial phosphorus concentration will affect the phosphorus removal efficiency to different extents. In the filter material preparation and sewage adsorption phosphorus removal test, Zheng Jun ,et.al [14] explored the key factors affecting the removal of phosphorus from the filter material, and obtain the optimal pH value, dosage and initial phosphorus concentration best. It was found that two factors of Ca^{2+} and pH affect the phosphorus removal effectively. The filter material has the function of retaining, adsorbing and inducing crystallization [7-9], and the phosphate and calcium ions in the wastewater will precipitate, which will promote the crystallization of the crystal, so the adsorption capacity of the filter material for phosphorus is more remarkable.Therefore, it can be seen that the four key factors are the filter feed amount, initial pH, reaction time and calcium-phosphorus molar ratio (initial concentration of phosphorus), and the range of the items is as follows: dosage 2-4 cm^3; initial pH=5-7; reaction time: 1-3 h; Ca: P (molar ratio) 1.0-3.0.

The response surface analysis test plan was designed by taking three levels from each factor. The factors and levels are shown in Table 1.

Table1. Factors and levels of response surface analysis

Level	Factor			
	Dosing amount/cm3	Initial pH	Ca:P	Reaction time/h
-1	2.0	5.0	1.0	1.0
0	3.0	6.0	2.0	2.0
1	4.0	7.0	3.0	3.0

3 Experimental results and analysis

3.1. Box-Behnken test design

This experiment uses the response surface method combined with the orthogonal experimental idea, and then according to the selection of suitable filter material dosage range 2-4cm^3, initial pH range 5-7, calcium-phosphorus molar ratio 1.0-3.0, reaction time 1-3h, and four factors and response values of the experimental design are shown by Box-Behnken test design in Table 2:

Table 2. Response surface experimental scheme and results

serial number	A: Dosing amount /cm3	B: Initial pH	C: Ca:P	D: Reaction time/h	Phosphorus removal /mg
1	4	5	2	2	1.574
2	3	5	2	1	1.52
3	3	7	1	2	1.942
4	2	6	3	2	1.921
5	3	6	3	1	1.875
6	3	6	2	2	1.9
7	2	5	2	2	1.531
8	2	6	2	1	1.9
9	3	5	1	2	1.5
10	3	7	3	2	1.965
11	3	5	3	2	1.5
12	4	6	2	3	1.97
13	3	6	2	2	1.94
14	3	6	2	2	1.94
15	4	6	2	1	1.969
16	2	6	2	3	1.931
17	3	7	2	1	1.977
18	3	7	2	3	2.01
19	3	6	1	3	1.875
20	3	6	2	2	1.9
21	3	5	2	3	1.54
22	3	6	1	1	1.875
23	4	6	1	2	1.96
24	3	6	3	3	1.88
25	2	7	2	2	1.94
26	4	7	2	2	2
27	3	6	2	2	1.9
28	4	6	3	2	1.96
29	2	6	1	2	1.92

Multivariate nonlinear fitting of the data in the table yields a quaternary quadratic regression model:

phosphorus removal = -5.24479-0.16108 × dosage + 2.20667 × initial pH + 0.050833 ×(Ca:P)+0.018167×Reaction time+4.25000E-003×dosing amount×initial pH-2.50000E-004×dosing amount×(Ca:P)-7.50000E-003×dosing amount×reaction time +5.75000E-003×initial pH ×(Ca:P)+3.25000E-003×initial pH×reaction time+1.25000E-003×(Ca:P)×reaction time+0.029208×dosing amount 2-0.16792×initial pH2-0.021167×(Ca:P)2-2.54167E-003×reaction time 2.

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Table 3 .Test plan and model analysis table

Source	Sum of Squares	df	Mean Squares	F Value	P-value Prob>F	Significant
Model	0.81	14	0.058	105.11	< 0.0001	significant
A- Dosing amount	7.01E-03	1	7.01E-03	12.69	0.0031	
B- Initial pH	0.59	1	0.59	1075.2	< 0.0001	
C-Ca:P	7.01E-05	1	7.01E-05	0.13	0.7269	
D- Reaction time	6.75E-04	1	6.75E-04	1.22	0.2875	
AB	7.23E-05	1	7.23E-05	0.13	0.7229	
AC	2.50E-07	1	2.50E-07	4.53E-04	0.9833	
AD	2.25E-04	1	2.25E-04	0.41	0.5335	
BC	1.32E-04	1	1.32E-04	0.24	0.6321	
BD	4.23E-05	1	4.23E-05	0.077	0.7861	
CD	6.25E-06	1	6.25E-06	0.011	0.9168	
A^2	5.53E-03	1	5.53E-03	10.02	0.0069	
B^2	0.18	1	0.18	331.26	< 0.0001	
C^2	2.91E-03	1	2.91E-03	5.26	0.0378	
D^2	4.19E-05	1	4.19E-05	0.076	0.787	
Residual	7.73E-03	14	5.52E-04	-	-	
Lack of Fit	5.81E-03	10	5.81E-04	1.21	0.4623	not significant
Pure Error	1.92E-03	4	4.80E-04	-	-	
Cor Total	0.82	28	-	-	-	

Note: $P < 0.0001$ indicates extremely significant, $P < 0.05$ indicates significant, and $P > 0.05$ indicates no significant.

It can be seen from Table 4 that the response value of each parameter of the mathematical model is "significant", the significance is good, and "Lack of Fit" is "not significant". That is, the established model is in line with the actual experiment. The Ca:P (molar ratio) Pr=0.7269>the reaction time Pr=0.2875>the dosage of Pr=0.0031>the initial pH value Pr<0.0001. It can be seen that the degree of influence of each factor on the magnetic field strength is initial pH>filter feed amount>reaction time>Ca:P (molar ratio).

3.2. Response surface analysis

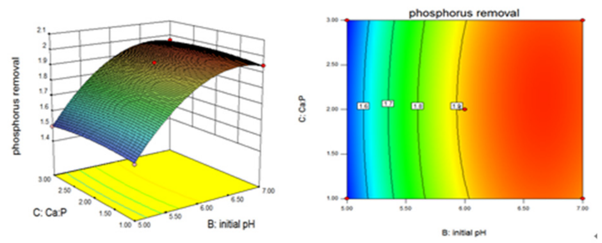

Fig.2. Response surface map and contour map of initial pH and Ca:P (dosing amount =3cm^3, reaction time=2h)

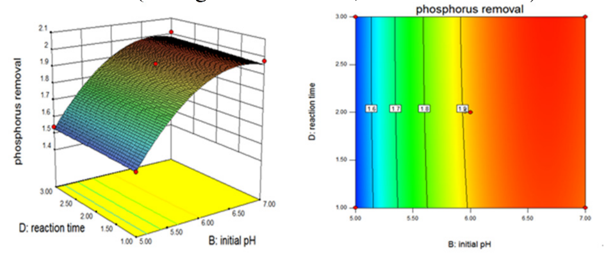

Fig.3. Response surface plot and contour plot of initial pH and reaction time (dosing amount = 3cm^3, Ca: P =2)

In the response surface diagram of Fig. 2, when the pH is in the range of 5-7, the removal amount of phosphorus shows a significant increase with the increase of pH value. The regression analysis of model variance (P<0.0001) indicates the removal of phosphorus by pH, which impact is extremely significant. When Ca:P was changed within the range of 1-3, the difference between the removal of phosphorus by Ca:P (molar ratio) was not significant (P>0.05). The interaction between the two is very significant, and the effect of initial pH on phosphorus removal is much greater than the effect of Ca:P (molar ratio). Figure 3 reflects the interaction between the initial pH and the reaction time. The surface map and contour plot analysis plus the reaction time of 1-3h, the variance model analysis table (P>0.05), the difference effect is not significant. Therefore, the effect of initial pH on phosphorus removal is much greater than the reaction time. At the same time, the optimum initial pH =7can be determined.

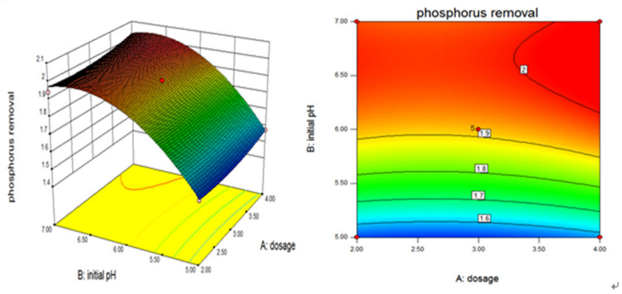

Fig.4. Response surface plot and contour plot of dosage and initial pH (Ca: P = 2h, reaction time = 2h)

It can be seen from Fig. 4 that when the pH is in the range of 5-7, the amount of phosphorus removed shows a significant increase with the increase of pH. Since the steel slag containing a large amount of calcium is in the crystal precipitation reaction, an increase in pH promotes the induction of the crystallization reaction, so that the reaction proceeds in the positive direction. The interaction between the initial pH of the solution and the dosage is very significant, and the effect of pH on the amount of phosphorus removed is greater than the effect of the dosage. At the same time, in combination with Fig. 3 and Fig. 4, the optimal reaction time = 2h can be determined.

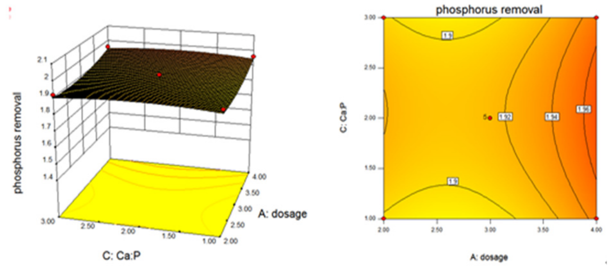

Fig.5. Response surface and contour plot of dosage and Ca:P (initial pH=7, reaction time=2h)

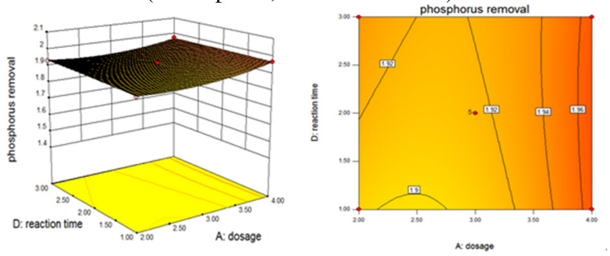

Fig.6. Response surface and contour map of the dosage and reaction time (initial pH=7, Ca:P=2)

It can be seen from Fig. 5 that when the dosage is in the range of 2-4 cm^3, the amount of phosphorus removed decreases first and then increases with the increase of the dosage, and the optimum dosage = 2 cm^3 can be selected. The influence of Ca:P (molar ratio) on the removal amount of phosphorus is basically consistent with the trend of dosage. The significance of the difference in the analysis of the variance model is also shown: the dosage of $P=0.0031<0.05$, the significance of Ca:P $=0.7269>0.05$. Therefore, the effect of dosage is greater than the effect of Ca:P. It can be seen from Fig. 6 that when the reaction time within 1-3 h, the removal amount of phosphorus does not change significantly, and the difference in the effect of phosphorus removal ($P>0.05$) is not significant. At the same time, it can be seen that the interaction between the two is not very significant, but the effect of the dosage on the amount of phosphorus removal is greater than the effect of the reaction time.

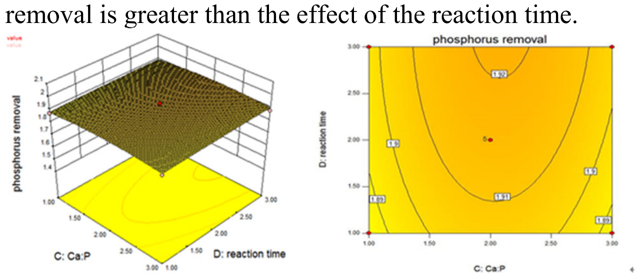

Fig.7. Ca: Response surface curve and contour map of P and reaction time (when dosage = 3 cm^3, initial pH = 6)

When the Ca:P (molar ratio) is in the range of 1-3, the amount of phosphorus removal increases first and then decreases with the increase of Ca:P (molar ratio), and when the reaction time changes within 1-3 hours, there was no significant change in the amount of phosphorus removal. The difference between the reaction time and the response value ($P=0.28705>0.05$) was not significant. It can be concluded from Fig.7 that the interaction between the two is not obvious, so the degree of influence of calcium and phosphorus molar ratio and reaction time is small. At the same time, the optimal calcium to phosphorus molar ratio is Ca: P = 2.

4 Conclusions

1) Taking the removal rate of phosphorus as the response value, the dosage of the filter material, the initial pH, the reaction time, and the molar ratio of calcium to phosphorus as the key factors, a multivariate quadratic response surface regression model for the adsorption and phosphorus removal of the steel slag filter material is obtained. The effect of the model is extremely significant, the missing term is not significant, the degree of variance is high, and the accuracy is high.

2) The interaction between initial pH and steel slag dosage is the largest, and the interaction between initial pH and reaction time is second, and the interaction between initial pH and Ca:P (molar ratio) is the smallest. According to the regression model analysis of variance, the order of influence of various factors on phosphorus removal rate is as follows: initial pH>filter feed amount>reaction time>Ca:P (molar ratio).

3) The optimal conditions for the key factors affecting the adsorption of phosphorus by steel slag were analyzed by response surface methodology. The initial pH=7, the steel slag dosage=2cm^3,Ca:P=2, and the reaction time=2h, the removal efficiency of the steel slag to phosphorus is optimal.

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