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Application of response surface methodology to optimize the bipolar membrane electrodialysis process of preparing polyferric sulphate

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ABSTRACT

Response surface methodology (RSM) is employed to optimize the bipolar membrane electrodialysis (BMED) process of preparing the polyferric sulphate (PFS). An experimental design is carried out based on Box-Behnken design to evaluate the effects of current density, operation time and feed molar ratio on basicity of polyferric sulphate. Results show that all the independent variables and quadratic of feed molar ratio have significant effect on the response values. High current density and feed molar ratio can promote the effect of operation time on basicity. Be different from the interaction between current density and feed molar ratio and the interaction between operation time and feed molar ratio, the interaction effect between current density and operation time is slight. In addition, the optimal operation condition is as follows: current density is 20 mA/cm^2, operation time is 180 mins and feed molar ratio is 3.04. Moreover, the actual basicity under the optimal condition is 19.15% ± 0.84%, which is agreed with predicted value (19.46%), indicating that RSM is an accurate tool to predict the PFS basicity and optimize the BMED process of preparing PFS.

Keywords: Electrodialysis; Response surface methodology; Polyferric sulphate; Box-Behnken design; Ion exchange membrane

1. Introduction

Coagulation-flocculation is a relatively simple physical-chemical technique used for water and wastewater treatment commonly. Generally, coagulation provides a method to remove suspended solids (SS), colloidal particles, natural organic matter (NOM) as well as heavy metal ions in surface water and wastewater [1]. The core of this technique is coagulant, which includes inorganic coagulant, organic coagulant and inorganic polymeric coagulant. Among them, inorganic polymeric coagulant, which is less expensive than organic coagulant, shows higher removal efficiency than inorganic coagulant [2,3]. Hence, more and more attention has been paid to inorganic polymeric coagulant.

As one of inorganic polymeric coagulants, polymeric ferric sulfate (PFS) is a pre-hydrolyzed coagulant, which is prepared through partially neutralization of ferric sulfate [4]. PFS contains a large number of poly-nuclear complex ions, such as $Fe_2(OH)_2^{4+}$ and $Fe_3(OH)_4^{5+}$, formed by OH bridges and lots of inorganic macromolecular compounds [5]. Moreover, PFS exhibits superior capability in removing turbidity, color, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [4,5]. Basicity, which can indicate the degree that the iron is hydrolyzed, is a more important index than others, such as density and the total iron content. Generally speaking, higher basicity can result in a better coagulation performance. Hence, much research has been done to increase the PFS basicity. Zouboulis et al. tried to improve the PFS basicity by adjusting the base concentration, hydrolysis and oxidation duration, but results showed that there was no obvious improvement [6]. Chen et al. tried to increase the PFS basicity through adding modifiers (polyethylene glycol, oxalic acid and phosphoric acid) into the reaction system, and results illustrated that the basicity can be increased from 11.61% to 17.75%, but the addition of modifiers can influence

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the water quality simultaneously [7]. In our previous research [8], bipolar membrane electrodialysis (BMED) was integrated with PFS preparation process. Under the direct current field, bipolar membrane can generate sufficient OH^- ions to participate in the PFS preparation process. Results showed that PFS basicity can be improved dramatically without addition of any chemical, and the influence parameters of basicity included current density, feed molar ratio ($n(FeSO_4)$: $n(H_2SO_4)$) and operation time. However, this research only investigated the effect of individual parameter on basicity, while "synergistic" or "antagonism" effects among these parameters on basicity were not studied. Actually, the interactive effects are also important to guide and optimize the BMED process of preparing the PFS. Hence, it is necessary to study the interactive effects of these parameters comprehensively.

In recent years, response surface methodology (RSM) has been a popular optimization method. RSM is a combination of mathematical and statistical techniques, which are based on the fit of a polynomial equation to the experimental data. The aim of RSM is to optimize the levels of independent variables and their interactions to obtain the optimum system performance [9]. The advantages of RSM include less times of experiments, high efficiency, and high cost-effectiveness in terms of both manpower and resources [10,11]. Now, RSM has been used to evaluate the operation parameters in some chemical and biochemical processes, such as the COD removal of acid dye effluent [12], the production of kaline protease from *Bacillus mojavensis* [13], and the recovery of tartaric acid from winery lees [14]. An experimental design, such as the central composite design (CCD) and Box-Behnken design (BBD), can be used to fit a polynomial model by least squares technique in RSM [15]. In addition, the adequacy of the proposed model can be revealed by using the diagnostic checking tests provided by analysis of variance (ANOVA) [16].

Hence, the objective of the present work is to optimize the PFS preparation process through BMED. RSM is designed to systemically analyze and optimize the effects of influence parameters (current density, molar feed ratio and operation time) on basicity. BBD, which only has three levels and needs fewer experiments, is used to develop a mathematical equation further.

2. Materials and methods

2.1. Materials

The anion exchange membrane and bipolar membrane used in this study are LabA and BPM–I, respectively. Their properties are listed in Table 1. All the chemicals, purchased from a domestic chemical regents' company (Sinopharm Chemical Reagent Co., Ltd., China), are of analytical grade. Their solutions were prepared without further purification with distilled water.

2.2. Experimental setup for the preparation process

The experimental setup used in this study is similar to that illustrated in our previous literature [8], and its schematic diagram is shown in Fig. 1. The stack configuration of BMED membrane module (1) is BP–A configuration, which includes three pieces of bipolar membranes and two pieces of anion exchange membranes, constituting two electrode compartments, two acid compartments and two reaction compartments. The effective area of each membrane is about 0.02 × 0.10 m^2. Apart from the five pieces of membranes, compartments are also separated by plastic partition nets (thickness ≈ 1.0 mm) and silicone gaskets (thickness ≈ 0.8 mm). The electrodes of BMED membrane module (1), which are made of titanium coated with ruthenium, are connected with a direct current power supply (2) (RLD–3005D1, Shanghai Huanzhen electronics Co., Ltd., China). Three submersible pumps (3) (JY-PG70, Hangzhou Jiyin Culture and the Arts Co., Ltd., China, with the maximum flow rate of 500 L/h) are placed in tanks (4)–(6) to pump the solutions into the membrane stack. Acid solution tank (4) is filled with 200 mL 0.15 mol/L H_2SO_4 solution. Reaction solution tank (5) is full of reaction feed (~65 mL, 1.10–2.25 mol/L H_2SO_4, 4.30 mol/L $FeSO_4$ and 0.75 mol/L $KClO_3$). 200 mL 0.3 mol/L Na_2SO_4 solution is added into electrode rinse tank (6). Constant current operation mode is adopted in this study. Voltage drop across the membrane module is monitored during the operation. After the operation, the liquid PFS product can be obtained through aging for over 24 h sequentially. All the operations are conducted at room temperature (28 ± 3°C).

2.3. Analysis of samples

Acid concentration in acid solution tank is analyzed by titrating with a standard NaOH solution with phenolphthalein as an indicator.

Basicity is determined according to the Chinese National Standard GB 14591-2006. Firstly, KF solution is used to cover the iron ions in sample. Then the sample is titrated

Table 1
The main properties of the membranes used in the experiments*

Membrane type	Thickness (μm)	IEC (meq·g⁻¹)	Water content (%)	Area resistance (Ω·cm²)	Transport number (%)	Burst strength (Mpa)	Company
LabA	~0.20	0.8~1.0	35~40	0.5~1.5	>98	>0.35	Chemjoy, Hefei, China
BPM-I	0.16~0.23	Positive side: 1.4~1.8 Negative side: 0.7~1.1	35~40	–	–	>0.25	Tingrun, Beijing, China

*The data were referred to the relative company websites: www.cj-membrane.com, www.tingrun.com.

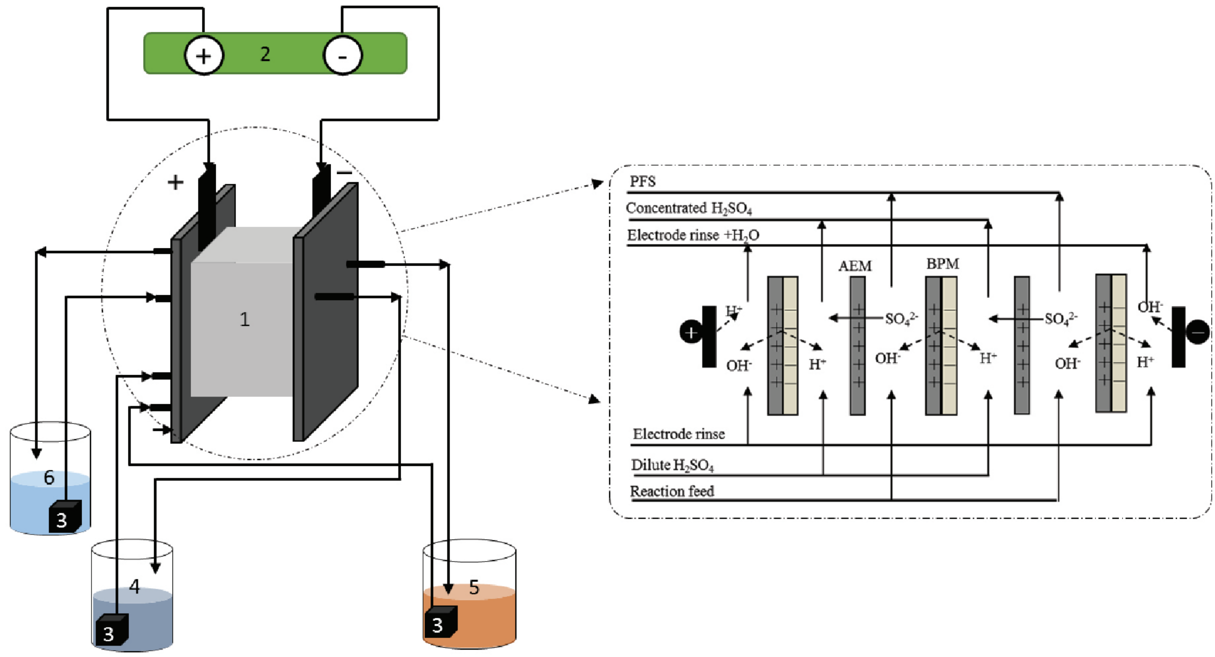

Fig. 1. The schematic diagram of experimental apparatus. (1) BMED membrane module; (2) DC power supply; (3) Submersible pump; (4) Acid solution tank; (5) Reaction solution tank; (6) Electrode rinse tank.

by standard NaOH solution with phenolphthalein as an indicator. Moreover, a distilled water blank test is conducted synchronously. Basicity can be calculated as follows.

$$B = \frac{\left[(V_0 - V)C_{NaOH} \cdot 0.017\right]/17.0}{m \cdot X_2 / 18.62} \times 100\% \tag{1}$$

where B (wt. %) represents the basicity, V (mL) is the consumed NaOH solution volume, V_0 (mL) is the consumed NaOH solution volume of distilled water blank test, C_{NaOH} (mol/L) is the standard NaOH solution concentration, m (g) is the liquid PFS sample mass, X_2 (wt.%) is the reductive substance content, 0.017 (g) is the mass of 0.001 mol OH^-, 17.0 (g) is the mass of 1 mol OH^-, 18.62 (g/mol) is the 1/3 mol Fe mass.

For the reductive substance content, it is also analyzed according to GB 14591–2006. Above of all, H_3PO_4 buffered solution is added into the sample to provide an acidic solution environment. After that, the sample is titrated by standard $KMnO_4$ solution. Simultaneously, a distilled water blank test is conducted. The calculation formula of reductive substance content (X_2, wt. %) is shown in Eq. (2).

$$X_2 = \frac{(V - V_0)C_{KMnO_4} \cdot 0.05585}{m} \times 100\% \tag{2}$$

where V (mL) is the consumed $KMnO_4$ solution volume, V_0 (mL) is the consumed $KMnO_4$ solution volume of distilled water blank test, C_{KMnO_4} (mol/L) is the standard $KMnO_4$ solution concentration, 0.05585 (g/mol) is the 0.001 mol iron mass, m is the liquid PFS sample mass.

2.4. Experimental design

In this study, response surface methodology (RSM) with Box-Behnken design (BBD) is selected to optimize the three important operation variables: current density, operation time and feed molar ratio. Based on the results of the previous literature [8], current density, operation time and feed molar ratio are selected as 0~20 mA/cm^2, 60~180 min and 2.01~4.08, respectively. As shown in Table 2, the three independent variables are converted to the dimensionless ones (x_1, x_2, x_3) with the coded values at 3 levels: –1, 0, + 1. What's more, BBD is arranged with second-order polynomial function, in which the variable for each factor is partitioned into linear, quadratic and interactive components [17].

$$y = \alpha_0 + \sum \alpha_i x_i + \sum \alpha_{ii} x_i^2 + \sum \alpha_{ij} x_i x_j \tag{3}$$

where y is the predicted response that can be correlated to the intercept coefficient α_0, the linear coefficients α_i, quadratic coefficients α_{ii} and interaction coefficients α_{ij}. x_i

Table 2
Independent variables and their levels for the Box-Behnken design (BBD) used in this study.

Coded variable levels	x_1	x_2	x_3
	Current density (mA/cm^2)	Operation time (min)	Feed molar ratio
–1	0	60	2.01
0	10	120	3.05
+1	20	180	4.08

and x_j (i = 1~3; j = 1~3) represent the coded independent variables.

In addition, analysis of variance (ANOVA) is performed. The accuracy and general ability can be evaluated by coefficient R^2, R_{adj}^2 and F-test. What's more, response surface plots and contour plots can be constructed using the fitted quadratic polynomial equation from regression analysis.

Moreover, some additional independent experiments under the optimal experimental condition will be conducted to validate the equation.

3. Results and discussions

3.1. Statistical analysis

The level of factors (current density, operation time and feed molar ratio) and the effect of their interactions on basicity was determined through BBD. 17 experiments, containing 5 replicates at the center of the design, were performed at different combinations of the factors (seen in Table 3). The fitting result of the second-order polynomial function is illustrated in Table 4 and the application of RSM yielded the following regression equation.

$$y = -11.54 - 0.24x_1 + 0.03x_2 + 11.01x_3 + 1.44\times10^{-3}x_1x_2 + 0.038x_1x_3 + 0.014x_2x_3 + 0.0104x_1^2 - 2.038\times10^{-4}x_2^2 - 1.70x_3^2 \quad (4)$$

F-test is used to check the statistical significance in this study. The significance of the F-value depends on the degrees of freedom (DF) number and can be shown in p-value column (95% confidence level). That is to say, when the p-value is less than 0.05, it can be regarded that the model is significant [18]. Table 4 also shows the ANOVA result. Firstly, the high F-value (18.55) and low p-value (0.0004) illustrate the high significance of the fitted model. Secondly, the significance of each variable and the interaction strength between each independent variable is determined using p-values [19]. As seen the p-values from the third to fifth line in Table 4, it can be found that the three linear items (x_1, x_2 and x_3) are all significant (p-value<0.01) for basicity, and the order of them is $x_3 > x_1 > x_2$. As to the interactive and quadratic terms, they have a very minor influence on basicity since the p-values are larger than 0.05, except for x_3^2. Thirdly, the lack of fit is used to measure the failure of the model to represent the data in the experimental domain at points which are not included in the regression [17]. In this study, F-value and p-value of the lack of fit are 4.05 and 0.1049, indicating that the model is fit to predict the basicity under any combination of variable values. Fourthly, the determination coefficient (R^2) and the adjusted determination coefficient (R_{Adj}^2) are also used to evaluate the model. R^2 value provides a variability measurement in the observed response values, while R_{Adj}^2 value is the correlation measurement for testing the goodness-of-fit of the regression equation. Generally, if the R^2 value is higher than 0.90, the regression model can be considered to have a very high correlation [20]. With regard to R_{Adj}^2, the closer its value to 1.0 can illustrate the smaller difference between predicted and observed values [21]. In this case, R_{Adj}^2 and R^2 are equal to 0.9080 and 0.9598, indicating that the model is significant and there is a high degree of correlation between observed and predicted data. Finally, the coefficient of variation (CV), that is the ratio of the estimated standard error to the mean value of the observed response, can define the reproducibility of the model [11]. If the CV value is less than 10%, the model can be regarded to be reproducible [13]. In this case, the CV value is 8.22%, suggesting a better precision and reliability of the experiments carried out.

Table 3
Experimental values of the BBD

No.	Current density (x_1, mA/cm^2)	Operation time (x_2, mins)	Feed molar ratio (x_3)	Basicity (wt. %)
1	10	120	3.05	13.12
2	20	60	3.05	13.55
3	10	180	4.08	15.9
4	0	180	3.05	12.22
5	10	120	3.05	13.28
6	20	120	2.01	10.95
7	10	60	4.08	10.09
8	20	180	3.05	20.18
9	20	120	4.08	18.55
10	10	120	3.05	12.55
11	10	60	2.01	7.58
12	10	120	3.05	14.26
13	0	60	3.05	9.05
14	10	180	2.01	9.95
15	0	120	4.08	13.58
16	0	120	2.01	7.55
17	10	120	3.05	13.99

3.2. Response surface analysis

3D response surface plots and 2D contour plots are the graphical representations of regression function, and they can visualize the relationship between responses and experimental levels of each variable, and the interaction type between two best variables [17]. In contour plots, the interaction between the variables can be determined through the contour plot shape. When the shape is circular, interaction between the variables is negligible; when the shape is elliptical, interaction is significant [22]. Figs. 2–4 show the response surface plots and contour plots generated by the model, and two variables are illustrated in a 3D response surface plot when the rest is set at 0 level. It's pretty clear that basicity is sensitive to the tiny change of investigated variables (current density, feed molar ratio and operation time).

Fig. 2 shows the response surface plot and contour plot of operation time and current density on basicity when the feed molar ratio is at center point. As seen from Fig. 2a, to be specific, as current density increases, basicity increases correspondingly. The main reason is that more OH^- ions, generated by bipolar membrane, can participate in the PFS

Table 4
ANOVA results for regression model

	Source	*SS*	*DF*	*MS*	*F*	*Pr > F*	Remarks
Basicity	Model	182.60	9	20.29	18.55	0.0004	Significant
	x_1	54.24	1	54.24	49.59	0.0002	
	x_2	40.41	1	40.41	36.95	0.0005	
	x_3	61.00	1	61.00	55.78	0.0001	
	$x_1 x_2$	2.99	1	2.99	2.74	0.1420	
	$x_1 x_3$	0.62	1	0.62	0.56	0.4773	
	$x_2 x_3$	2.96	1	2.96	2.71	0.1440	
	x_1^2	4.59	1	4.59	4.19	0.0798	
	x_2^2	2.27	1	2.27	2.07	0.1931	
	x_3^2	14.04	1	14.04	12.84	0.0089	
	Residual	7.66	7	1.09			
	Lack of fit	5.76	3	1.92	4.05	0.1049	Not significant
	Pure error	1.90	4	0.47			
	Cor. total	190.26	16				
					$RAdj^2 = 0.9080$	$R^2 = 0.9598$	$CV = 8.22\%$

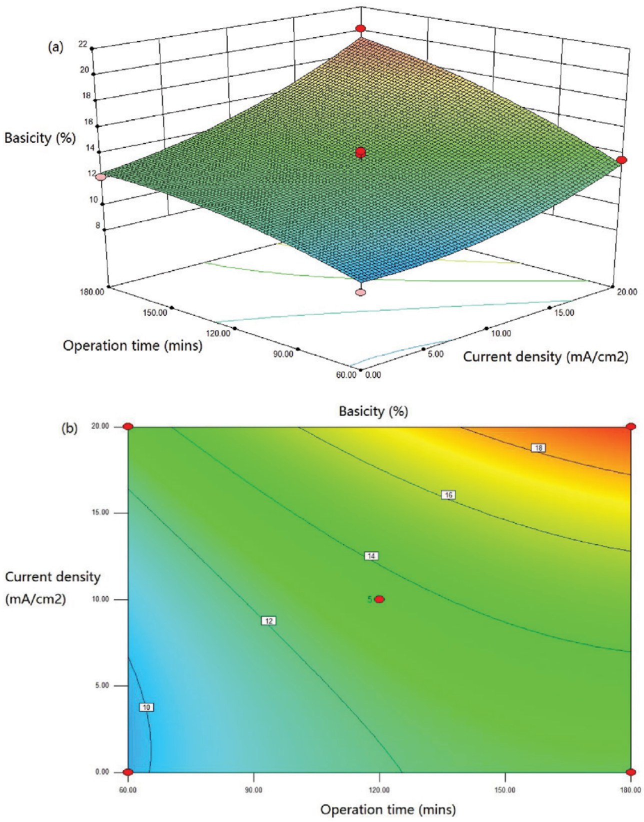

Fig. 2. Response surface plots (a) and contour plots (b) of operation time and current density on basicity.

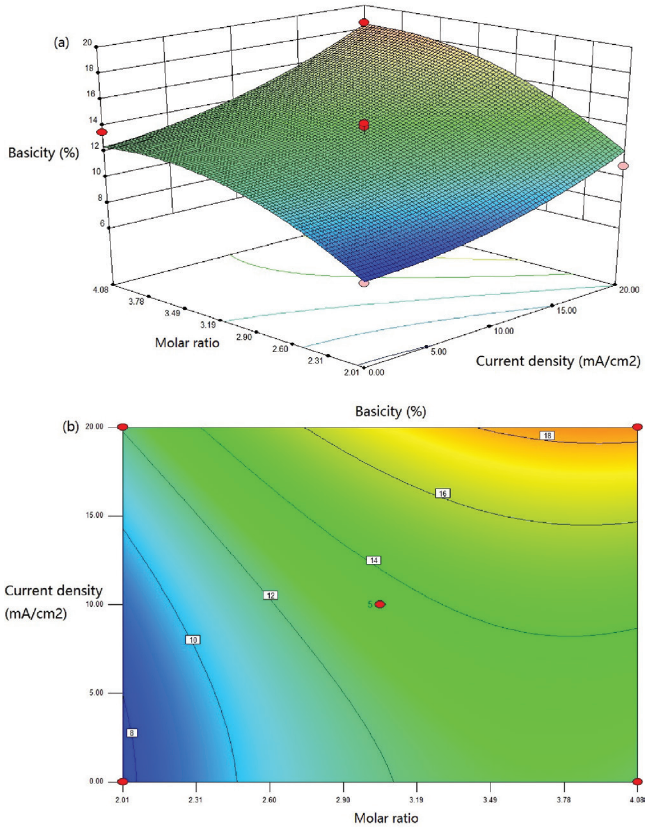

Fig. 3. Response surface plots (a) and contour plots (b) of feed molar ratio and current density on basicity.

production process under stronger electric field. Moreover, as current density increases, effect of operation time on basicity turns more obvious. For example, as operation time increases from 60 to 180 min, basicity increases from about 10% to 12% at current density of 0 mA/cm^2, while it increases from about 13.2% to 20% at current density

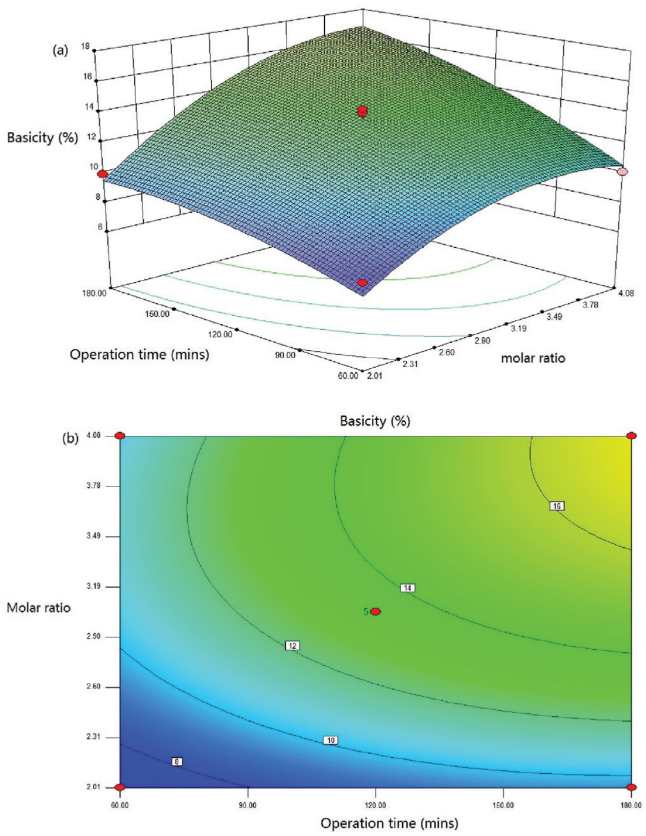

Fig. 4. Response surface plots (a) and contour plots (b) of feed molar ratio and operation time on basicity.

of 20 mA/cm^2. As shown in Fig. 2b, the interaction effect between current density and operation time is relatively slight, in spite of that the current density is the major factor affecting the basicity. This can also be confirmed by the quadratic polynomial equation, since the interactive constant coefficient of the two variables is minimum.

Fig. 3 demonstrates the quadratic effect of current density and feed molar ratio on basicity, when the operation time is at the center point. Firstly, no matter what the current density is high or low, effect of feed molar ratio on basicity is remarkable. This phenomenon can be explained that higher feed molar ratio can promote more Fe^{2+} ions to take part in the hydrolytic reaction to produce more OH^- ions. Secondly, as seen the contour plot shape shown in Fig. 3b, it can be concluded that the effect of feed molar ratio on basicity is more remarkable than that of current density. Thirdly, the interaction between current density and feed molar ratio affects the response significantly, and the biggest interact constant coefficient of the two variables in quadratic polynomial equation can also demonstrate this.

When current density is at center point, effect of feed molar ratio and operation time on basicity is shown in Fig. 4. Basicity increases with an increase of operation time and feed molar ratio. That because more OH^- ions can be generated during the Fe^{2+} hydrolytic reaction when the feed molar is higher, and water dissociation reaction of the bipolar membrane when the operation time is longer. Hence, it can be concluded that longer operation time and higher feed molar ratio can result in a higher basicity. In addition, higher feed molar ratio can promote the effect of operation time on basicity. From Fig. 4a, when the feed molar ratio is set as 2.01, basicity increases from 7.58% to 9.95% with the increment of operation time; when the feed molar ratio is 4.08, basicity increases from 10.09% to 15.90% dramatically. The contour plot shape in Fig. 4b is elliptical, suggesting that the interaction between operation time and feed molar ratio is relatively significant. In addition, according to the contour plot shape, effect of feed molar ratio on basicity is more obvious than that of operation time.

3.3. Process optimization

With multiple responses, ridge minimum and canonical analysis is used to determine the optimal condition. When the result expresses a saddle point in response surfaces, this analysis method can generate an estimated ridge of maximum or minimum response through increasing radii from the center of design [23]. Analysis results show that the maximum basicity (19.46%) can be achieved at current density of 20 mA/cm^2, operation time of 180 min and feed molar ratio of 3.04. In addition, at least seven independent experiments under the optimal condition have been conducted to confirm the adequacy of the predicting model. As shown in Table 5, basicity obtained from the experiments and predicted by model is in close agreement.

What is more, Figs. 5, 6 show the normal plot of residuals and the plot of the actual basicity vs. the predicted ones,

Table 5
The predicted and experimental value of response at optimal conditions.

Items	Value
Current density (mA/cm^2)	20
Operation time (mins)	180
Feed molar ratio	3.04
Predicted basicity (%)	19.46
Actual basicity (%)	19.15 ± 0.84

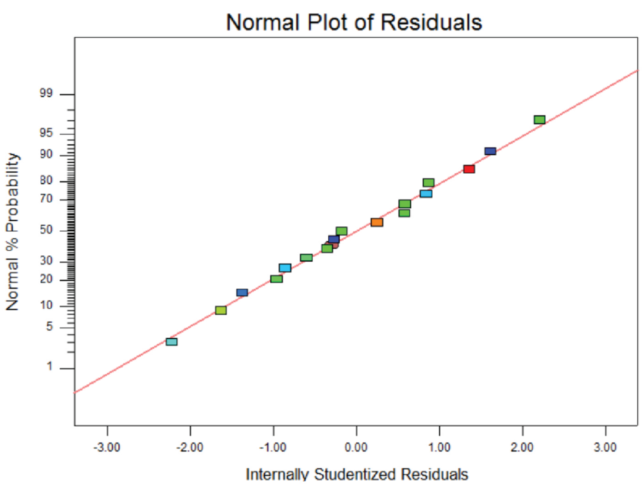

Fig. 5. Normal plot of residuals.

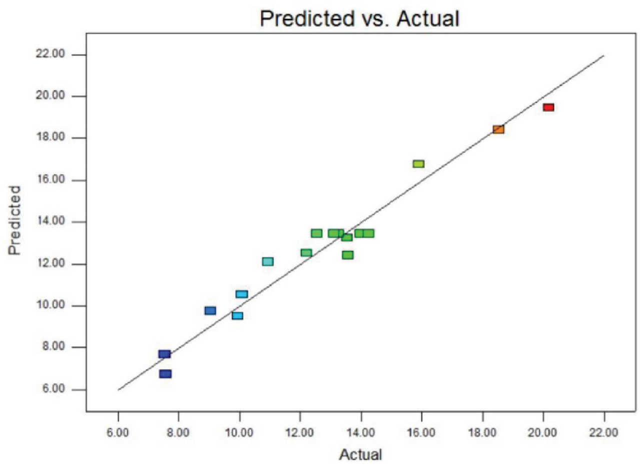

Fig. 6. Plot of actual vs. predicted values.

respectively. As seen a straight line that residuals fall along in Fig. 5, it can be concluded that the normality assumption is satisfactory. What's more, the points cluster around the diagonal line in Fig. 6, suggesting that the deviation between the actual and predicted ones is small.

4. Conclusions

In this research, response surface methodology is used to optimize the experimental variables (current density, operation time and feed molar ratio) to prepare polyferric sulphate with high basicity by bipolar membrane electrodialysis.

Firstly, a second-order polynomial mathematical model, established in terms of the three variables, is gained to predict the PFS basicity accurately. All the independent variables and quadratic of feed molar ratio have significant effect on the response values. Secondly, according to the response surface plots and contour plots, it can be summarized that high current density and feed molar ratio can promote the effect of operation time on basicity; the effect of feed molar ratio on basicity is more remarkable than that of current density and operation time; the interaction between current density and feed molar ratio and the interaction between operation time and feed molar ratio is relatively significant, while the interaction effect between current density and operation time is slight. In addition, the optimal experimental condition for the process is as the following: current density is 20 mA/cm^2, operation time is 180 mins and feed molar ratio is 3.04. Under the optimal condition, the actual basicity is 19.15% ± 0.84%, which is agreed with predicted value (19.46%).

To sum up, response surface methodology analysis is a useful and accurate technique to predict and optimize the bipolar membrane electrodialysis process of preparing polyferric sulphate.

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