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Determination of optimal conditions for separation of metal ions through membrane dialysis using statistical experimental methods

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ABSTRACT

Statistical experimental methods were used to optimize the variable conditions of membrane dialysis process with a complex agent. Permselectivity of metal ions has been investigated in a two-compartment dialyzer with reflux flow. Cu^{+2}–Ni^{+2} ion system was chosen for the experimental investigation. Oxalic, malonic acid, acid and citric acid were selected as a complex agent used in the investigated solution in order to increase the discrepancy between transport fluxes of metal ions. The concentration ratio of complex agent to metal ions (X_1), pH value of investigated solution (X_2) and concentration of metal ions (X_3) were conducted to be optimized. The Box-Behnken design and response surface methodology were employed in the design of experiments and the analysis of results. The experimental results indicated that oxalic acid is a better complex agent in this study. For the case of oxalic acid as complex agent, the maximal permselectivity of metal ions was obtained when concentration ratio of complex agent to metal ions, pH value of solution and concentration of metal ions were 0.96, 5.48 and 0.011 (mol/m^3), respectively. The corresponding maximal permselectivity of metal ions is 11.91.

Keywords: Optimization; Complex agent; Dialysis; Permselectivity

1. Introduction

Membrane dialysis is an efficient separation process which can simultaneously solve two environmental problems, for recovery and enrichment of valuable ions and for the removal of undesirable ions from wastewater [1]. Based on the Donnan membrane equilibrium principle [2], the permeation behavior across the membrane depends on an electrochemical equilibrium established when two solutions are separated by a membrane that is impermeable to some of the ions in the solution. One of the prominent features in the development of modern technology is the cross-fertilization of ideas among different disciplines [3,4]. Therefore, a separation process combined use of complex agents with ion exchange membranes for the enhancement of separation efficiency has received much attention in recent years [5–7].

Some fundamental works on the preferential transport behaviors of ions through an ion exchange membrane with dialysis and electrodialysis in the presence of complex agents have been studied for binary ion systems in our previous papers [8–10]. The experimental results show that the uptake of metal ions in the cation exchange membrane is changed by adding a complex agent in the solution phase, and both the anion ligands and the kinds of metal ions can differentiate the equilibrium uptake of metal ions so as to increase the membrane selectivity of the metal ions. These results are in concordance with the reports of other investigators [4,11–15]. As a result, the combined use of a cation exchange membrane with a complex agent seems to be a feasible process for the simultaneous separation and concentra-

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tion of metal ions. However, many factors such as membrane and complex agent sources, pH of solution, concentrations of complex agent and metal ions are important variables affecting permselectivity of metal ions. It seems to need a simple model to optimize such an ion fractionation process that the enrichment of metal ions as well as the separation of metal ions from wastewater in industrial practice.

Conventional practice of single variable optimization by maintaining other variables involved at a specified constant level does not depict the combined effect of all the variables involved. It was reported that the complexities and uncertainties associated with industry separation usually come from lack of knowledge of the sophisticated interactions among various variables. These limitations of a single variable optimization can be eliminated by using an experimental design and response surface methodology [16]. A combination of variables generating a certain optimum response can be identified through Box-Behnken design and the use of response surface methodology [17]. This pattern is designed by using statistical methods to yield the most information by a minimum number of experiments and had been successfully applied to the optimization of various engineering processes [18,19].

The present investigation is aimed at optimization of concentration ratio of complex agents to metal ions, concentration of metal ions and pH of the feed solution, which were observed to be the primary variables in enhancing permselectivity of metal ions. The Box-Behnken design and response surface methodology were combined to optimize the variable conditions for separation of metal ions by membrane dialysis in a continuous dialyzer.

2. Experimental

2.1. Permeation measurements of dialysis

The ion exchange membranes and dialysis unit used in this work have been described in an earlier paper [8,9]. The feed solution containing metal ions, a complex agent, and 0.1 M NaCl was placed in the feed compartment. To the stripping compartment, only 1.0 M NaCl was added except for the other specifications. The complex agent used in this work included oxalic acid ($HO2CCO_2H$), malonic acid ($CH_2[COOH]_2$), and citric acid (C_6H_8O7). A pseudo-steady-state was attained by pre-dialysis for a half-hour, and then the solution in the compartments was replaced with fresh solutions. During the dialysis, 2 ml of solution were taken from the stripping compartment at each preset time interval. The concentrations of metal ions were determined by use of an atomic absorption spectrophotometer (Model 551, Instrumentation Laboratory, Inc.). The permeation fluxes of the metal ions were calculated from linear slopes of the ionic concentration vs. time curve with using the least squares method. The permselectivity of metal ions, Y, was calculated from $(J_{Ni}/C_{Ni})/(J_{Cu}/C_{Cu})$ [10].

2.2. Experimental design and optimization by RSM

Response surface methodology (RSM) [18,19] is an empirical modeling technique used to evaluate the relationship between a set of the controlled experimental variables and the measured responses. A prior knowledge and understanding of the process and process variables under investigation are necessary for achieving a more realistic model. Based on the results of preliminary experiments, we selected the following three variables as experimental variables for each complex agent: (1) concentration ratio of complex agent to metal ions (X_1), (2) pH value of investigated solution (X_2) and (3) concentration of metal ions (X_3). The Box-Behnken design and response surface methodology (RSM) were employed to obtain the optimal variable conditions for higher permselectivity of metal ions. Each variable had three levels to be examined at high level (+1), medium level (0) and low level (–1). The high and low levels we selected for this study represented the extremes of normal operating ranges. The range and the levels of the experimental variables investigated in this study are given in Table 1. Based on Box-Behnken design, a set of 17 experiments was carried out for each complex agent, respectively. In developing regression model, the experimental variables were coded according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X} \tag{1}$$

where x_i is the coded value of the variable X_i, X_0 is the value of X_i at the center point and ΔX is the step change value. Once the experiments were performed, the regression model could be constructed by fitting the experimental results. According to the RSM methodology, a second-order polynomial model was used to fit the experimental variables using the following equation

Table 1
The actual and code levels of the variables

Variable	Code levels		
	–1	0	+1
X_1: concentration ratio of complex agent to metal ions	0	0.5	1
X_2: pH of solution	1.5	3.5	5.5
X_3: concentration of metal ions (mol/m^3)	0.005	0.01	0.015

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1^2 + b_5x_2^2 + b_6x_3^2 + b_7x_1x_2 + b_8x_1x_3 + b_9x_2x_3 \quad (2)$$

where Y is the permselectivity of metal ions; b_0, …, b_9 are coefficients of the model; x_1, x_2, x_3 are the coded variables.

In this study, Design-Expert package (version 6.0., Stat-ease Inc., Minneapolis, USA) was used for regression analysis of the data obtained, to estimate the coefficients of regression model and to search the optimal conditions. The fit of regression model attained was checked by the multiple correlation coefficients (R^2).

3. Results and discussion

3.1. Regression models of response

The Box-Behnken design and experimental results are shown in Table 2. The experimental data indicates that permselectivity of metal ions can be enhanced with the use of a complex agent. This is due to the fact that metal ions will compete with each other to react with complex ligands to form complexes which are hardly permeated through the membrane, while the complex agent is added in the feed. The difference in the concentration gradients of free metal ions across the membrane can be obtained because of the difference in stability and quantity of complexes [8–10]. Thus, the various permselectivities of metal ions can be observed in Table 2 for various kinds of complex agents including oxalic acid, malonic acid and citric acid. From the experimental results in Table 2, the means of permselectivity of metal ions are 2.31 for malonic acid as complex agent; 4.24 for oxalic acid as complex agent; 1.95 for citric acid as complex agent, respectively. It shows that the effect of the complex agent on permselectivity of metal ions for Cu^{+2}–Ni^{+2} ion system has the following order: oxalic acid > malonic acid > citric acid. The permselectivity of metal ions can be enhanced with a complex agent under suitable conditions. The difference in the concentration gradients of free metal ions across the membrane can be obtained because of the difference in stability and quantity of complexes. The larger the difference that exists between stability constants of metal ion complexes, the higher the difference that the permselectivity of metal ions can be obtained [9–11]. Theses experimental results were analyzed using statistical software package Design-Expert 6.0.

Table 2
The Box-Behnken design and experimental results

Trial No.	Variables			Permselectivity (Y)		
	x_1	x_2	x_3	Oxalic	Malonic	Citric
1	–1	–1	0	0.91	0.91	0.91
2	1	–1	0	2.20	1.30	1.25
3	–1	1	0	0.95	0.95	0.95
4	1	1	0	10.88	5.25	4.13
5	–1	0	–1	0.87	0.87	0.89
6	1	0	–1	6.00	3.86	3.03
7	–1	0	1	0.93	0.93	0.93
8	1	0	1	5.78	3.53	2.40
9	0	–1	–1	2.43	1.53	1.20
10	0	1	–1	5.50	2.34	2.78
11	0	–1	1	1.13	1.03	1.03
12	0	1	1	9.43	4.30	3.78
13	0	0	0	5.03	2.53	1.88
14	0	0	0	4.95	2.45	1.98
15	0	0	0	5.20	2.40	2.05
16	0	0	0	4.95	2.53	1.89
17	0	0	0	5.20	2.45	1.99

3.1.1. For oxalic acid as complex agent

According to the RSM methodology, a second-order polynomial model, Eq. (2), was used to fit the experimental variables. Multiple regression analysis of the experimental results gave the following equation [16]:

$$Y = 5.07 + 2.65x_1 + 2.65x_3 + 0.42x_3 - 1.14x_1^2 - 0.19x_2^2 - 0.53x_3^2 + 2.16x_1x_2 - 0.07x_1x_3 + 1.08x_2x_3 \quad (3)$$

The results of the analysis of variables (ANOVA) for regression model are given in Table 3. The R^2 (multiple correlation coefficient) of the regression equation obtained from the analysis of variance is always larger than 0.9685 (a value > 0.75 indicates aptness of the model) [18], which means that the model can explain 96.85% variation in the response. The results of the analysis of variables for testing the significant terms in the regression model are given in Table 4. The results show that x_1, x_2, x_1^2, x_1x_2 and x_2x_3 have significant effect on permselectivity of metal ions because the value of Prob > F is less than 0.05 [19].

3.1.2. For malonic acid as complex agent

From the analysis of sequential model and lack of fit, a second-order regression model was suggested. Mul-

Table 3
ANOVA for regression in the case of oxalic acid as a complex agent

Source	Sum of squares	DF	Mean square	F-value	Prob > F
Regress	144.39	9	16.04	30.22	< 0.0001
Residual	3.72	7	0.53		
Total	148.10	16			

R^2 = 0.9685, Adjusted R^2 = 0.9281

Table 4
ANOVA to test significant terms in the regression model for the case of oxalic acid

Effect	Sum of squares	DF	Mean square	F-value	Prob > F
Model	144.39	9	16.04	30.22	< 0.0001
x_1	56.18	1	56.18	105.82	< 0.0001
x_2	59.13	1	59.13	105.72	< 0.0001
x_3	1.42	1	1.42	2.67	0.1460
x_1^2	5.49	1	5.49	10.34	0.0147
x_2^2	0.15	1	0.15	0.28	0.6105
x_3^2	1.18	1	1.18	2.22	0.1797
x_1x_2	18.66	1	18.66	35015	0.0006
x_1x_3	0.020	1	0.020	0.037	0.8531
x_2x_3	4.69	1	4.69	8.83	0.0208

tiple regression analysis of the experimental results gave the following equation:

$$Y = 2.47 + 1.28x_1 + 1.02x_2 + 0.16x_3 - 0.18x_1^2 - 0.20x_2^2 + 0.98x_1x_2 - 0.098x_1x_3 + 0.59x_2x_3 \quad (4)$$

The results of the analysis of variables (ANOVA) for regression model are given in Table 5. The results showed the R^2 (multiple correlation coefficient) of the regression equation obtained from the analysis of variance is 0.9807 (a value > 0.75 indicates aptness of the model) [18], which means that the model can explain 98.07% variation in the response. The results of the analysis of variables for testing the significant terms in the regression model are given in Table 6. The results show that x_1, x_2, x_1x_2 and x_2x_3 have significant (P < 0.05) effect on permselectivity of metal ions [19].

3.1.3. For citric acid as complex agent

From the analysis of the sequential model and lack of fit, a second-order regression model was suggested. Multiple regression analysis of the experimental results gave the following equation:

Table 5
ANOVA for the regression in the case of malonic acid as a complex agent

Source	Sum of squares	DF	Mean square	F-value	Prob > F
Regress	27.32	9	3.04	39.63	< 0.0001
Residual	0.54	7	0.077		
Total	27.38	16			

R^2 = 0.9807, Adjusted R^2 = 0.9560

Table 6
ANOVA to test significant terms in the regression model for the case of malonic acid

Effect	Sum of squares	DF	Mean square	F-value	Prob > F
Model	27.32	9	3.04	39.63	< 0.0001
x_1	13.21	1	13.21	172.46	< 0.0001
x_2	8.34	1	8.34	108.93	< 0.0001
x_3	0.21	1	0.21	2.72	0.1434
x_1^2	0.13	1	0.13	1.64	0.2417
x_2^2	0.16	1	0.16	2.09	0.1915
x_3^2	0.00	1	0.00	0.00	1.0000
x_1x_2	3.82	1	3.82	49.90	0.0002
x_1x_3	0.038	1	0.038	0.50	0.5038
x_2x_3	1.39	1	1.39	18.18	0.0037

$$Y = 1.96 + 0.89x_1 + 0.91x_2 + 0.03x_3 - 0.27x_1^2 + 0.12x_2^2 + 0.12x_3^2 + 0.71x_1x_2 - 0.17x_1x_3 + 0.29x_2x_3 \quad (5)$$

The results of the analysis of variables (ANOVA) for regression model are given in Table 7. The R^2 (multiple correlation coefficient) of the regression equation obtained from the analysis of variance is always larger than 0.9680 (a value > 0.75 indicates aptness of the model) [18], which means that the model can explain 96.80% variation in the response. The results of the analysis of variables for testing the significant terms in the regression model are given in Table 8. The results show that x_1, x_2 and x_1x_2 have significant (P < 0.05) effect on permselectivity of metal ions [19].

In comparison with Eqs. (3), (4) and (5), it can be found that three variables of permselectivity including the concentration ratio of complex agent to metal ions (X_1), pH value of investigated solution (X_2) and concentration of metal ions (X_3), are not independent and the interactions among them are complicated. It is difficult to find a general equation governing the permselectivity behavior of metal ions. However, a second-order polynomial model with using the RSM methodology was suitable to simu-

Table 7
ANOVA for regression in the case of citric acid as a complex agent

Source	Sum of squares	DF	Mean square	F-value	Prob > F
Regress	15.80	9	1.76	23.53	0.0002
Residual	0.52	7	0.075		
Total	16.32	16			

R^2 = 0.9680, Adjusted R^2 = 0.9269

Table 8
ANOVA to test the significant terms in the regression model for the case of citric acid

Effect	Sum of squares	DF	Mean square	F-value	Prob > F
Model	15.80	9	1.76	23.537	0.0002
x_1	6.35	1	6.35	85.17	< 0.0001
x_2	6.57	1	6.57	88.06	< 0.0001
x_3	7.2×10^{-3}	1	7.2×10^{-3}	0.097	0.7651
x_1^2	0.30	1	0.30	4.01	0.0854
x_2^2	0.06	1	0.06	0.79	0.4029
x_3^2	0.06	1	0.06	0.83	0.3936
x_1x_2	2.02	1	2.02	27.03	0.0013
x_1x_3	0.11	1	0.11	1.50	0.2597
x_2x_3	0.34	1	0.34	4.59	0.0695

late the permselectivity behaviors of metal ions through membrane dialysis with a complex agent.

3.2. *Optimization of permselectivity behaviors*

In the case of oxalic acid used as a complex agent, the permselectivity of metal ions can be predicted based on the regression model in Eq. (3). Table 9 lists that the comparisons of the experimental values and predicted values of the regression model. It can be observed from Table 9 that the predicted values are in reasonable agreement with experimental values. Fig. 1 shows the contour plot of the effect of the concentration ratio of the complex agent on metal ions (x_1) and pH value of solution (x_2) by keeping the concentration of metal ions (x_3) at medium level. The results also indicate that the oxalic acid is an optimal complex agent for separation of the Cu^{2+}–Ni^{2+} ion system. The predicted maximum permselectivity was calculated to be 11.22 from Eq. (3). The corresponding optimal variable conditions were 0.96 for concentration ratio of the complex agent to metal ions, 5.48 for pH value of solution, and 0.011 (mol/m^3) for concentration of metal ions with oxalic acid as a complex agent.

Based on the regression model in Eq. (4), the permselectivity of metal ions can be predicted in the case of malonic acid. Comparisons of the experimental values and predicted values of the regression model are shown in Table 9. It can be also seen from Table 9 that the predicted values agree well with experimental values because the residual values are always less than ±0.34. Fig. 2 illustrates the contour plot of the effect of concentration ratio of complex agent on metal ions (x_1) and pH value of solution (x_2) by keeping concentration of metal ions (x_3) at medium level. The maximum permselectivity was calculated to be 5.69 from Eq. (4). The corresponding optimal variable conditions were 0.98 for concentration ratio of the complex agent to metal ions, 5.40 for pH value

Table 9
Comparisons of the predicted values and actual values in the cases of the respective complex agent used as oxalic acid, malonic acid and citric acid

Trial No.	Permselectivity								
	Oxalic acid			Malonic acid			Citric acid		
	Actual	Predicted	Residual	Actual	Predicted	Residual	Actual	Predicted	Residual
1	0.91	0.79	0.12	0.91	0.77	0.14	0.91	0.72	0.19
2	2.20	1.58	0.62	1.30	1.39	–0.09	1.25	1.09	0.17
3	0.95	1.57	–0.62	0.95	0.86	0.09	0.95	1.12	–0.17
4	10.88	11.19	–0.31	5.25	5.39	–0.14	4.13	4.32	–0.19
5	0.87	0.25	0.62	0.87	0.75	0.12	0.89	0.72	0.17
6	6.00	5.69	0.31	3.86	3.52	0.34	3.03	2.84	0.19
7	0.93	1.24	–0.31	0.93	1.27	–0.34	0.93	1.12	–0.19
8	5.78	6.40	–0.62	3.53	3.65	–0.12	2.40	2.57	–0.17
9	2.43	2.36	0.07	1.53	1.68	–0.15	1.43	1.55	–0.12
10	5.50	5.49	0.01	2.34	2.55	–0.21	2.78	2.78	0.00
11	1.13	1.04	0.09	1.03	0.82	0.21	1.03	1.03	0.00
12	9.43	8.95	0.48	4.30	4.05	0.25	3.78	3.43	0.35
13	5.03	5.07	–0.04	2.53	2.47	0.06	1.88	1.96	–0.08
14	4.95	5.07	–0.12	2.45	2.47	–0.02	1.98	1.96	0.02
15	5.20	5.07	0.13	2.40	2.47	–0.07	2.05	1.96	0.09
16	4.95	5.07	–0.12	2.52	2.47	0.05	1.89	1.96	–0.07
17	5.20	5.07	0.13	2.45	2.47	–0.02	1.99	1.96	0.03

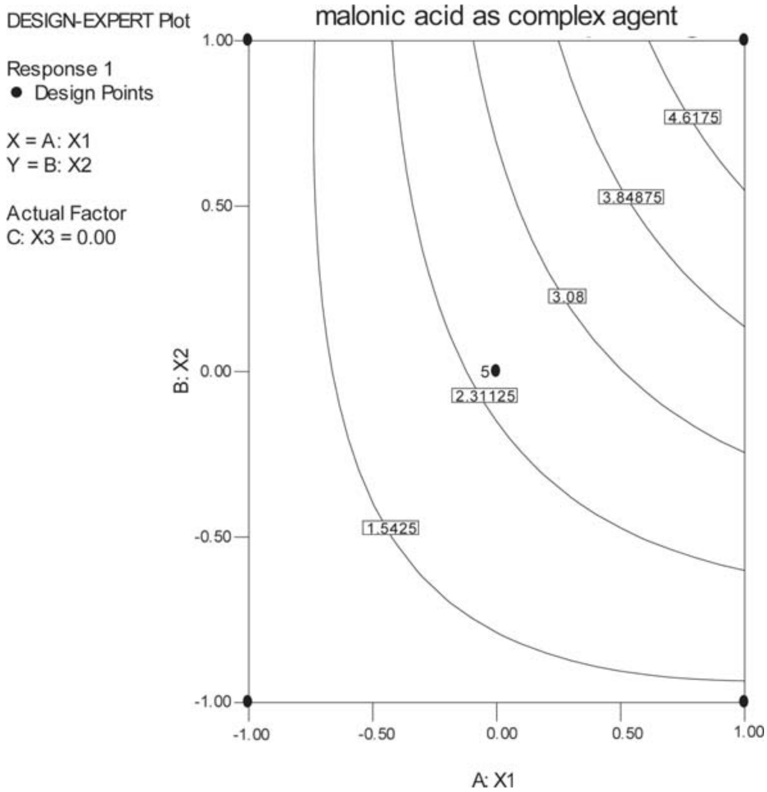

Fig. 1. Contour plot of the effect of x_1 and x_2 for oxalic acid as a complex agent.

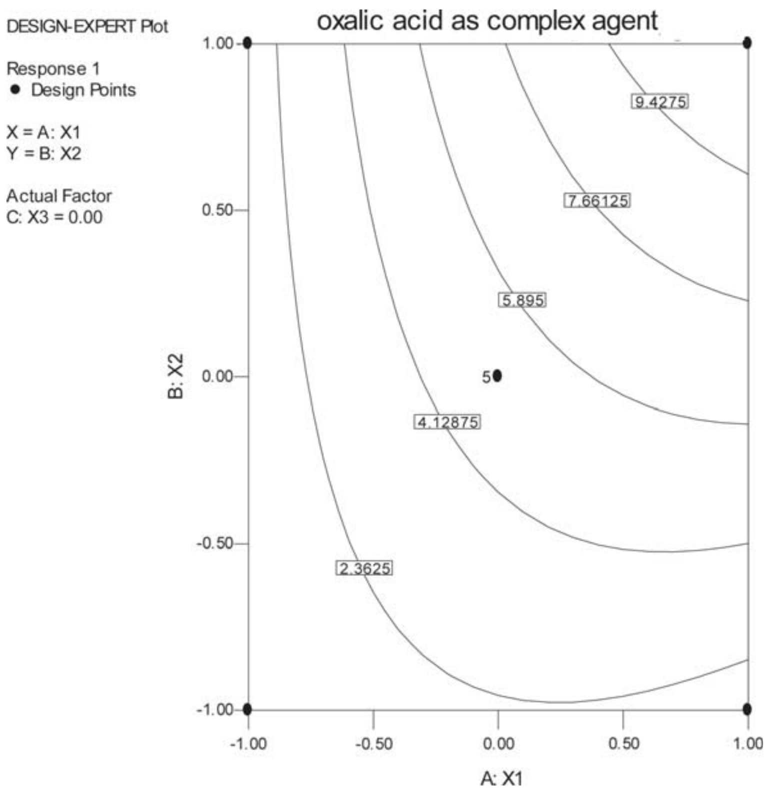

Fig. 2. Contour plot of the effect of x_1 and x_2 for malonic acid as a complex agent.

of solution, and 0.014 (mol/m^3) for concentration of metal ions with malonic acid as a complex agent.

Based on the regression model in Eq. (5), the permselectivity of metal ions can be predicted in the case of citric acid. Comparisons of the experimental values and predicted values of the regression model are tabulated in Table 9. The results revealed that the predicted values are in accordance with experimental values because the residual is less than ±0.35. Fig. 3 depicts the contour plot of the effect of concentration ratio of complex agent on metal ions (x_1) and pH value of solution (x_2) by keeping concentration of metal ions (x_3) at medium level. The maximum permselectivity was calculated to be 4.35 from Eq. (5). The corresponding optimal variable conditions were 0.98 for concentration ratio of complex agent to metal ions, 5.30 for pH value of solution, and 0.015 (mol/m^3) for concentration of metal ions with using citric acid as a complex agent.

3.3. Confirmation test for optimization of permselectivity behaviors

Once the optimal level of the process varables was identified for each complex agent, the confirmation experiment was conducted to validate the optimization model. As shown in Table 10, the predicted optimal values agree well with the experimental results. The results also indicate that the model could be a simple method to stimulate the permselectivity behaviors of metal ions through membrane dialysis with a complex agent

Table 10
Confirmation test for optimization experiments

Complex agent	Variables			Permselectivity	
	x_1	x_2	x_3 (mol/m^3)	Predicted	Measured
Oxalic acid	0.96	5.48	0.011	11.22	11.91
Malonic acid	0.98	5.40	0.014	5.69	5.98
Citric acid	0.98	5.30	0.015	4.35	4.30

4. Conclusion

The preferential transport of metal ions with binary system across the cation-exchange membrane can be effectively enhanced by the addition of a complex agent. The kinds of complex agents, the concentration ratio of complex agent to metal ions, the pH value of solution are the primary factors on the preferential transport behavior of metal ions across the cation-exchange membrane. Data from the present investigation have shown that statistical experimental method is an effective tool to find the optimal separation conditions for the ion

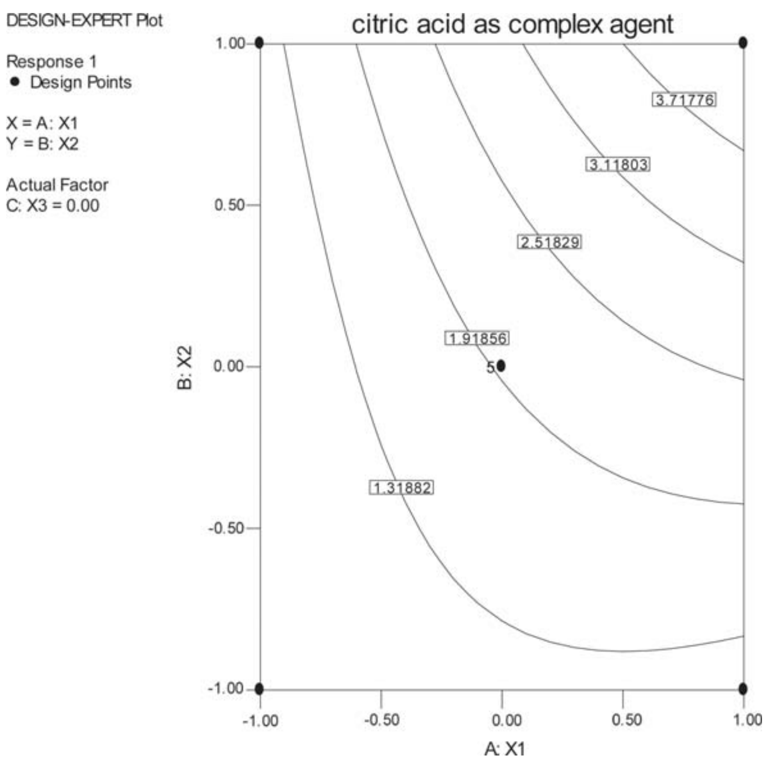

Fig. 3. Contour plot of the effect of x_1 and x_2 for citric acid as a complex agent.

membrane dialysis process combined use a complex agent. The effect of complex agent has the following order: oxalic acid > malonic acid > citric acid for separation of Cu^{2+}–Ni^{2+} ion system. The maximal permselectivity of Cu^{2+}–Ni^{2+} ion system is 11.91 and the corresponding optimal variable conditions were 0.98 for concentration ratio of complex agent to metal ions, 5.48 for pH value of solution, and 0.011 (mol/m^3) for concentration of metal ions with oxalic acid as a complex agent. It was also highlighted that an effective multi-ion fractionation process could be built from the cation-exchange membrane being the separation interface; the driving force being the concentration gradient of counter ion; the suitable complex agent being the separation agent and the pH value is the separation index. The optimal operating condition could be determined by statistical experimental methods.

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