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Micellar-Enhanced Ultrafiltration to Remove Nickel Ions: A Response Surface Method and Artificial Neural Network Optimization

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Abstract: Nickel ions from aqueous solutions were removed by micellar-enhanced ultrafiltration (MEUF), using the surfactant sodium dodecyl sulfate (SDS) as a chelating agent. Process variables and indicators were modeled and optimized by a response surface methodology (RSM), using the Box–Behnken design (BBD). The generated quadratic models described the relationship between a performance indicator (nickel rejection rate or permeate flux) and process variables (pressure, nickel concentration, SDS concentration, and molecular weight cut-off (MWCO)). The analysis of variance (ANOVA) showed that both models are statistically significant. To remove 1 mM of nickel ions, the optimal condition for maximum nickel removal and flux were: pressure = 30 psi, $C_{\text{SDS}} = 10.05$ mM, and MWCO = 10 kDa, resulting in a rejection rate of 98.16% and a flux of 119.20 L/h·m². Experimental verification indicates that the RSM model could adequately describe the performance indicators within the examined ranges of the process variables. An artificial neural network (ANN) modelling followed to predict the MEUF performance and validate the RSM results. The obtained ANN models showed good fitness to the experimental data.

Keywords: nickel removal; optimization; micellar-enhanced ultrafiltration (MEUF); response surface methodology (RSM); Box–Behnken design (BBD); artificial neural network (ANN)

1. Introduction

Nickel is a common heavy metal generated from various industrial activities such as mining, electroplating, batteries manufacturing, metal finishing, and forging. It is carcinogenic, non-biodegradable, and could accumulate and persist in the nature and living organisms [1,2]. Even at low concentrations, nickel can be toxic to the environment and humans. Conventional methods (e.g., chemical precipitation, adsorption, ion exchange, electrodialysis) when treating large-volume aqueous solution containing low concentration of heavy metals (e.g., nickel) can be challenged by secondary pollution of deposition, high cost, low selectivity, and difficulties of recycling metals [3,4]. Although membrane technologies such as reverse osmosis have been successfully used to remove metal ions from aqueous solution with high removal efficiency, their high operational and maintenance costs hinder their wider application. To overcome these drawbacks, micellar-enhanced ultrafiltration (MEUF) provides an alternative for heavy metal removal as it can achieve high removal rate and high permeate flux under mild conditions with lower energy costs [5]. An MEUF integrates a surfactant, which with sufficient dose self-assembles and forms micelles. The micelles then bind metal ions through electrostatic interactions and can be retained by an ultrafiltration membrane [6].

Most MEUF studies for nickel removal used the conventional one-factor-at-a-time method, namely, to examine one operational variable while fixing the others. For example, Karate and Marathe [7]

examined the MEUF removal of nickel by testing a series of factors individually: flow rate, surfactant to metal (S/M) ratio, pH, feed metal ion concentration, pressure, and presence of electrolyte. Tanhaei, et al. [8] investigated the MEUF removal of nickel using single and mixed surfactants. Similarly, they determined the optimum SDS and nickel concentrations by separately examining the effect of SDS concentration, nickel concentration, pressure, and pH. Danis and Aydinler [9] examined the MEUF performance in four stages, by changing surfactant concentrations, nickel concentrations, transmembrane pressure, and electrolyte content separately.

System optimization is important in engineering applications because it is directly related to costs. In MEUF studies, it is crucial to find an optimal operating condition that yields high rejection and high permeate flux simultaneously, with minimal dosage of surfactant and power consumption. Though easy to conduct, the one-factor-at-a-time method tends to involve much labor and resources (many experimental runs) for a multi-variable system and does not provide adequate information on factor interactions or estimate the effects [10]. Besides, the method is difficult to find a true optimal condition with a reasonable number of experimental runs. These limitations can be avoided by using a more systematic experimental method, such as a response surface methodology (RSM). RSM is an experiment- and statistic-based technique that involves multiple factors and their interactions to optimize a process [11]. It has been increasingly used in environmental studies, such as to optimize the process condition for wastewater treatment [12–18]. However, only a few attempts of MEUF have been made to remove heavy metals using the RSM method, mostly focusing on copper, cadmium, and zinc [3,19]. Reports on RSM-based nickel removal using MEUF were rare.

Further, computer modeling can be integrated to describe a complex input-output relationship of a given system. Such approaches are suitable for uncertain or approximate reasoning when the systems are complex to describe with a mathematical model. In recent years, artificial neural network (ANN) has been developed to understand non-linear multi-variable systems [20]. It is a statistical modeling tool to approximate complex functions, especially nonlinear ones between system inputs and outputs, with few requirements for data. A typical ANN consists an input layer, one or more hidden layer with multiple hidden neurons, and an output layer. These layers are mathematically linked by weights and biases. ANN has become an attractive tool for non-linear modelling. It has been used in many fields of science and engineering [21–23] but extremely limited in MEUF studies. Table 1 summarizes the MEUF studies integrating RSM and other optimization models. The integration of ANN to RSM can provide additional information of the process behavior [24], but research efforts in MEUF are scarce (Table 1). These studies examined the removal of lead and zinc from cross-flow ultrafiltration systems, mostly conducted by the same researcher. Though the cross-flow operation could better scale-up to industrial application, most laboratory MEUF studies were carried out under batch operation. The removal of nickel ions from the common dead-end ultrafiltration system is desired.

Table 1. Summary of MEUF studies integrating RSM and other optimization models.

Solute	UF System (Surfactant and Flow)	RSM Design	Independent Variables	Optimization Model	References
Pb ²⁺	SDS, cross-flow	BBD (3 factors and 3 levels, 17 runs)	C _{SDS} (2–6 mM), S/M (5–15), pH (2–12)	ANN and ANFIS	[25]
Zn ²⁺	SDS and Brij-35, cross-flow	FFD (7 factors, 22 runs)	Pressure, pH, C _{SDS} , S/M, L/M, C _{NaCl} , Brij35/SDS ratio	ANN, R ² > 0.91	[26]
Pb ²⁺	SDS, cross-flow	BBD (3 factors, 3 levels)	C _{SDS} (2–6 mM), S/M (5–15), pH (2–12)	Fuzzy logic models, R > 0.91	[27]
Pb ²⁺	CTAB, cross-flow	BBD (3 factors, 3 levels)	C _{SDS} (1.61–6.43 mM), S/M (5.64–13.8), pH (2.34–12.1)	Interval type-2 fuzzy logic	[28]

Surfactant: SDS = surfactant sodium dodecyl sulfate, CTAB = cetyltrimethylammonium bromide. Models: ANFIS = adaptive neuro-fuzzy inference system; ANN = artificial neural network; BBD = Box–Behnken Design; FFD = full factorial design.

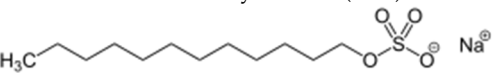
This study examines the process of MEUF to remove nickel ions from dilute aqueous streams. The objectives are to (1) optimize MEUF process conditions using RSM, (2) predict the maximum nickel removal and flux rate under optimal conditions, and (3) verify RSM results using ANN modeling.

2. Materials and Methods

2.1. Materials

All chemicals were of analytical grade and were used as received. The anionic surfactant sodium dodecyl sulfate (SDS, 20% in H₂O) was purchased from Sigma-Aldrich, Canada. Its properties are listed in Table 2. Nickel sulfate hexahydrate (NiSO₄·6H₂O, J.T. Baker) were used as sources of metal ions. The pH of feed solutions was adjusted to 8 ± 0.1. Nickel reference standard solutions (1000 ppm ± 1%/certified) for Flame Atomic Absorption (FAA) tests were purchased from Fisher Scientific and diluted as needed. Distilled water was used in all experimental procedures. Permeate samples were collected and stored using sorption-free materials.

Table 2. Properties of the surfactant used in this study.

Properties	Specifications
Name	Sodium dodecyl sulfate (SDS)
Chemical structure	
Ionic type	Anionic
Molecular weight	288.38 g/mol
Critical micellar concentration (CMC)	8.2–8.3 mM

2.2. Dead-End Ultrafiltration Experiments

Batch experiments were conducted in a stirred ultrafiltration Cell (Amicon Model 8400, EMD Millipore) with a maximum volume uptake of 400 mL. Regenerated cellulose membrane (EMD Millipore, Canada) was used, with 3, 5, and 10 kDa MWCO (diameter of 76 mm and effective area of 0.00418 m²). An initial 250-mL feed solution was filled and continuously stirred (at a constant rate to get effective agitation and prevent membrane fouling) in each experimental run. All experiments were conducted at room temperature (23 ± 1 °C). The applied transmembrane pressure was controlled by pressurized nitrogen gas.

For each ultrafiltration run, 250 mL of feed solution was prepared with designated nickel and surfactant concentrations. When an ultrafiltration run starts, the first 10 mL sample was discarded, then every 20 mL permeate was sampled. The run was terminated when successive five samples were collected and timed. Nickel concentrations of the permeate samples were measured, and their permeate fluxes and rejection rates were determined. For both rejection rate and permeate flux, the average values of five permeate samples for each experimental run were calculated and used as inputs for RSM and ANN modeling. The membrane was cleaned after each run to recover its permeability (indicated by the flux rate of distilled water measured at 40 psi) and can be repeatedly used if over 90% of the original water flux (i.e., flux of distilled water passing the clean membrane at 40 psi) was recovered. Pretreatment of sampling apparatus, storage of samples, and recovery of membranes followed the procedures described by Lin et al. [29]. The experimental scheme and mechanism of MEUF are illustrated in Figure 1.

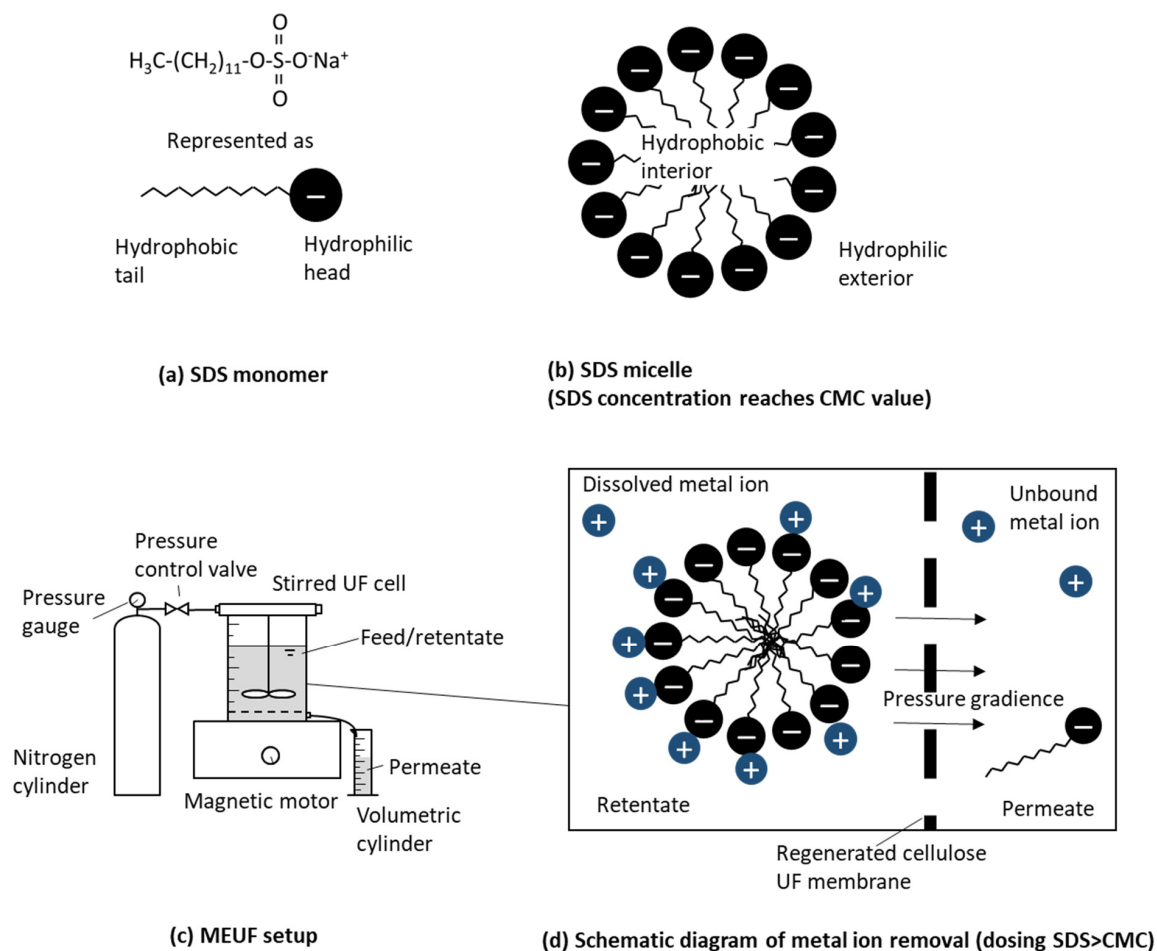


Figure 1. A Schematic diagram of (a) SDS monomer, (b) SDS micelle (when SDS concentration > CMC) (c) micellar-enhance ultrafiltration (MEUF) setup, and (d) mechanism of MEUF removal of metal ions.

2.3. Sample and Data Analysis

The nickel concentration in permeate samples (C_p) were measured using a Varian Model 55B SpectrAA FAA Spectrophotometer at 232.0 nm. The mean values of triplicate measurements for each permeate sample were calculated (%RSD $\leq 1.3\%$). FAA calibration curves were made before each set of measurement ($R^2 > 0.999$).

To evaluate the removal efficiency of nickel ions using MEUF, the nickel rejection rate (R) and permeate flux (J) of the metal were calculated as follows:

$$R(\%) = \left(1 - \frac{C_p}{C_r}\right) \times 100 \quad (1)$$

where C_p and C_r denote the nickel concentration in the permeate and retentate, respectively. C_r was calculated using material balance.

$$J(L/h \cdot m^2) = \frac{V_p}{t \times A_m} \quad (2)$$

where V_p is the volume of the permeate sample; t is the sampling time; and A_m is the effective area of the membrane.

2.4. Response Surface Modeling

The RSM modeling and optimization consist the following steps: (1) statistical design of experiment, where all process variables vary simultaneously over experimental runs; (2) define coefficients of

variables (and their interactions) in the mathematical model based on experimental results; (3) check the adequacy of the regressed model; and (4) predict the optimal experimental condition and responses using the model.

2.4.1. Design of Experiments

In this study, an RSM model based on Box–Behnken design (BBD) was used to optimize the four independent variables (factors) and to observe their effect on MEUF performance in terms of rejection rate and permeate flux. A BBD entails factors at high (+1), basic (0), and low (−1) levels. The center points (coded level 0 or the basic level), which were the midpoints between the high and low levels, were repeated multiple times. Table 3 presents the factors and levels set by the BBD. The design consists of 29 experimental runs, including 5 replicates of the central experiments to check the analysis repeatability and to estimate the experimental error. The responses (rejection rate and permeate flux) were determined experimentally according to designed runs. Design-Expert (version 11.1) was used for RSM modeling.

Table 3. Factors and levels set by Box–Behnken design (BBD).

Factors	Levels		
	Minimum (−1)	Center (0)	Maximum (+1)
(A) Pressure (psi)	30	40	50
(B) Ni concentration (mM)	0.5	1.25	2
(C) SDS concentration (mM)	8.3	16.6	24.9
(D) Molecular weight cut-off, or MWCO (kDa)	3	5*	10

* The center point 5 kDa MWCO was used instead of 6.5k Da due to the size of commercial membrane.

2.4.2. RSM Modeling

To determine the mathematical relationship between the responses and factors the following second-order polynomial equation was used to fit the experimental data obtained from the BBD experimental design. The response surface model includes the main, quadratic, and interactions terms:

$$Y = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} X_i X_j \quad (3)$$

where Y is the predicted response; b_0 the constant coefficient, b_i the linear coefficients, b_{ii} the quadratic coefficients, b_{ij} the interaction coefficients; n the number of design variables, and X_i , X_j the coded levels of design variables.

Stepwise regression procedure was performed using backward elimination method to excludes non-significant terms (p-values > 0.05) from the initial response surface model. The regression coefficients of the reduced model are computed by multiple linear regression (MLR) method to minimize the sum of square of the residuals. The validity of the empirical model was tested using analysis of variance (ANOVA) at 95% confidence level. The fitted model was assessed by the R-squared (R^2), the adjusted R-squared (R^2 -adj), and the predicted R-squared (R^2 -pre). The R^2 value increases with the number of model terms, even when non-significant terms are added to the model. Therefore, the R^2 value of a refined model is usually smaller than that of the full model. The R^2 -adjusted coefficient is used to adjust to the number of model terms, where the addition of non-significant terms usually decreases the R^2 -adjusted value. The predicted R-squared shows how well a model predicts responses for new observations. Based on the obtained response surface models, optimal conditions were determined by maximizing the nickel rejection and the permeate flux.

2.5. Artificial Neural Network (ANN) Modeling

The BBD design (factors and levels) and the corresponding responses were used to develop the ANN model, using the neural network toolbox for MATLAB 2016b. An ANN model with one hidden layer was trained to simulate nickel removal by MEUF. The inputs were pressure, feed nickel concentration, feed SDS concentration, and MWCO, whereas the outputs were rejection rate and permeate flux. All inputs and outputs were normalized into the range of (0, 1) to avoid putting too much weight on variables with a large variance. Twelve neurons in the hidden layer were optimized for the ANN model following Jing, et al. [30]. Datasets were randomly divided into training (70%), validation (15%), and testing (15%) subsets. The model was trained by minimizing the mean squared error (MSE) while maximizing the correlation coefficients (R) between the experimental and modeling outputs. The two outputs, i.e., rejection rate and permeate flux, were given equal weightings when calculating R^2 for the ANN model. For comparison purposes, an inverse range scaling was performed on all modeling outputs to transfer them from (0, 1) to their original scales.

3. Results and Discussion

3.1. Ultrafiltration Experimental Results

Experimental results (i.e., nickel rejection rates and permeate flux) of the BBD design are reported in Table 4. The maximum rejection rate of nickel is 98.70% (flux = 23.03 L/h·m²) in run 17, with a transmembrane pressure of 30 psi, nickel concentration of 1.25 mM, SDS concentration of 16.6 mM, and MWCO of 3 kDa. The maximum flux 178.28 L/h·m² ($R = 91.83\%$) was found in run 26 with 50 psi pressure, 1.25 mM nickel, and 16.6 mM SDS using membrane MWCO of 10 kDa. It can be seen that higher rejection (or flux) tends to compromise on lower flux (or rejection), yet in practice high values of both rejection (indicates MEUF effectiveness) and flux (indicates efficiency) are desired. As such, an operating condition generating high rejection and flux is needed.

Table 4. Design layout and experimental results of BBD design.

Std.	Run	Factor Input Variables				Response Variable	
		Factor A Pressure (psi)	Factor B Ni conc. (Mm)	Factor C SDS conc. (Mm)	Factor D MWCO (kDa)	Rejection ^a (%)	Flux ^a (L/h·m ²)
13	1	40	0.5	8.3	5	94.86	37.93
18	2	50	1.25	8.3	5	92.98	45.15
25	3	40	1.25	16.6	5	98.13	36.83
7	4	40	1.25	8.3	10	94.30	158.67
29	5	40	1.25	16.6	5	97.09	37.43
20	6	50	1.25	24.9	5	98.13	43.31
6	7	40	1.25	24.9	3	97.15	29.96
19	8	30	1.25	24.9	5	98.17	28.74
22	9	40	2	16.6	3	97.98	31.03
23	10	40	0.5	16.6	10	97.76	148.64
14	11	40	2	8.3	5	88.06	37.41
10	12	50	1.25	16.6	3	98.67	38.25
3	13	30	2	16.6	5	96.15	29.27
28	14	40	1.25	16.6	5	96.59	39.51
11	15	30	1.25	16.6	10	97.84	115.56
27	16	40	1.25	16.6	5	96.32	37.78
9	17	30	1.25	16.6	3	98.70	23.03
26	18	40	1.25	16.6	5	96.47	36.45
8	19	40	1.25	24.9	10	80.53 ^b	149.23
4	20	50	2	16.6	5	95.70	45.36
2	21	50	0.5	16.6	5	95.08	46.16
17	22	30	1.25	8.3	5	91.31	28.78

Table 4. Cont.

Std.	Run	Factor Input Variables				Response Variable	
		Factor A Pressure (psi)	Factor B Ni conc. (Mm)	Factor C SDS conc. (Mm)	Factor D MWCO (kDa)	Rejection ^a (%)	Flux ^a (L/h·m ²)
16	23	40	2	24.9	5	98.20	35.00
21	24	40	0.5	16.6	3	98.40	29.10
1	25	30	0.5	16.6	5	90.43 ^b	30.19
12	26	50	1.25	16.6	10	91.83	178.28
15	27	40	0.5	24.9	5	96.94	35.67
24	28	40	2	16.6	10	93.53	138.17
5	29	40	1.25	8.3	3	92.61	28.96

^a Rejection/flux values of an ultrafiltration run are the mean values of rejection/flux of all permeate samples (n=5) in that run. ^b Observed outliers; eliminated from analysis.

3.2. RSM Models

Goodness-of-fit of the regression model is evaluated using ANOVA by testing the significance of the regression model, significance of individual model coefficients, and lack-of-fit. For both rejection and flux models the assumptions for ANOVA are met, e.g., the residuals are normally and randomly distributed (figures not shown). Tables 5 and 6 summarize the ANOVA analysis for rejection and flux, respectively, showing the goodness-of-fit of the quadratic models. The regression models for nickel rejection and permeate flux are statistically significant at the 95% confidence level in the studied range.

Table 5. ANOVA for reduced quadratic model (response: rejection).

Source	Sum of Squares	df	Mean Square	F-Value	p-Value	
Model	158.79	8	19.85	12.61	<0.0001	significant
A-Pressure	12.24	1	12.24	7.78	0.0121	
B-C-Ni	10.51	1	10.51	6.68	0.0187	
C-C-SDS	17.18	1	17.18	10.92	0.0039	
D-MWCO	13.18	1	13.18	8.37	0.0097	
AD	12.10	1	12.10	7.69	0.0125	
BC	16.26	1	16.26	10.33	0.0048	
CD	7.33	1	7.33	4.66	0.0447	
C ²	27.39	1	27.39	17.40	0.0006	
Residual	28.33	18	1.57			not significant
Lack of Fit	26.16	14	1.87	3.46	0.1200	
Pure Error	2.16	4	0.5409			
Cor Total	187.12	26				

Fit statistics: $R^2 = 0.8486$, Adjusted $R^2 = 0.7813$, Predicted $R^2 = 0.4481$. df = degree of freedom.

Table 6. ANOVA for reduced quadratic model (response: flux).

Source	Sum of Squares	df	Mean Square	F-Value	p-Value	
Model	10.68	4	2.67	2173.32	<0.0001	significant
A-Pressure	0.5914	1	0.5914	481.41	<0.0001	
C-C-SDS	0.0033	1	0.0033	2.67	0.1151	
D-MWCO	7.65	1	7.65	6229.95	<0.0001	
D ²	0.3832	1	0.3832	311.97	<0.0001	
Residual	0.0295	24	0.0012			not significant
Lack of Fit	0.0256	20	0.0013	1.31	0.4387	
Pure Error	0.0039	4	0.0010			
Cor Total	10.71	28				

Data were transformed into natural log. $R^2 = 0.9972$, Adjusted $R^2 = 0.9968$, Predicted $R^2 = 0.9958$.

The significance of the model on rejection rate was determined by Fisher test, indicated by the F-value. The model F-value of 12.61 indicates that the model is significant, with a 0.01% chance that an F-value could occur due to noise. The lack-of-fit F-value of 3.46 indicates that there is a 12% chance

that an F-value could occur due to noise. The calculated R^2 (0.8486) and adjusted R^2 (0.7813) was reasonably close to 1, showing good fitness of the regressed model. The difference between predicted R^2 and the adjusted R^2 is over 0.02. This may be due to the close values of the response (which can be sensitive to experimental and measurement errors).

The flux model shows great fitness. The model F-value of 2171.32 indicates that the model is highly significant, with only 0.01% chance that the value could occur due to noise. Non-significant lack-of-fit ($p = 0.4387$) also indicates good fitness of the model. Both R^2 (0.9972) and adjusted R^2 (0.9968) show good fitness of the regressed model. High predicted R^2 (0.9958) indicates that the model can well predict response for new observations.

Regression model for nickel rejection:

Significant model terms ($p < 0.05$) are coded factors A, B, C, D, AD, BC, CD, and C^2 . The reduced regression model (coded factors) for nickel rejection was determined as:

$$\text{Rejection} = 96.48 - 1.15 A - 0.99 B + 1.77 C - 1.17 D - 1.65 AD + 2.02 BC - 1.84 CD - 2.17 C^2 \quad (4)$$

where coded factor subject to the level of $(-1,1)$.

The regressed model in terms of actual factors is:

$$\text{Rejection} = 80.35 + 0.19 \text{ Pressure} - 6.69 C_{\text{Ni}} + 1.26 C_{\text{SDS}} + 2.60 \text{ MWCO} - 0.05 (\text{Pressure}) (\text{MWCO}) + 0.32 C_{\text{Ni}} C_{\text{SDS}} - 0.06 (C_{\text{SDS}})(\text{MWCO}) - 0.03 (C_{\text{SDS}})^2 \quad (5)$$

where factors subjected to: $30 \leq \text{pressure} \leq 50$ psi, $0.5 \leq C_{\text{Ni}} \leq 2$ mM, $8.3 \leq C_{\text{SDS}} \leq 24.9$ mM, $3 \leq \text{MWCO} \leq 10$ kDa. Equations (4) and (5) can be used to predict the nickel rejection for given levels of each factor.

The coefficients of coded factors indicate that the importance of the factor is in the order: $BC > CD > C > AD > D \approx A > B$, i.e., interaction of nickel concentration and SDS concentration $>$ interaction of SDS concentration and MWCO $>$ SDS concentration $>$ interaction of pressure and MWCO $>$ MWCO $\approx$ pressure $>$ nickel concentration.

Regression model for permeate flux:

Table 6 shows that A, D, AD, A^2 , D^2 are significant model terms. The final equation in terms of coded factors is:

$$\ln(\text{Flux}) = 3.89 + 0.22 A - 0.02 C + 0.80 D + 0.30 D^2 \quad (6)$$

where coded factor subject to the level of $(-1,1)$.

Final equation in terms of actual factors is:

$$\ln(\text{Flux}) = 2.59 + 0.02 \text{ Pressure} - 0.002 C_{\text{SDS}} - 0.09 \text{ MWCO} + 0.024 (\text{MWCO})^2 \quad (7)$$

where factors subjected to: $30 \leq \text{pressure} \leq 50$ psi, $0.5 \leq C_{\text{Ni}} \leq 2$ mM, $8.3 \leq C_{\text{SDS}} \leq 24.9$ mM, $3 \leq \text{MWCO} \leq 10$ kDa.

The importance of factors is: $D > A > C$, i.e., MWCO $>$ pressure $>$ C_{SDS} .

3.3. Effect of Factors on Rejection Rate and Permeate Flux

The response surface plots show the effect of pressure, nickel concentration, SDS concentration, and MWCO on rejection rate and permeate flux. The response surface and contour plot enable visualization of parameter interaction. Based on the ANOVA results, three interaction effect (i.e., pressure and MWCO, feed nickel and SDS concentration, feed SDS concentration and MWCO) on rejection rate and three individual effect (i.e., pressure, feed SDS concentration, and MWCO) on flux will be discussed.

3.3.1. Effect of Factors on Rejection

ANOVA results indicate significant interaction effect between pressure and MWCO on rejection. Figure 2 shows the effect of pressure and MWCO on rejection, when feed nickel and SDS concentrations

were fixed at their central levels. Pressure seems to affect the rejection rate more at higher MWCO than the lower end. The rejection rate was relatively stable with the increase in pressure at MWCO of 3 kDa but considerably dropped at MWCO of 10 kDa (Figure 2a). Previous one-factor-at-a-time studies showed that pressure alone had a small effect on the rejection rate. For example, Huang, et al. [31] examined the rejection under a transmembrane pressure of 40 to 800 kPa and found that pressure did not significantly change the rejection rate. Mulligan et al. (2011) reported similar conclusions for a pressure range from 30 to 140 kPa. This observation can be explained, because the pressure does not affect the interaction between metal ions and the surfactant but mainly provides a driving force for mass transport across the membrane.

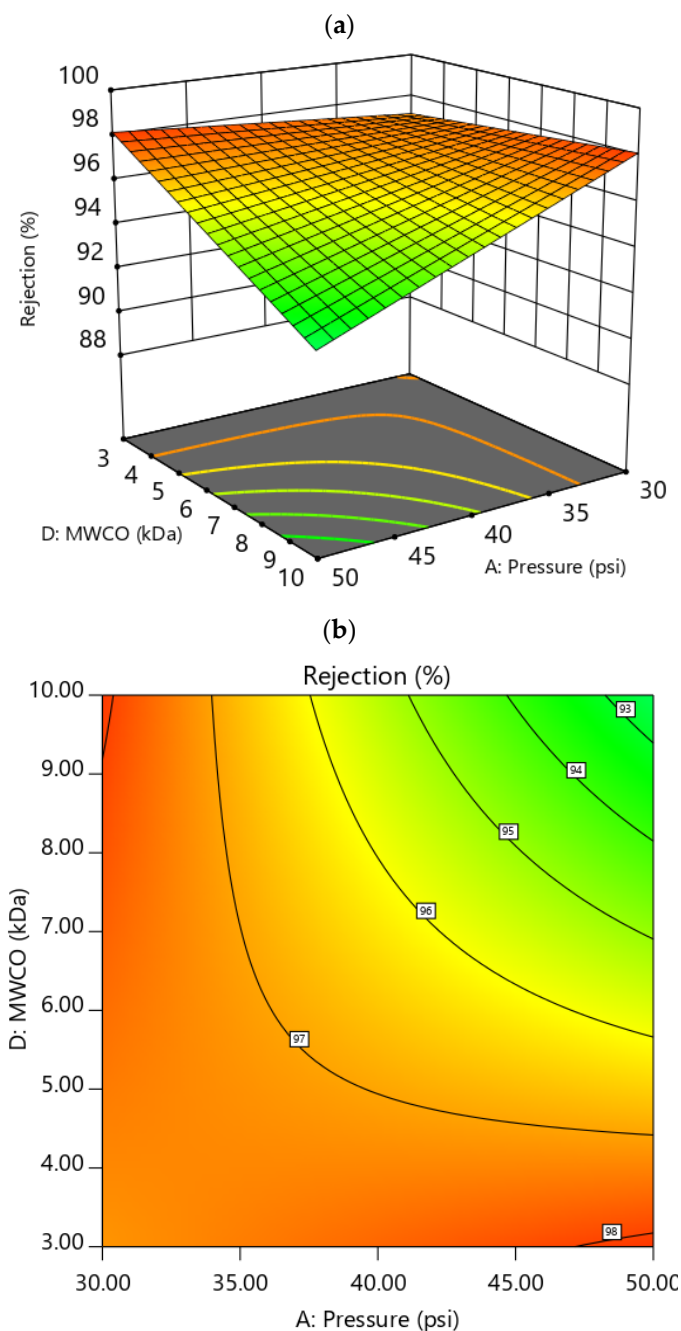


Figure 2. Response surface (a) and contour (b) showing the effect of pressure and MWCO on rejection rate. $C_{Ni} = 1.25\text{mM}$, $C_{SDS} = 16.6\text{mM}$.

In terms of MWCO, smaller MWCO tend to generate higher rejection (Figure 2 and Figure 4). The observation is in agreement with previous findings. For example, Baek and Yang [32] reported higher chromate rejection (>99%) using membrane MWCO of 3 kDa than that of 10 kDa (98%). Bade and Lee [33] reported 98% rejection of chromate using the surfactant cetylpyridinium chloride (CPC) with 100 kDa membrane and 97% with 300 kDa membrane.

Figure 3 shows the predicted response under different metal and surfactant concentrations, when the pressure and MWCO were fixed as their central values. It can be seen that, at a lower SDS concentration (1 CMC), low metal concentrations result in high rejection rate. At higher nickel concentration, the decrease in rejection might be attributed to a lack of available binding sites. To sum up, MEUF is more efficient to treat dilute (i.e., low concentration) nickel streams, showing an advantage to traditional techniques (e.g., precipitation) that are inefficient at dilute streams. Alternatively, MEUF could be used as a secondary treatment method.

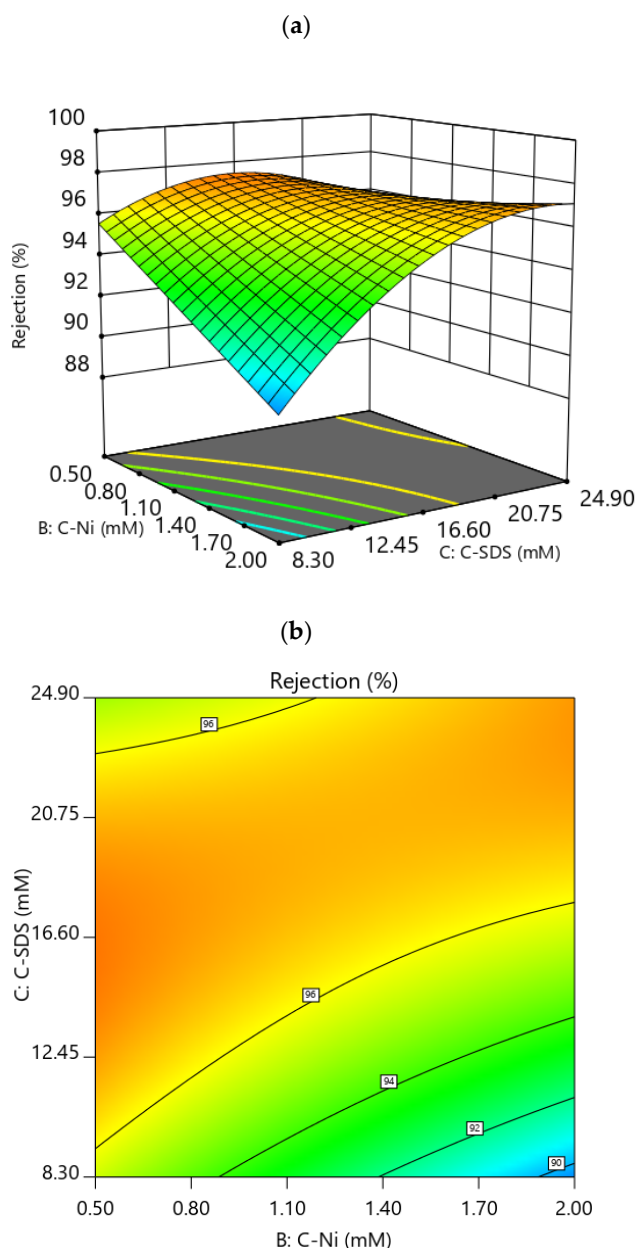


Figure 3. Response surface (a) and contour (b) showing the effect of nickel and SDS concentrations on rejection rate. Pressure = 40 psi, MWCO = 5 kDa.

In the examined concentration range, higher SDS concentration resulted in higher rejection of nickel ions. When SDS concentration increased to approximately 20 mM no further increase in rejection is observed. Therefore, increasing the SDS feed concentration enhances the rejection of heavy metals until certain limits. The maximum rejection might be due to the competition between the surfactant sodium ions and nickel ions. The electrostatic interaction between the anionic micellar surface and nickel cations depends on the ion charge and concentration. At first, when increasing the SDS feed concentration, a higher fraction of surfactants will be in the micellar form. This will increase the surface charge; hence, more divalent nickel ions will be adsorbed on the micellar surface displacing the sodium ions. This ion exchange will consequently enhance heavy metal rejection. However, at low heavy metal feed concentration, when SDS concentration is further increased to concentration up to 20 mM, the sodium counter ion concentration might increase to an extent that the adsorption of sodium counter ions is favored. Therefore, no further increase in nickel rejection is achieved, as shown in Figures 3a and 4a.

3.3.2. Effect of Factors on Flux

Pressure, SDS concentration, and MWCO significantly contribute to the flux rate. When the pressure was increased from 30 to 50 psi, the permeate flux rate increased. The permeate flux follows the Darcy's law [34], i.e., $J = L_p \times \Delta P$ where the membrane permeability $L_p = 1/(\eta \cdot R_M)$, where η is the viscosity of the solution and R_M is the membrane resistance. If the permeate flux linearly increases with pressure, the separation process is under the pressure controlled region, where the concentration polarization is negligible [4]. This linear relationship was observed in the present study (figure not shown), indicating that concentration polarization was not obvious, and that the membranes performed well.

SDS concentration was found negatively and linearly related to the flux rate. Increasing amount of SDS forms more SDS micelles which are retained by the membrane. The retained micelles may concentrate on the membrane surface or in its pores, hence reducing the permeate flux. The decrease in flux rate with the increase in surfactant concentration has been reported in literature [34]. In addition, nickel concentration seems to have little effect on flux. This can be explained by the small size of nickel ions which can easily pass the ultrafiltration membrane.

A higher MWCO (i.e., bigger pore size) of the membrane increases the permeate flux. Nonlinear relationship between MWCO and flux was observed. Flux rate gradually increases with MWCO in its lower ranges (3–7 kDa) and quickly increase at higher ranges (7–10 kDa).

3.4. RSM Optimization

The economic operation of the membrane processes draws attention to achieve lower costs in practice. As such, the MEUF process desires to use lower transmembrane pressures (minimize pressure) and lower dosages of surfactant (minimize C_{SDS}) to treat large volumes of water (maximize flux rate), as well as obtaining a high efficiency in removing nickel ions (maximize rejection).

The optimal conditions of the MEUF of nickel were obtained using the desirability function approach in Design Expert. The condition was found by maximizing rejection and flux (defined by equations 5 and 7, respectively) when setting minimum pressure, $C_{Ni} = 1$ mM, minimum C_{SDS} , and $3 \leq MWCO \leq 10$ kDa. The predicted maximum rejection rate (major response) and flux (secondary response) are 98.16% and 119.20 L/h·m², respectively, where pressure = 30 psi, $C_{Ni} = 1.0$ mM, $C_{SDS} = 10.05$ mM, and MWCO = 10 kDa.

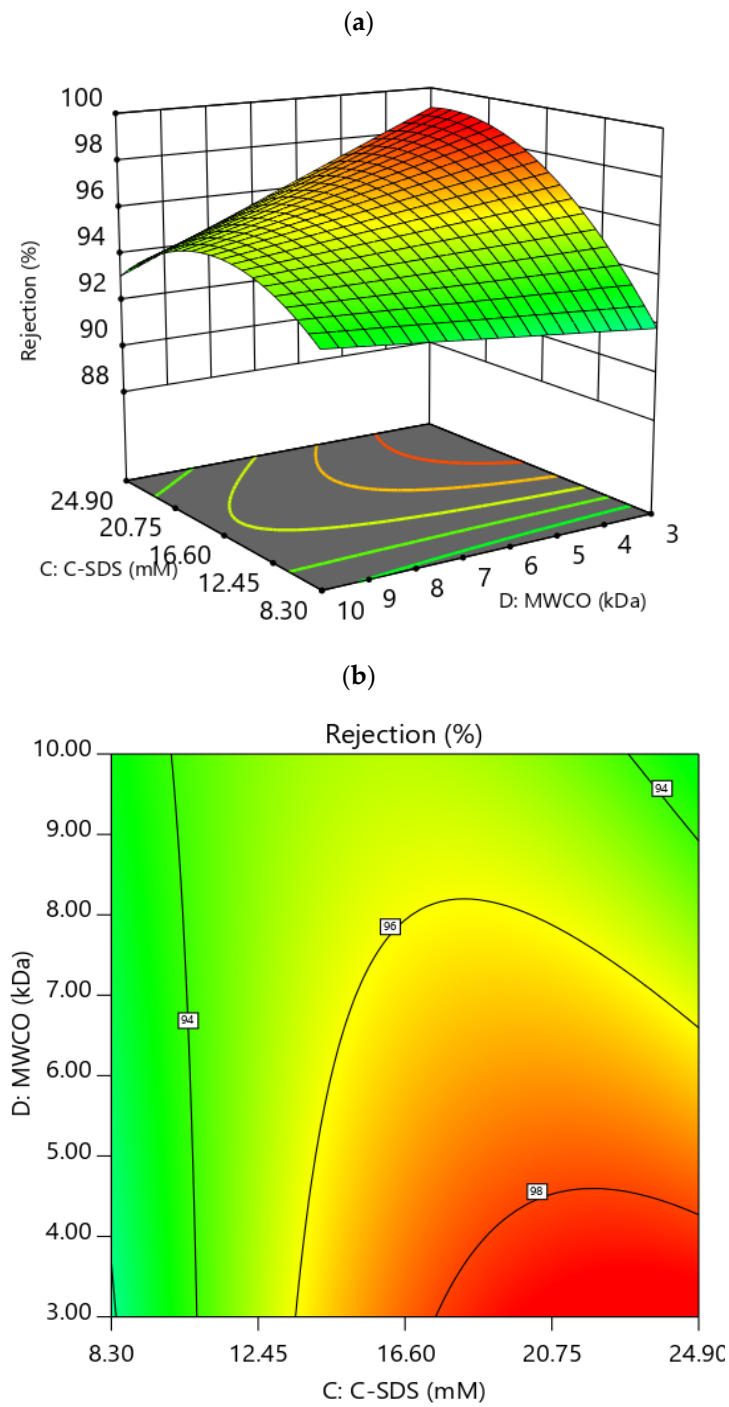


Figure 4. Response surface (a) and contour (b) showing the effect of SDS concentration and MWCO on rejection rate. Pressure = 40 psi, $C_{Ni} = 1.25$ mM.

3.5. ANN Modeling

To predict the values of rejection rate and permeate flux using the ANN model, 75% of the data were randomly used for training purpose. The remainders were categorized as testing and validation data. In order to evaluate the ANN model, the model was presented with new values of rejection and flux that were not used during the training. The rejection and flux values estimated by ANN models were then compared with their corresponding actual values. The scatter regression plots of the ANN model shows the predicted values of rejection and flux against their experimental values (Figures 5 and 6, respectively). Due to the inverse rescaling, two outputs, i.e., rejection rate and permeate flux, were first converted from (0, 1) and then plotted together within their original ranges. The best linear fit equations for the training, validation, testing, and overall subsets mostly had a slope between 0.99 and 1, and the values of R^2 were all higher than 0.99 (except for the testing values for rejection model, $R^2 = 0.719$), indicating a close match between the experimental and modeling results. Therefore, the trained ANN model was able to accurately simulate the rejection rate and permeate flux for nickel removal process.

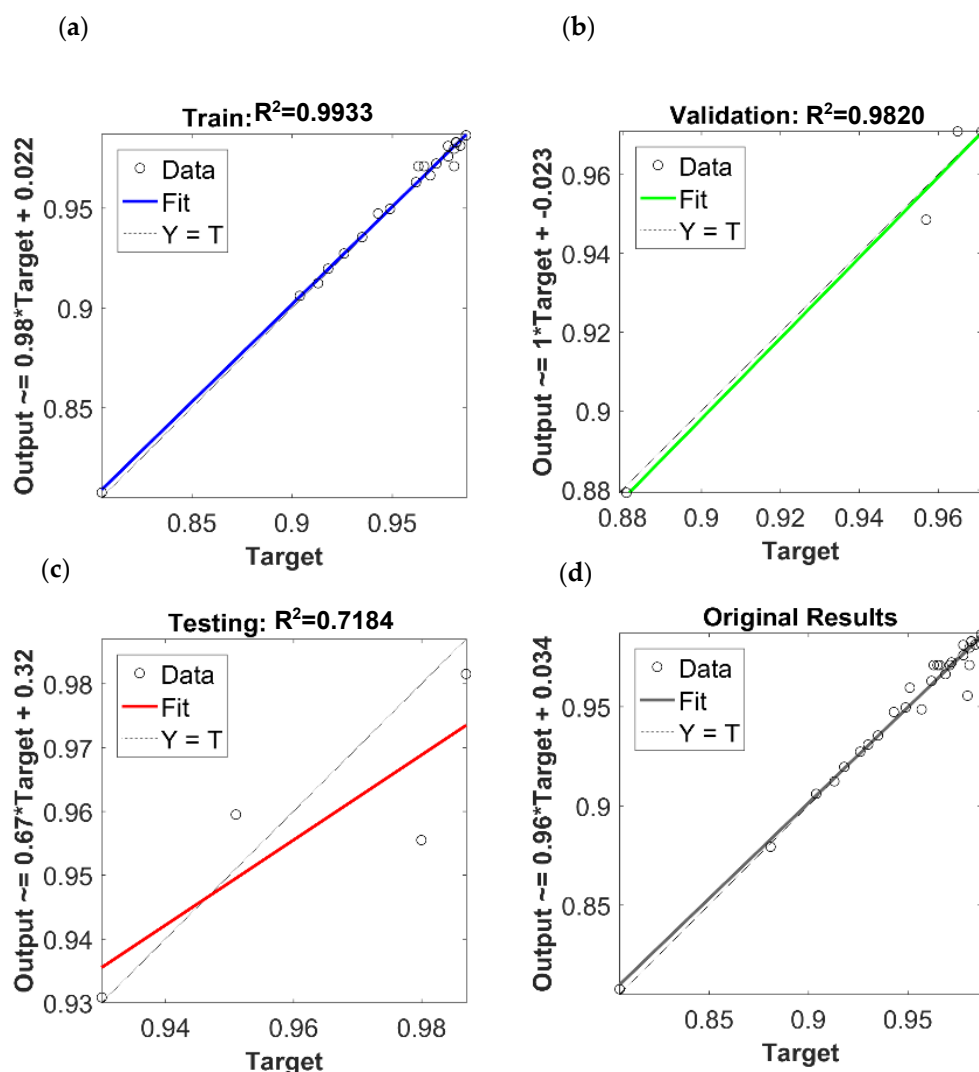


Figure 5. The scatter plots of ANN model predicted values (rejection rate of nickel ions) versus experimental values for (a) training, (b) validation, (c) testing, and (d) all data sets.

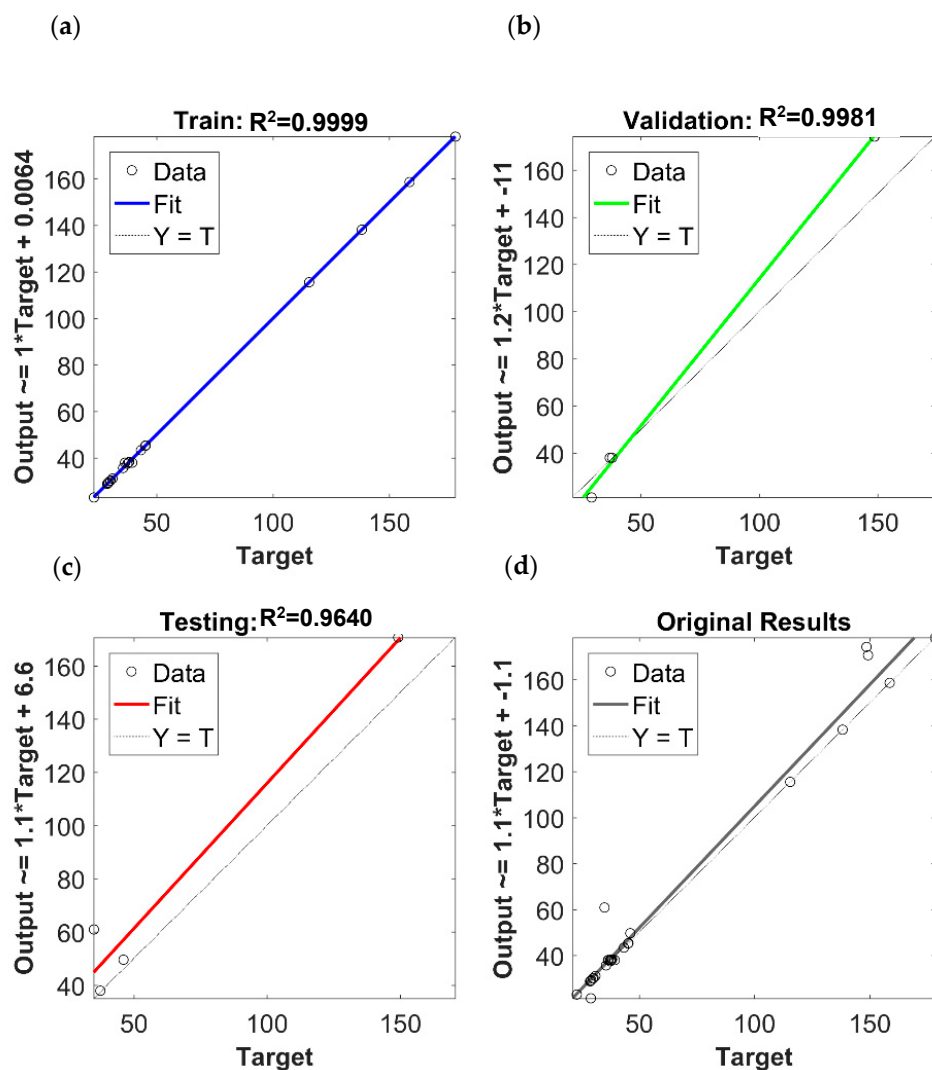


Figure 6. The scatter plots of ANN model predicted values (permeate flux) versus experimental values for (a) training, (b) validation, (c) testing, and (d) all data sets.

4. Conclusions

This paper demonstrated the feasibility of using BBD (an RSM design) to study the effect of process variables (pressure, nickel concentration, SDS concentration, and MWCO) on MEUF performance to remove nickel ions from aqueous solutions. RSM generated quadratic models for rejection and flux, respectively. The results showed that all factors significantly contribute to the rejection rate, namely the effectiveness of a MEUF process (importance follows: SDS concentration > MWCO $\approx$ pressure > nickel concentration). Pressure and MWCO are significant factors contributing to the permeate flux (importance: MWCO > pressure). Among the range of factors in the study, the optimal conditions to remove 1 mM nickel ions from aqueous solutions while obtaining the highest rejection (98.16%) and flux (119.20 L/h·m²) are: pressure = 30 psi, C_{SDS} = 10.05 mM, and MWCO = 10 kDa. Verification experiments showed that the quadratic models could adequately predict the MEUF performance. Furthermore, ANN modeling showed good model fitness to the experimental data. This study shows that RSM and ANN models could be used and provide information for the MEUF treatment of nickel-contaminated water. In future works, a cross-flow MEUF system will be used to better reflect the industrial practice. Furthermore, the recycle and reuse of SDS will be attempted to further reduce the capital cost.

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