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Statistical-Based Modeling and Optimization of Chlorophenol Removal from Wastewater Using Reverse Osmosis Process

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This paper focuses on the modelling and optimisation of the removal of chlorophenol from wastewater using multifactorial analysis. The development of the corresponding mathematical model is based on a specific set of experimental data of chlorophenol removal from wastewater derived from the literature. An analysis of variance (ANOVA) is used to investigate the most important independent variables and their interaction(s), which affect process performance. This in turn is used to develop two empirical model correlations for the rejection of chlorophenol and recovery rate using the multiple linear regression technique. The linear coefficients of the model correlations are estimated using the statistical software SPSS. The predictions of the model developed are compared to observed data and show high confidence level of R^2. Finally, the optimised control variables, which achieved both optimal rejection and recovery rate were explored further based on the upper and lower limits of the associated independent variables.

1. Introduction

Reverse Osmosis (RO) process has been proved in several studies to offer an effective and economic method for destroying unwanted organic compounds in wastewater including more particularly phenolic compounds (Reverberi et al., 2014). Several analytical models developed based on the principles of solution diffusion model have been successfully used to predict the removal of chlorophenol from wastewater using spiral wound RO process (Al-Obaidi and Mujtaba, 2016). Similarly, other advanced techniques have been used successfully to model and investigate the interactions of the independent variables on the performance of the RO process in respect of rejection and recovery rate. They include the use of Artificial Neural Network (ANN), Response Surface Method (RSM) and Factorial Design (FD) (Khayet et al., 2011). To the best of authors' knowledge, no modelling and optimisation method for the removal of phenolic compounds from wastewater using statistical analysis has yet been explored.
This research centres on the development of a statistical-based model for the removal of chlorophenol from wastewater in a spiral wound RO process. A multifactorial design methodology including analysis of variance (ANOVA) is used to investigate the interaction of the independent variables; i.e. feed concentration, pressure, temperature, and flow rate on the dependent variables; i.e. chlorophenol rejection and recovery rate using the experimental data of Sundaramoorthy et al. (2011). Multifactorial design has been selected because it facilitates the identification of the main factors, which have high impact on process performance using an optimised number of designed experiments. It will also yield an empirical model based on a second-grade quadratic equation. The consistency of which will be determined dependent on the R^2 value between model prediction results and experimental data of the removal of chlorophenol from wastewater. Finally, the optimisation of the model is realised using the desirability function available in the statistical software SPSS.

2. Review of the Experimental Work of Sundaramoorthy et al. (2011) and Data Generation

A pilot-scale cross-flow RO filtration system of a spiral wound RO process has been used by Sundaramoorthy et al. (2011) to remove chlorophenol from wastewater. The characteristic of the membrane used, and the transport parameters of water and chlorophenol are given in Table 1. The operating conditions used are:

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2.166x10^{-4}–2.583x10^{-4} m³/s, 0.778x10^{-3}–6.226x10^{-3} kmol/m³, 5.83–13.58 atm and 29.5–32.5 °C of feed flow rate, concentration, pressure, and temperature respectively. This set of data represents a reasonable range of pressure and concentration. However, the feed flow rate and temperature limit investigated was insignificant. This paper explores further this limitation by analysing extended limits of these variables and investigate their impact(s) on the process rejection and recovery rate. This is carried out by compiling a new set of data based on the experimental data of Sundaramoorthy et al. (2011). Sundaramoorthy et al. (2011) have developed a model that has been validated against the experimental data of chlorophenol and represents a high degree of consistency. This same model has been coded in the gPROMS software suite and used to solve a wide range of operating parameters. This also confirmed the ability of this model to predict process performance. The same code has now been used to generate new data for the extended limits of feed flow rate and temperature. The model has been extended to include two new equations to investigate the impact of operating temperature on the transport water $A_{w(T)}$ (m/s atm) and chlorophenol $B_{s(T)}$ (m/s) parameters as shown in Eq(1) and Eq(2).

$$A_{w(T)} = A_{w(T_o)} \frac{\mu_{b(T_o)}}{\mu_{b(T)}} \tag{1}$$

$$B_{s(T)} = B_{s(T_o)} \frac{(T+273.15)}{(T_o+273.15)} \frac{\mu_{b(T_o)}}{\mu_{b(T)}} \tag{2}$$

$A_{w(T_o)}$, $B_{s(T_o)}$ and $\mu_{b(T_o)}$ are the water and chlorophenol transport parameters and viscosity (kg/m s) at reference temperature respectively. The reference temperature is taken as 31 °C due to generating the transport parameters at such temperature (Sundaramoorthy et al., 2011). While the new selected range of feed flow rate and temperature (lower and upper) are 1.5x10^{-4}–2.7x10^{-4} m³/s and 25–40 °C respectively. Note that the selected limits are within the membrane manufacturer specification. Moreover, this study keeps the same operating conditions of pressure and concentration used by Sundaramoorthy et al. (2011).

Table 1: Membrane specifications (Ion Exchange, India Ltd)

Parameter	Unit	Value
Length (L), width (W) and area (A)	$(\mathrm{m})\ (\mathrm{m}^2)$	0.934, 8.4 and 7.9
Feed (t_f) and permeate (t_p) channel thickness	(mm)	0.8 and 0.5
Water and chlorophenol transport parameters (A_w) and (B_s)	$\left(\frac{\mathrm{m}}{\mathrm{atm\ s}}\right)\left(\frac{\mathrm{m}}{\mathrm{s}}\right)$	9.5188x10^{-7} and 8.468x10 -8

3. Application of the Factorial Design Method

Here, the methodology of Factorial Design Method (FDM) is used to quantify the interaction effects between the independent variables including concentration C_f (kmol/m³), flow rate Q_f (m³/s), pressure P_f (atm), and temperature T (°C) with the chlorophenol rejection Rej (-) and recovery rate Rec (-). The proposed first order linear regression model of chlorophenol rejection and recovery rate for two-way levels main interactions of four independent variables (factors) factorial design is given in the counter of Eq(3) and Eq(4).

$$Rej = A_0 + A_1Q_f + A_2C_f + A_3P_f + A_4T + A_{12}Q_fC_f + A_{13}Q_fP_f + A_{14}Q_fT + A_{23}C_fP_f + A_{24}C_fT + A_{34}P_fT \tag{3}$$

$$Rec = B_0 + B_1Q_f + B_2C_f + B_3P_f + B_4T + B_{12}Q_fC_f + B_{13}Q_fP_f + B_{14}Q_fT + B_{23}C_fP_f + B_{24}C_fT + B_{34}P_fT \tag{4}$$

A_0, B_0 are the coefficients representing the mean of responses of all the simulation runs. A_1 to A_4 and B_1 to B_4 are the linear coefficient representing the effect of each parameter on rejection and recovery rate respectively. A_{12} to A_{34} and B_{12} to B_{34} are the linear coefficient representing the effect of two interactions of operating parameters in rejection and recovery rate respectively. the statistical package SPSS has been used to generate the linear regression model by predicting the constants of the empirical model presented in the above two equations. This in turn generates a linear model using the least square technique as described in the next section. SPSS is used later on to analyse the experimental data using ANOVA (analysis of variance).

3.1 Model Development and Consistency

The linear regression model developed provided by SPSS is illustrated in Eq(5) and Eq(6) based on the experimental data used.

$$Rej = -0.689 + 1550.404\ Q_f + 108.582\ C_f + 0.003\ P_f + 0.037\ T - 50062.36\ Q_fC_f + 13.065\ Q_fP_f - 38.2\ Q_fT + 0.104\ C_fP_f - 2.268\ C_fT + 6.013x10^{-5}\ P_fT \tag{5}$$

$$Rec = -26.613 + 169037.141\, Q_f - 2681.945\, C_f + 2.862\, P_f + 0.652\, T + 5699869.565\, Q_f C_f - 15667.483\, Q_f P_f - 5026.5\, Q_f T - 102.562\, C_f P_f + 39.383\, C_f T + 0.122\, P_f T \quad (6)$$

The model developed is validated against the expanded set of experimental data of Sundaramoorthy et al. (2011). The validation methodology is based on finding the coefficient of determination (R^2) which is used to measure the adequacy of the model developed. Figure 1 shows the normal P-P plot of chlorophenol rejection and recovery rate. It can readily be seen that the residual data lies reasonably close and best fit to the line across the bisection of the graph. Therefore, this figure shows no big deviation from normality I.e. the empirical data are normally distributed. The simple comparison between the model prediction and experimental data shows a high coefficient of determination (R^2) of 0.941 and 0.99 for chlorophenol rejection and recovery rate respectively at probability value less than 0.05. This confirms the agreement between the model prediction and experimental data. Table 2 shows summary model results for chlorophenol rejection and recovery rate.

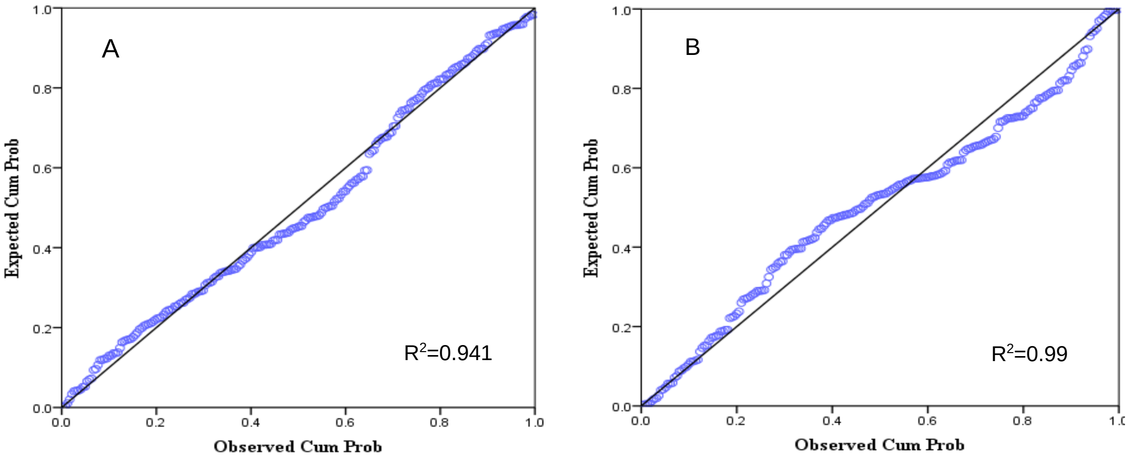

Figure 1: Normal P-P of regression standardised residual dependent of rejection (A) and recovery rate (B)

Table 2: Model summary of chlorophenol rejection [b]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
Rej	.970 [a]	.941	.938	.0318	.941	326.643	10	205	.000
Rec	.995 [a]	.990	.990	1.3020	.990	2052.808	10	197	.000

[a] Predictors: (Constant), $Q_f, P_f, C_f, T, P_f - T, C_f - T, C_f - P_f, Q_f - P_f, Q_f - C_f, Q_f - T$

4. Analysis of variance (ANOVA)

The experimental data of Sundaramoorthy et al. (2011) were further used to perform an analysis of variance ANOVA which in turn aids to optimise the process performance. Figure 2 shows a symmetrical pins-shaped histogram of the frequency distribution of errors from experimental data. This means that the proposed model can describe the pattern of experimental data due to randomly distributed residuals. Table 3 can be used to assess if the model proposed is statistically significant to predict the outcome pattern of this process. It is easy to see that the p value is less than 5%, which indicates that the model can accurately predict the chlorophenol rejection. Moreover, the F-Statistic available in SPSS to compare variances confirms the significance of the model evidenced by the large value of F-Statistics shown in Table 3. Tables 4 and 5 show the impact of each independent and two-factor interaction variables on chlorophenol rejection and recovery rate respectively. It can be observed that the temperature has the most significant impact on chlorophenol rejection followed by concentration, pressure, and flow rate. However, the pressure has the most significant impact on recovery rate followed by flow rate, temperature, and concentration. The impact of two-factor interaction on chlorophenol rejection and recovery rate is given in Tables 4 and 5 respectively. Specifically, all the independent variables have positive impact on chlorophenol rejection, as shown in Table 4. Whereas, Table 5 shows that only pressure and temperature have a positive impact on recovery rate compared to concentration and flow rate. Note that these results have shown that almost all the independent variables and the two-factor interaction independent variables are statistically significant (5% i.e. p<0.05). This confirms that the model is statistically significant.

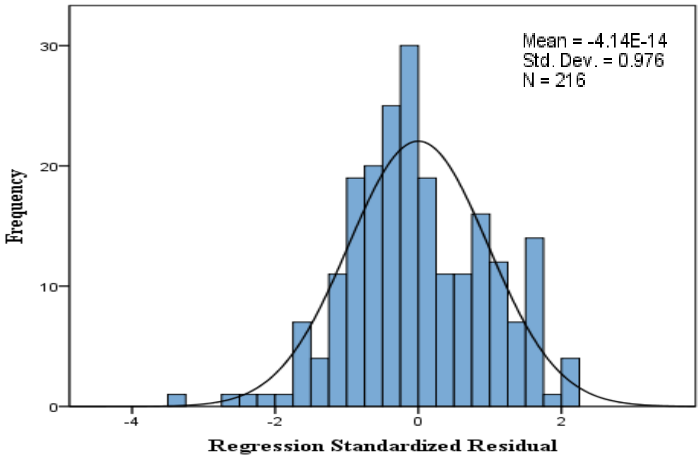

Figure 2: The histogram of distribution of errors from the experimental data of chlorophenol rejection

Table 3: ANOVA analysis of chlorophenol rejection Rej

Model	Sum of Squares	Df [a]	Mean Square	F	Sig.
Regression	3.315	10	.331	326.643	.000 [b]
Residual	.208	205	.001		
Total	3.523	215			

[a] Degree of freedom; [b] Predictors: $Q_f, P_f, C_f, T, P_f - T, C_f - T, C_f - P_f, Q_f - P_f, Q_f - C_f, Q_f - T$

Table 4: Correlations of chlorophenol rejection Rej

		Rej	C_f	P_f	T	Qf	Qf_Cf	Qf_Pf	Qf_T	Cf_Pf	Cf_T	Pf_T
Pearson correlation	Rej	1.000	.376	.206	.841	.015	.350	.175	.460	.405	.516	.546
	C_f	.376	1.00	.015	-.016	.002	.930	.014	-.006	.884	.966	.003
	P_ff	.206	.015	1.00	.023	-.008	.012	.782	.007	.400	.016	.891
	T	.841	-.016	.023	1.00	-.079	-.037	-.028	.475	-.011	.199	.455
	Q_f	.015	.002	-.008	-.079	1.00	.307	.594	.829	.000	-.013	-.040
	Qf_Cf	.350	.930	.012	-.037	.307	1.00	.195	.248	.821	.891	-.008
	Qf_Pf	.175	.014	.782	-.028	.594	.195	1.00	.504	.316	.005	.675
	Qf_T	.460	-.006	.007	.475	.829	.248	.504	1.00	-.005	.098	.213
	Cf_Pf	.405	.884	.400	-.011	.000	.821	.316	-.005	1.000	.853	.344
	Cf_T	.516	.966	.016	.199	-.013	.891	.005	.098	.853	1.00	.098
	Pf_T	.546	.003	.891	.455	-.040	-.008	.675	.213	.344	.098	1.00
Sig. (1-tailed)	Rej	.	.000	.001	.000	.413	.000	.005	.000	.000	.000	.000

Table 5: Correlations of recovery rate Rec

		Rec	C_f	P_f	T	Q_f	Qf_Cf	Qf_Pf	Qf_T	Cf_Pf	Cf_T	Pf_T
Pearson correlation	Rec	1.00	-.177	.685	.383	-.558	-.324	.161	-.289	.086	-.087	.795
	C_f	-.177	1.00	.005	.003	-.007	.930	-.001	-.002	.888	.966	.005
	P_ff	.685	.005	1.00	.010	-.003	.003	.775	.003	.378	.006	.880
	T	.383	.003	.010	1.00	-.081	-.019	-.042	.481	.006	.214	.463
	Q_f	-.558	-.007	-.003	-.081	1.00	.297	.606	.824	-.007	-.022	-.039
	Qf_Cf	-.324	.930	.003	-.019	.297	1.00	.183	.249	.826	.892	-.006
	Qf_Pf	.161	-.001	.775	-.042	.606	.183	1.00	.504	.289	-.008	.657
	Qf_T	-.289	-.002	.003	.481	.824	.249	.504	1.00	-.001	.101	.221
	Cf_Pf	.086	.888	.378	.006	-.007	.826	.289	-.001	1.00	.859	.334
	Cf_T	-.087	.966	.006	.214	-.022	.892	-.008	.101	.859	1.00	.103
	Pf_T	.795	.005	.880	.463	-.039	-.006	.657	.221	.334	.103	1.00
Sig. (1-tailed)	Rec	.	.005	.000	.000	.000	.000	.010	.000	.108	.106	.000

5. Design of full factorial experiments

The estimation of the relative strength of independent variables is carried out using the design of full factorial experiments test. This in turn would explore the factors' effects independently and more precisely on chlorophenol rejection and recovery rate. In this study, the 2-level factorial experiments design involving n factors that has 2^n runs is used. The idea is to calculate the subtraction of mean response at high level (+ sign) and mean response at low level (- sign), which identifies the main effect of that factor. Moreover, the interaction between two factors at all combinations can be explored using the same principles. Table 6 shows the design of a balanced array of full factorial experiments of four independent variables.

Figure 3 is the Pareto bar chart that shows the relative main effects of each individual and interacted variable on chlorophenol rejection and recovery rate respectively within the selected lower and upper limits of each variable. It is observed that the temperature has a considerable effect on rejection compared to pressure for recovery rate. The mean response, which has the most significant change for the selected limits of any independent variable confirms that this variable has the strongest impact on that response. Therefore, it can be said that the temperature has the most important positive impact on rejection followed by concentration, pressure, and flow rate. Whereas, the consequence of recovery rate is pressure, feed flow rate, temperature, and concentration despite the negative impact of flow rate and concentration. Moreover, Figure 3 shows the two-way interaction impact of independent variables on all such combinations. This means that the effect of each factor is dependent on the level of the combined factor. It is obvious that C_fT has a significant positive impact on rejection followed by P_fT. However, C_fT has the strongest impact on recovery.

Table 6: Design a balanced array of full factorial experiments test

Run	A0	A1 (Q_f)	A2 (C_f)	A3 (P_f)	A4 (T)	Exp. Rej	Exp. Rec
1	1	-1	-1	-1	-1	0.3573	16.237
2	1	+1	+1	+1	+1	0.9390	33.522
3	1	+1	-1	-1	-1	0.4179	8.130
4	1	-1	+1	-1	-1	0.5936	10.588
5	1	-1	-1	+1	-1	0.3122	44.941
6	1	-1	-1	-1	+1	0.8128	24.436
7	1	+1	+1	+1	-1	0.6970	17.535
8	1	+1	+1	-1	+1	0.8738	10.180
9	1	+1	-1	+1	+1	0.8886	37.416
10	1	-1	+1	+1	+1	0.9374	58.435
11	1	+1	+1	-1	-1	0.6347	5.523
12	1	+1	-1	+1	-1	0.3844	24.527
13	1	-1	+1	-1	+1	0.8755	20.273
14	1	-1	-1	+1	+1	0.8817	68.238
15	1	-1	+1	+1	-1	0.6578	30.170
16	1	+1	-1	-1	+1	0.8200	12.138

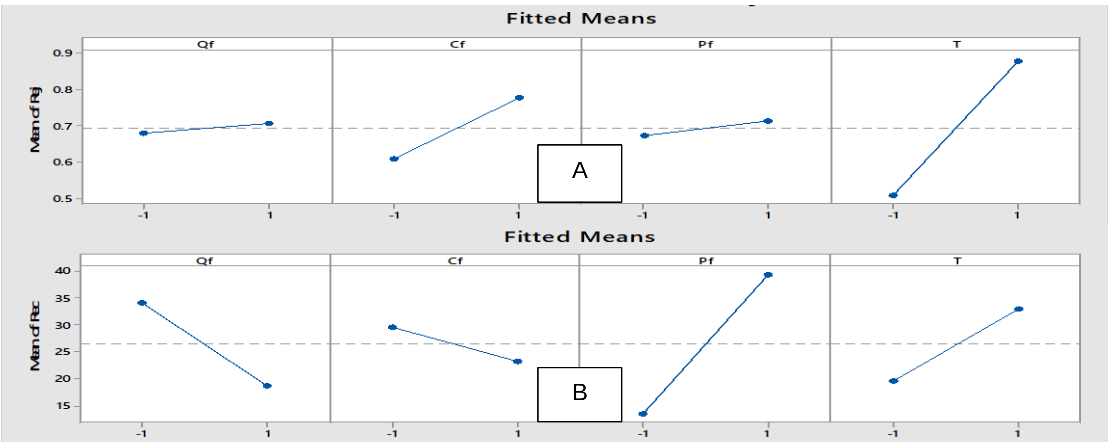

Figure 3: Main effect plot of independent variables on rejection (A) and recovery rate (B)

6. Optimisation of chlorophenol rejection and recovery rate

The aim of this part of the research is to investigate which independent variables can generate the maximum chlorophenol rejection and recovery rate simultaneously. The desirability function is therefore used to optimise the independent variables within their upper and lower limits to satisfy the maximum values of rejection and recovery rate. This is carried out using the design of experiments shown in section 5. The optimisation output results are given in Figure 4. It is concluded that the optimum independent variables are 1.5×10^{-4} m³/s, 0.778×10^{-3}, 13.58 atm, and 40 °C. This yields the maximum 0.865 and 67.4% of chlorophenol rejection and recovery rate respectively at the maximum desirability function of 0.88 and 0.98 respectively. The solution of chlorophenol rejection can be improved by selecting an individual optimisation response compared to simultaneous optimisation responses.

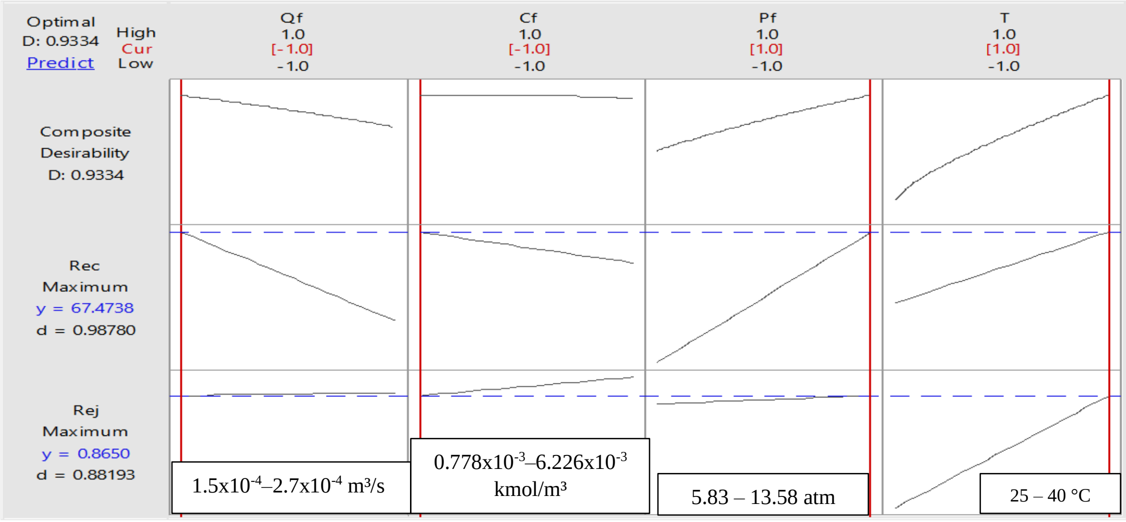

Figure 4: Optimisation results

7. Conclusions

This paper shows the development of a full factorial predictive model to estimate the removal of chlorophenol from wastewater and recovery rate (response) of an individual spiral wound RO process based on experimental data and using the least squares fitting regression method in SPSS. The results clearly suggest a significant linear strong regression correlation between the independent variables and the rejection and recovery rate with a high determination coefficient of 0.941 and 0.99 respectively. The model can investigate the response within the limits of four independent variables of feed flow rate (1.5×10^{-4}–2.7×10^{-4} m³/s), concentration (7.78×10^{-4}–6.226×10^{-3} kmol/m³), pressure (5.83–13.58 atm), and temperature (25–40 °C). The method of design of experiment is used to investigate the effect of individual and two-way interactions of four independent variables on the process response. Analysis results indicate that both the temperature and pressure have the most important effect on rejection and recovery rate. Finally, the optimisation results confirm the desirable values of the independent variables commensurate with the simultaneous optimal rejection and recovery rate.

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