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*Corresponding author

Corby G Anderson PE, Kroll Institute for Extractive Metallurgy, Mining Engineering Department, Colorado School of Mines, Golden, Colorado USA

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Research Article

A DOE Based Comparison of Resins and Factors Affecting Direct Lithium Extraction

Cahyo A Putra[1], Corby G Anderson PE[1]* and Todd S Fayram QP[2]

[1]*Kroll Institute for Extractive Metallurgy, Mining Engineering Department, Colorado School of Mines, USA*

[2]*Continental Metallurgical Services, USA*

Abstract

Lithium has been identified as a critical or near-critical element in several recent studies, owing to its significance in green technology. The threat of global warming from the combustion of fossil fuels, along with the awareness that a shift to electric and hybrid vehicles powered by lithium batteries might significantly reduce the nation's carbon footprint and dependency on foreign oil. Continental brines make the highest contribution to lithium production by supplying 59% of overall lithium production. Because of the increased demand over the years, the current and projected productions are feared to be too short to handle the demands. Hence, better recovery and processing method for lithium is needed to establish more economical and environmentally friendly outcome. Direct Lithium Extraction (DLE) is the most recent trend in lithium extraction [1-3]. DLE's large scale economics are still unknown, but it is carving out a niche for lower-grade brine and petroleum brine projects for the time being. Adsorption, ion exchange, and solvent extraction are the three major types of DLE technology. This study attempted to contribute to the DLE technology development by performing experimental research on the ion exchange process in DLE. It also included an ancillary, comprehensive Pourbaix diagram thermodynamic evaluation for the elements found in the system. The experiments were performed to investigate the factors affecting direct lithium extraction during the ion exchange process. Factors that were studied included pH, Temperature, Time, and Resin Dose. The results show that pH, Temperature, and Time are the significant factors which affect the amount of extracted lithium. Time and Temperature give positive effects which means the extraction is better as Time and Temperature increase. On the other hand, pH regulated the condition in which the extraction could or could not occur. In this experiment, Resin A extracted lithium at pH 7, and Resin B extracted lithium at pH 6. In summary, Resin B is better than Resin A since it extracts lithium at lower pH, which means it has fewer consumption requirements of caustic during pre-treatment.

Experimental Methodology

The primary materials utilized for ion exchange were two unidentified resins provided by the sponsor of this research, noted as A and B due to proprietary restrictions. The lithium-clay leachant solutions used in this experiment were provided by the sponsor of this research (Table 1).

Table 1: Device specification for the experiments.

Devices	Specification
Magnetic Stirring Device	VWR; Hotplate Stirrer
Shaking Device	Benchmark Scientific; Multitherm shaker H5005-H
pH meter	Fisher Scientific; accumet AE150 pH Benchtop Meter
ORP meter	Ohrus; ST-20 R Pen Meter

The experimental procedure was as follows

a. Put the specific amount of resin (depending on the DOE matrix) into the filtered head solution (with initial pH and Eh) determined in the plastic vials.
b. After that, attach the vials to the shaking device. Set the time and temperature needed on the shaking device setting (depends on the Design of Experimentation matrix).
c. Start shaking.
d. After the shaking process is finished, filter the solution to separate the resin from its matrix solution.
e. Measure the final pH and Eh value of the matrix solutions.
f. Do an ICP analysis on the matrix solution to identify the metal content in the matrix solution.

The effects of time, temperature, pH, and resin dose on lithium, calcium, and magnesium recovery using Stat Ease Design Expert were then evaluated. Stat Ease is a commercial software product used for statistical analysis and optimization by utilization design of experimentation. Design-Expert is specifically dedicated to performing Design of Experiments (DOE). Design-Expert offers comparative tests, screening, characterization, optimization, robust parameter design, mixture designs and combined designs. Design-Expert provides test matrices for screening up to 50 factors. Statistical significance of these factors is established with Analysis of Variance (ANOVA). Graphical tools help identify the impact of each factor on the desired outcomes and reveal abnormalities in the data [4-9].

The DLE Recovery of Lithium with Resin A

After the experimental work was completed, it was tabulated in Tables 2-6. STD represent Std order or standard order; an index used to form designs that always have the same run settings. Sorting by standard order sorts the factors settings in a low to high pattern. It is only presented out of convenience for standard designs, the design will be sorted by run number by default (Table 2-6).

The following was observed from evaluating this data

a. The lithium, magnesium, and potassium recovery by the resin only occurs at pH 7 Head Solution. The highest lithium recovery at this pH range occur at STD 3 and STD 4.
b. The calcium recovery was not measurable through all pH ranges.
c. The aluminum recovery started taking place partly at pH 4.0 and was fully recovered on all STD matrix at pH 5,6, and 7 head solution, with high recoveries.
d. The manganese recovery by the resin uniquely happened at pH 3 with high recovery, and at pH 7 with low recovery.
e. The iron recovery by the resin occurs at every pH condition, with few exceptions on STD 1, 4, 5 at pH 3.5.

Table 2: Recovery of metals at pH 3.5 initial solution by resin A.

ph 3.5							
	Li recovery %	Mg recovery %	Ca recovery %	K recovery %	Al recovery %	Mn recovery %	Fe recovery %
STD 1	-34.51	-9.30	-30.76	-12.86	-21.81	89.13	-2.87
STD 2	-8.67	-2.22	-6.24	-4.70	-3.31	90.31	7.87
STD 3	-9.73	-4.45	-8.77	-5.56	-6.99	89.70	2.26
STD 4	-33.40	-11.76	-28.10	-21.39	-24.79	88.98	-3.56
STD 5	-38.11	-15.94	-28.10	-31.68	-29.79	88.60	-14.16
STD 6	-44.42	-26.05	-29.80	-37.80	-37.30	87.77	-14.84

Table 3: Recovery of metals at pH 4.0 head solution by resin A.

ph4							
	Li recovery %	Mg recovery %	Ca recovery %	K recovery %	Al recovery %	Mn recovery %	Fe recovery %
STD 1	-31.70	-12.22	-29.4	-22.00	7.79	-21.65	31.46
STD 2	-16.63	-15.18	-21	-24.86	11.33	-14.55	24.40
STD 3	-29.64	-18.97	-21.15	-33.84	2.29	-20.94	26.88
STD 4	-65.16	-26.45	-57.2	-57.78	-17.45	-37.86	13.15
STD 5	-54.93	-29.08	-52.7	-55.15	-14.15	-39.64	16.22
STD 6	-49.15	-34.77	-49.95	-53.43	-8.70	-32.10	14.98

Table 4: Recovery of metals at pH 5.0 head solution by resin A.

ph5						
	Li recovery %	Mg recovery %	K recovery %	Al recovery %	Mn recovery %	Fe recovery %
STD 1	-63.92	-20.71	-27.59	78.22	-13.48	47.25
STD 2	-62.00	-30.58	-45.20	90.46	-27.45	41.61
STD 3	-43.46	-26.22	-33.76	91.68	-24.61	46.43
STD 4	-76.50	-33.63	-47.06	85.36	-33.02	43.12
STD 5	-59.27	-34.75	-44.94	87.51	-29.64	43.37
STD 6	-46.26	-21.48	-31.41	90.61	-15.81	45.14

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Table 5: Recovery of metals at pH 6.0 head solution by resin A.

ph6							
	Li recovery %	Mg recovery %	Ca recovery %	K recovery %	Al recovery %	Mn recovery %	Fe recovery %
STD 1	-109.31	-48.65	-83.79	-79.72	76.18	-53.06	47.96
STD 2	-57.68	-35.54	-52.62	-58.13	93.94	-39.67	53.71
STD 3	-39.74	-24.25	-32.67	-37.97	93.39	-22.59	57.54
STD 4	-73.53	-41.27	-57.67	-65.82	86.80	-35.65	54.09
STD 5	-57.39	-39.06	-52.37	-57.29	91.90	-36.91	54.36
STD 6	-53.17	-31.38	-49.31	-49.99	93.33	-31.13	55.40

Table 6: Recovery of metals at pH 7.0 head solution by resin A.

ph7							
	Li recovery %	Mg recovery %	Ca recovery %	K recovery %	Al recovery %	Mn recovery %	Fe recovery %
STD 1	-5.78	6.72	-11.24	12.06	87.34	27.86	97.81
STD 2	9.95	8.89	-0.91	13.12	95.47	22.07	99.44
STD 3	18.64	18.04	4.71	13.16	95.71	23.96	98.56
STD 4	20.50	12.05	-8.20	13.40	92.47	21.89	95.95
STD 5	3.70	4.74	-4.56	5.32	94.20	21.71	99.40
STD 6	4.75	4.74	-5.27	11.17	94.70	22.43	99.40

The analysis result of matrices STD solution indicates that the extraction of lithium by resin A only occurs at pH 7 head solution. Therefore, the Design-Expert analysis is only performed for pH 7 head solution. The standard analysis (No Response Transformation) for lithium extraction shows that temperature is the only significant factor that affects the recovery. This model is proven to be significant as the p-value equals 0.0391 (Less than 0.05), and the insignificant "Lack of Fit" (0.1032) supports the idea that this model is fit to be utilized. However, this model has a flaw in the form of a large gap between "Adjusted R^2" and "Predicted R^2" which is 0.5215. The maximum allowable gap is 0.2 for the model to be considered "good." This large gap shows that the model is good enough to analyze the current experiment but cannot predict new experiments. To get a better model, a response transformation is needed. Transformation of the response is a vital component of any data analysis. Transformation is needed if the error (Residuals) is a function of the magnitude of the response (Predicted Values). A power transformation (lambda=2.2) is applied. Using this feature, we could find a new way to investigate the relationship between factors and responses. The half-normal plot (Figure 1) produced from this analysis shows that "Time" and "Temperature" are significant factors affecting lithium's recovery.

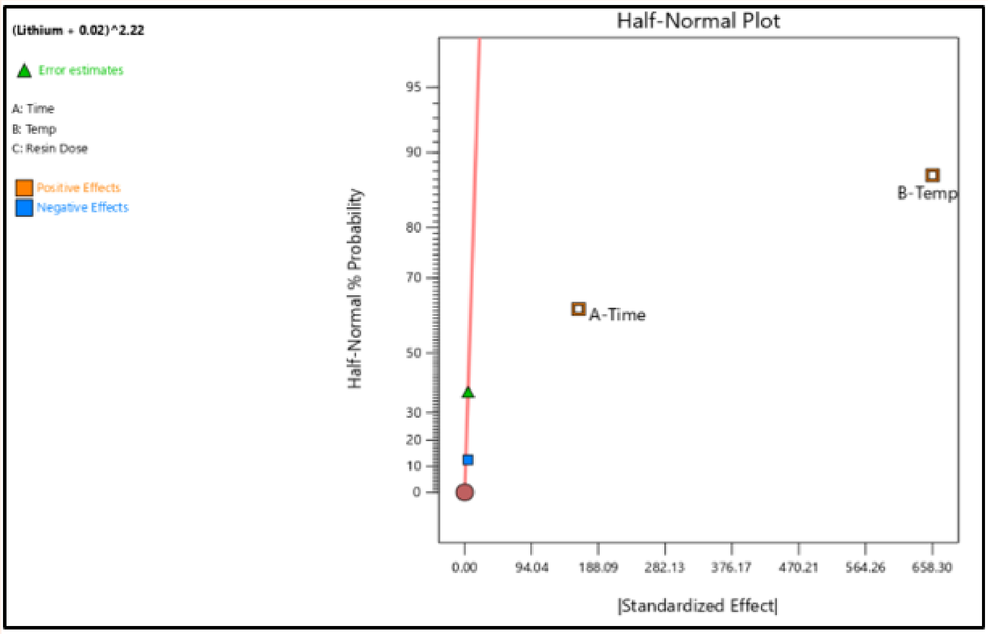

Figure 1: Lithium recovery stat ease's half normal plot (Resin A, Solution A, pH 7).

Figure 1 shows that "Time" and "Temperature" factors are distinguished from other factors. From the graph we can also imply that "Time" and "Temperature" factors give us the "signal" whereas other factor gives us the "noise." Pareto's Chart (Figure 2) is a graphical tool used to manage model selection for two-level factorial design. The primary use of the Pareto chart is to check for "one more significant effect" that was not obvious on the half-normal plot. There are two different t limits plotted on the graph [9,10]. The highest limit is based on the Bonferroni or family-wise corrected t-critical value. The lower limit is based on standard t-critical for individual effects tests. The limits are re-calculated as the terms selected for the model are changed.

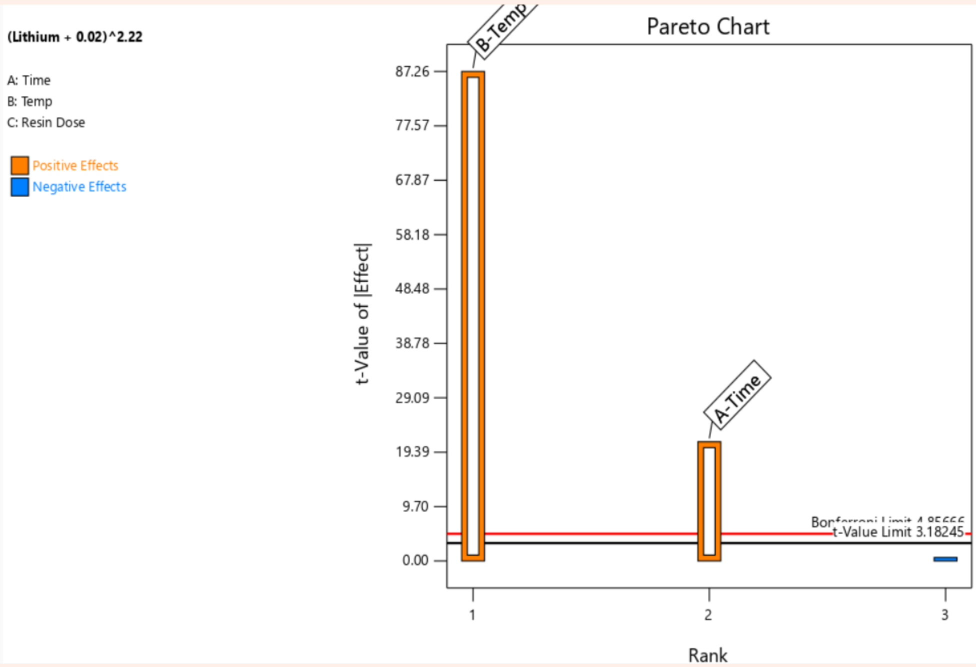

Figure 2: Pareto's chart of lithium extraction model (Resin A, Solution A, pH 7).

Selected effects that are above the Bonferroni Limit are certainly important and should be left in the model. Effects that are above the t-value Limit are possibly important and should be added if they make sense to the experimenter. Effects that are below the t-value limit should only be selected to support hierarchy. They can also be forced into the model by the analyst. Figure 2 shows that both "Time" and "Temperature" factors are important in the model since the t-value of those factors exceed the Bonferroni t-value Limit. Based on the Analysis of Variance (ANOVA) of the model (Table 7), the model F-value of 4033.26 implies the model is significant. F-value is a variable to compare the source's mean square to the residual mean square. There is only a 0.02% chance that an F-value this large could occur due to noise. P-value is the probability of seeing the observed F-value if the null hypothesis is true (There Are No Factor Effects). Small probability values call for rejection of the null hypothesis. This probability equals the integral under the curve of the F-distribution that lies beyond the observed F-value. P-value less than 0.05 indicate model terms are significant. In this case "Time" and "Temperature" are significant model terms. The Lack of Fit F-value of 0.23 implies that the Lack of Fit is insignificant relative to the pure error. There is a 71.61% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good. We want the model to fit (Table 8).

Table 7: Analysis of variance (ANOVA) of lithium recovery model (Resin A, Solution A, pH 7).

Response 1: Lithium (1) Transform: Power Lamda: 2.22, Constant: 0.0205						
Source	**Sum of Squares**	**df**	**Mean Square**	**F - Value**	**p - Value**	
Model	4.590E + 05	2	22.295E + 05	4033.26	0.0002	significant
A - Time	25687.07	1	25687.07	451.38	0.0022	
B - Temp	4.334E + 05	1	4.334E + 05	7615.13	0.0001	
Curvature	1.990E + 05	1	1.990E + 05	3496.37	0.0003	
Residual	113.82	2	56.91			
Lack of Fit	21.18	1	21.18	0.2286	0.7161	not significant
Pure Error	92.64	1	92.64			
Cor Total	6.581E + 05	5				

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Table 8: Fit of lithium recovery model (Resin A, Solution A, pH 7).

Std . Dev .	7.54	**R^2**	0.9998
Mean	282.82	**Adjusted R^2**	0.9995
C.V. %	2.67	**Predicted R^2**	0.9985
		Adeq Precision	132.8976

The Predicted R^2 of 0.9985 is in reasonable agreement with the Adjusted R^2 of 0.9995; the difference is less than 0.2. Adequate Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Our ratio of 132.89 indicates an adequate signal. This model can be used to navigate the design space. The Normal Plot of Residuals indicates whether the residuals follow a normal distribution, thus follow the straight line. A definitive pattern S-shaped curve indicates that the response may need further transformation [11-16]. Figure 3 shows no extreme S-shaped scattered data. Thus, this plot indicates a good model.

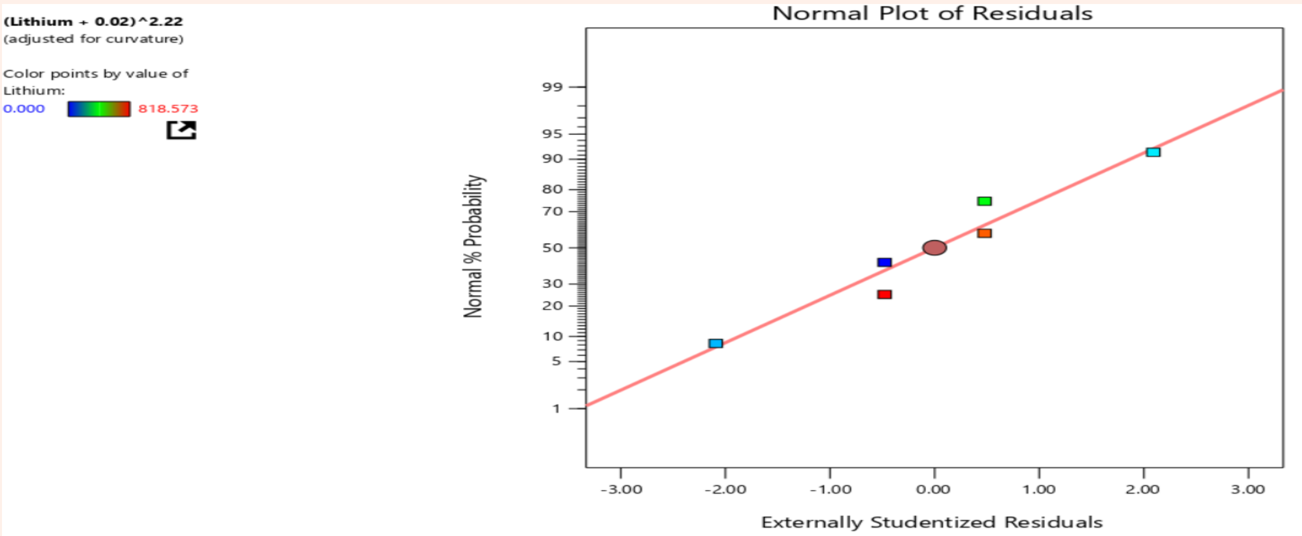

Figure 3: Normal plot of residuals (Lithium recovery by resin A).

The Residuals vs Predicted Plot tests the assumption of constant variance. The plot should be a random scatter (Constant Range of Residuals Across the Graph). Expanding variance (Megaphone Pattern) in this plot indicates the need for further transformation. Figure 4 shows no megaphone-shaped scattered data. Thus, this plot indicates a good model. Cook's Distance Plot is a measure of how much the entire regression function changes when the i[th] point is not included for fitting the model. It is the sum of differences in predictions at every point caused by leaving a point out for fitting the model. Figure 5 shows no data is plotted beyond the red line. Thus, this plot indicates a good model. The DFFITS vs Run Plot measures how much the prediction changes at the ith point when the ith point is not included for fitting the model. Figure 6 shows all data is plotted inside the boundary. Thus, this plot indicates a good model.

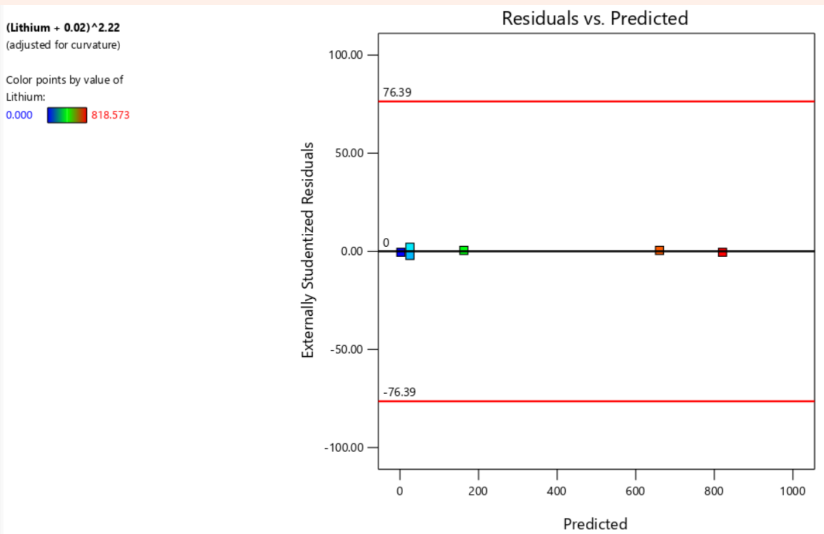

Figure 4: Residuals vs predicted plot of lithium extraction by resin A.

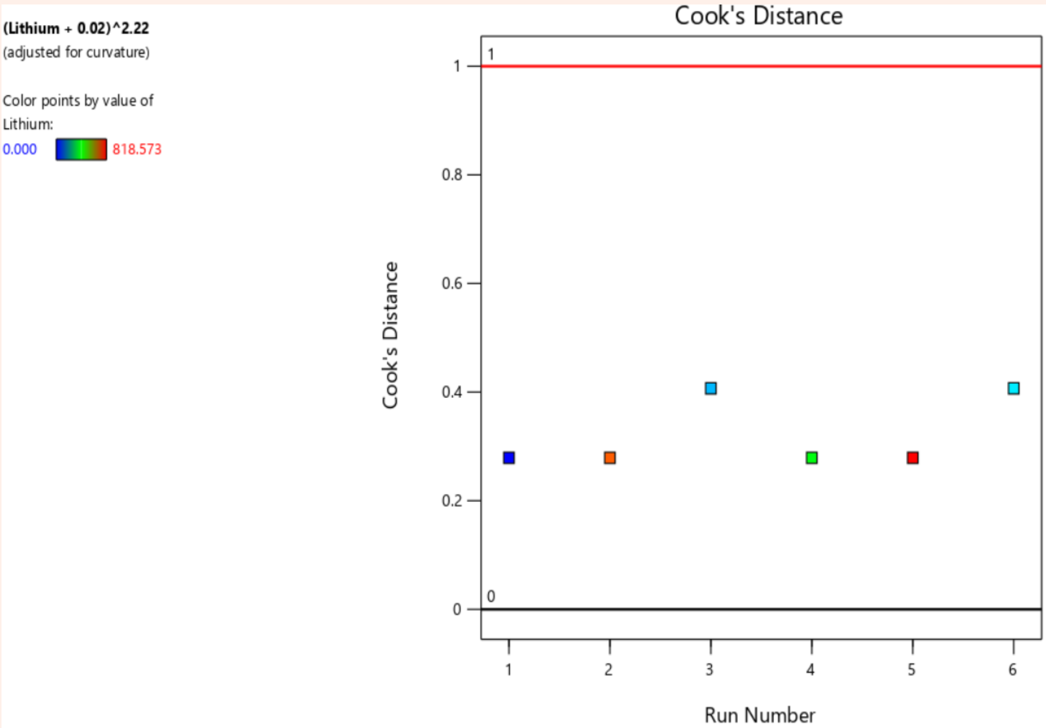

Figure 5: Cook's Distance plot of lithium extraction by resin A.

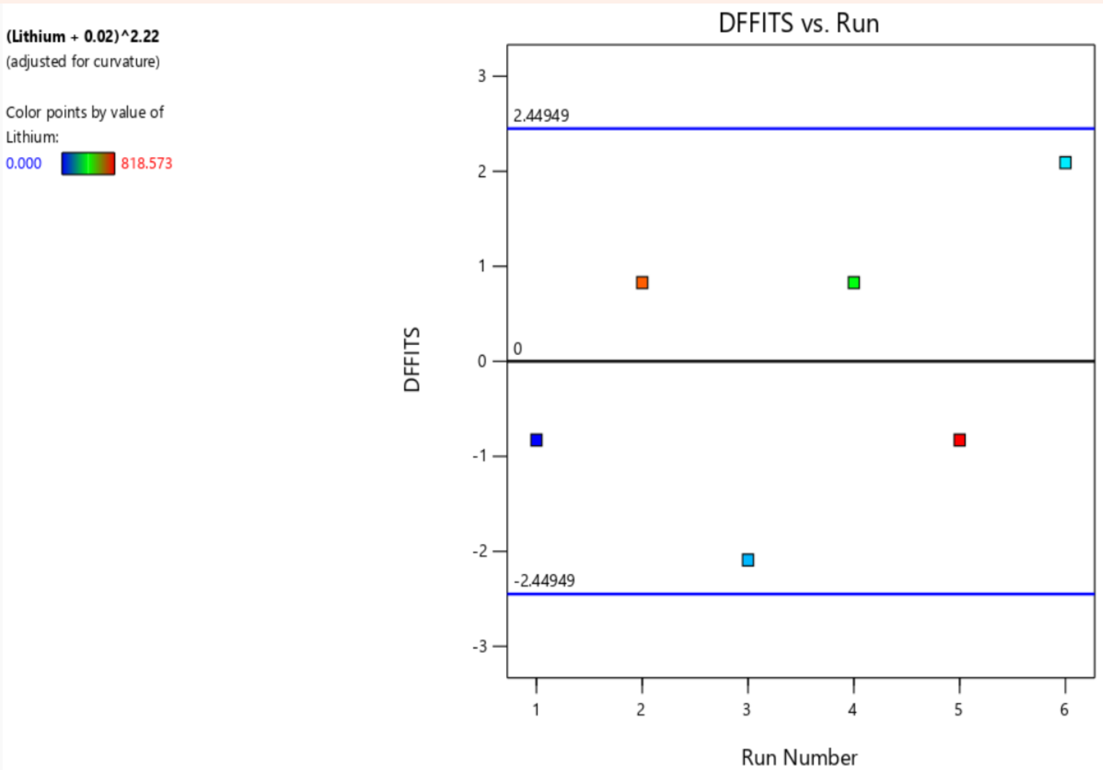

Figure 6: DFFITS vs Run plot of lithium extraction by resin A.

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We can interpret this model in 3D Surface Model Graph as illustrated by Figure 7. Based on this model, we can engineer lithium extraction optimization using the numerical optimization feature on Stat Ease. The outcome is a parameter setting recommendation to maximize lithium extraction (Figure 8). Figure 8 presents a set of parameters recommendation for lithium extraction by resin A optimization. It recommends "Time" set at 8 hours, "Temperature" at 55, and 0.2 grams of resin dose [17-21]. The expected maximum lithium recovery by implementing these parameters is 20.5%.

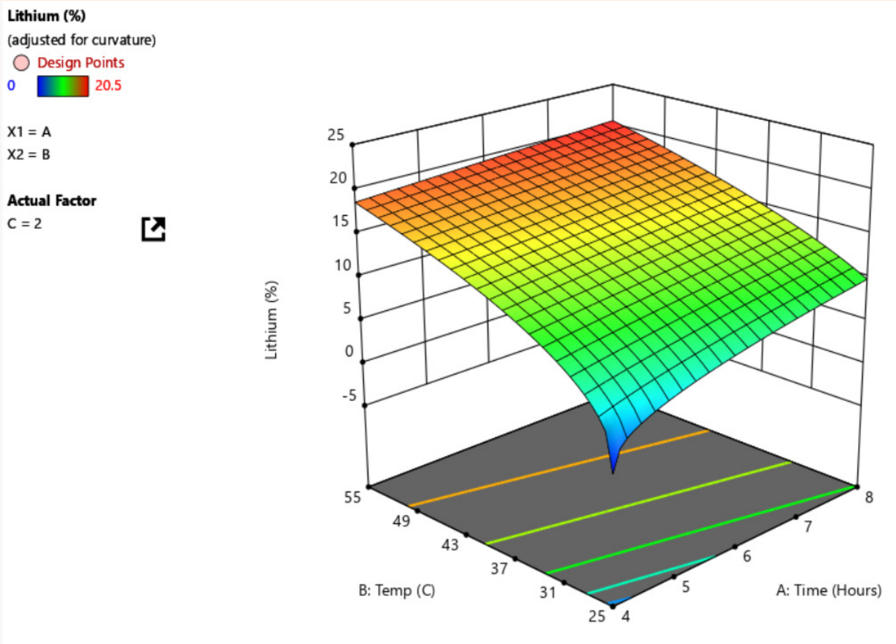

Figure 7: 3D surface model graph of lithium extraction by resin A.

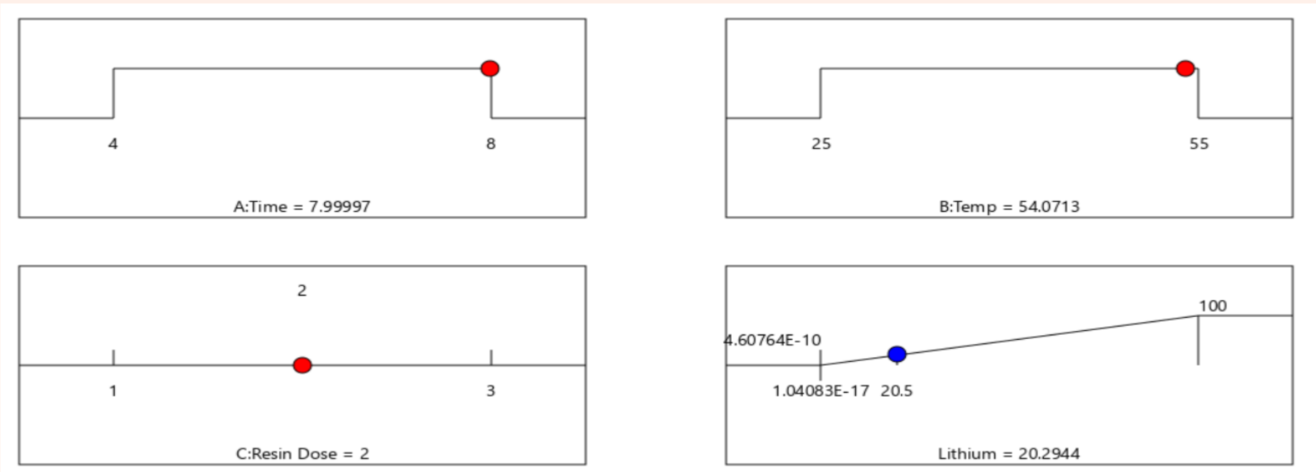

Figure 8: Set of parameters recommended for lithium extraction optimization (Resin A).

The DLE Recovery of Lithium with Resin B

Subsequently Resin B was evaluated in an analogous comparative manner as delineated before Resin A. These results follow (Table 9-13). The analysis result of matrix STD solution indicates that the extraction of lithium by resin B occurs at pH 6 head solution (All STD Matrix Solution), pH 4 head solution (STD 1 and STD 6), and pH 5 head solution (STD 1, STD 2, and STD 6). There is very few lithium recovery data that could be used for analysis on pH 5 and pH 6 head solution since majority of the data is "no response". Therefore, the Design-Expert analysis is only performed for pH 6 head solution. The standard analysis (No Response Transformation) for lithium extraction shows that temperature and time are the significant factors that affect the recovery. This model is proven to be significant as the p-value equals 0.0178 (Less than 0.05), and the insignificant "Lack of Fit F-value" (20.14) supports the idea that this model is fit to be utilized. However, this model has a flaw in the form of a large gap between "Adjusted R^2" and "Predicted R^2" which is 0.2395. The maximum allowable gap is 0.2 for the model to be considered "good." This large gap shows that the model is good enough to analyze the current experiment but cannot be used to predict new experiments [22-25].

Table 9: Recovery of metals at pH 3.5 initial solution by resin B.

ph3.5							
	Li recovery %	Mg recovery %	Ca recovery %	K recovery %	Al recovery %	Mn recovery %	Fe recovery %
STD 1	-4.46	-1.46	1.56	19.36	7.65	-0.19	12.50
STD 2	-4.84	-1.12	0.56	0.49	0.55	-1.16	-100.00
STD 3	-6.34	-3.63	0.01	-1.55	1.87	-2.90	56.25
STD 4	-11.31	2.79	12.69	15.51	14.44	-1.54	43.75
STD 5	-7.47	2.09	6.85	9.54	8.35	-2.51	-6.25
STD 6	-6.72	4.18	5.93	8.37	4.29	-5.41	-6.25

Table 10: Recovery of metals at pH 4 initial solution by resin B.

ph4							
	Li recovery %	Mg recovery %	Ca recovery %	K recovery %	Al recovery %	Mn recovery %	Fe recovery %
STD 1	5.13	-1.66	-5.30	-4.70	13.48	1.40	zero in head solution
STD 2	-2.72	-5.31	-8.69	-9.11	-0.53	-0.56	zero in head solution
STD 3	-15.75	-21.20	-27.70	-27.25	-10.08	-15.01	zero in head solution
STD 4	-1.56	-0.10	-3.63	6.05	19.45	2.38	zero in head solution
STD 5	-6.65	-3.36	-7.20	-7.88	6.50	-5.19	zero in head solution
STD 6	0.66	-0.54	-7.88	1.38	10.81	-0.98	zero in head solution

Table 11: Recovery of metals at pH 5 initial solution by resin B.

ph5							
	Li recovery %	Mg recovery %	Ca recovery %	K recovery %	Al recovery %	Mn recovery %	Fe recovery %
STD 1	19.54	7.56	2.42	8.73	7.40	9.32	zero in head solution
STD 2	5.82	-2.65	-1.21	-1.47	-16.88	0.00	zero in head solution
STD 3	-4.59	-7.48	-9.88	-10.03	-11.83	-6.13	zero in head solution
STD 4	-7.14	-9.41	-5.96	-2.28	16.91	-9.85	zero in head solution
STD 5	-7.82	-5.42	-3.17	-2.34	-2.58	-11.32	zero in head solution
STD 6	0.30	-0.38	2.80	7.79	11.65	-3.60	zero in head solution

Table 12: Recovery of metals at pH 6 initial solution by resin B.

ph6							
	Li recovery %	Mg recovery %	Ca recovery %	K recovery %	Al recovery %	Mn recovery %	Fe recovery %
STD 1	7.33	-5.33	-4.17	-11.34	3.02	-11.93	zero in head solution
STD 2	9.22	-8.24	-8.56	-14.67	-4.73	-13.12	zero in head solution
STD 3	12.16	-16.82	-17.95	-28.14	-13.07	-29.22	zero in head solution
STD 4	15.70	-9.36	2.24	-9.11	-17.93	-13.92	zero in head solution
STD 5	18.84	-5.38	-1.82	-6.80	-3.81	-15.71	zero in head solution
STD 6	19.10	-2.96	-3.05	-6.85	-3.61	-14.31	zero in head solution

Table 13: Recovery of metals at pH 6 initial solution by resin B.

ph7							
	Li recovery %	Mg recovery %	Ca recovery %	K recovery %	Al recovery %	Mn recovery %	Fe recovery %
STD 1	-5.60	1.85	5.72	3.24	9.39	3.23	zero in head solution
STD 2	-32.59	-17.62	-10.57	-18.70	-6.26	-16.94	zero in head solution
STD 3	-7.46	-3.86	2.41	-2.87	-2.27	1.61	zero in head solution
STD 4	-16.79	-0.34	2.53	8.75	-0.31	22.58	zero in head solution
STD 5	-5.35	4.31	7.24	9.88	4.60	20.97	zero in head solution
STD 6	-16.79	-0.34	2.53	8.75	-0.31	22.58	zero in head solution

To get a better model, a response transformation is needed. Transformation of the response is a vital component of any data analysis. Transformation is needed if the error (Residuals) is a function of the magnitude of the response (Predicted Values). Stat Ease recommends base log transformation in this case. A base log transformation is applied. Using this feature, we could find a new way to investigate the relationship between factors and responses. The half-normal plot (Figure 9) produced from this analysis shows that "Time" and "Temperature" are significant factors affecting lithium's recovery.

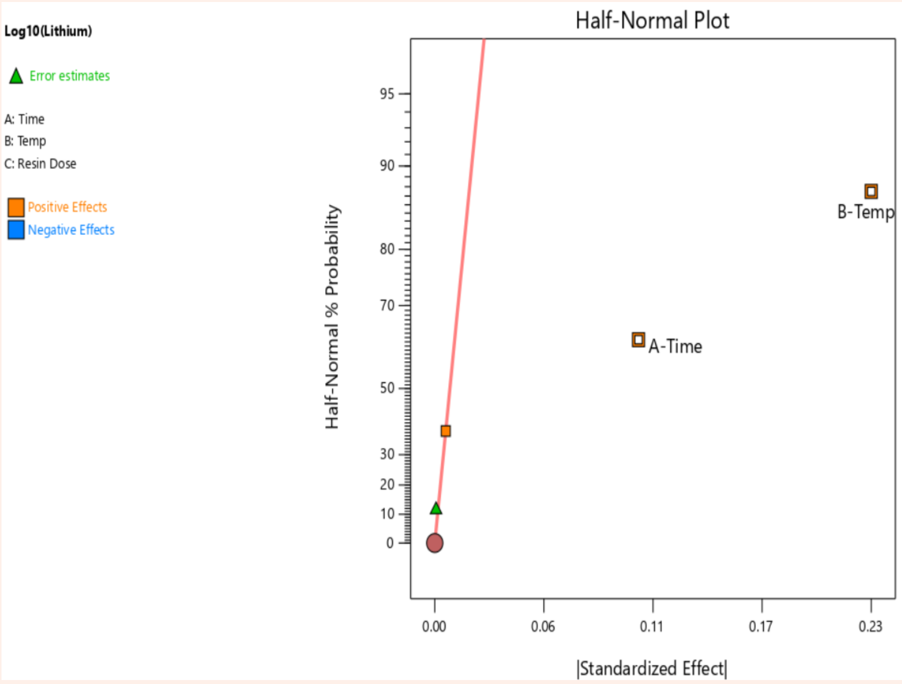

Figure 9: Lithium recovery stat ease's half normal plot (Resin B, Solution B, pH 6).

Figure 9 shows that "Time" and "Temperature" factors are distinguished from other factors. From the graph we can also imply that "Time" and "Temperature" factors give us the "signal" whereas other factor gives us the "noise." Pareto's Chart (Figure 10) is a graphical tool used to manage model selection for two-level factorial design. The primary use of the Pareto chart is to check for "one more significant effect" that was not obvious on the half-normal plot. There are two different t limits plotted on the graph [25-30]. The highest limit is based on the Bonferroni or family-wise corrected t-critical value. The lower limit is based on standard t-critical for individual effects tests. The limits are re-calculated as the terms selected for the model are changed. Selected effects that are above the Bonferroni Limit are certainly important and should be left in the model. Effects that are above the t-value Limit are possibly important and should be added if they make sense to the experimenter. Effects that are below the t-value limit should only be selected to support hierarchy. They can also be forced into the model by the analyst.

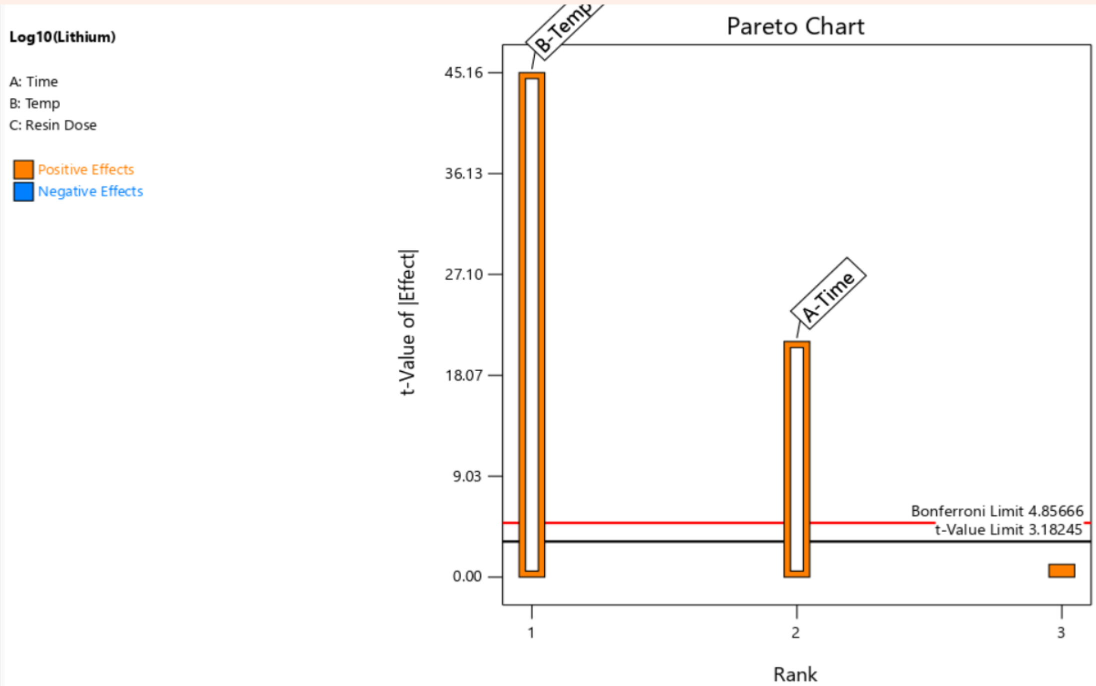

Figure 10: Pareto's chart of lithium extraction model (Resin B, Solution B, pH 6).

Figure 10 shows that both "Time" and "Temperature" factors are important in the model since the t-value of those factors exceed the Bonferroni t-value Limit. Based on the Analysis of Variance (ANOVA) of the model (Table 14), the model F-value of 1242.22 implies the model is significant. F-value is a variable to compare the source's mean square to the residual mean square. There is only a 0.08% chance that an F-value this large could occur due to noise. P-value is the probability of seeing the observed F-value if the null hypothesis is true (There Are No Factor Effects). Small probability values call for rejection of the null hypothesis. This probability equals the integral under the curve of the F-distribution that lies beyond the observed F-value. P-value less than 0.05 indicate model terms are significant. In this case "Time" and "Temperature" are significant model terms.

Table 14: Analysis of variance (ANOVA) of lithium recovery model (Resin B, Solution B, pH 6).

Response 1: Lithium (1) Transform: Base 10 Log Constant: 0						
Source	**Sum of Squares**	**df**	**Mean Square**	**F - Value**	**p - Value**	
Model	0.0619	2	0.0310	1242.22	0.0008	significant
A - Time	0.0111	1	0.0111	444.74	0.0022	
B - Temp	0.0508	1	0.0508	2039.71	0.0005	
Curvature	0.0836	1	0.0836	3353.14	0.0003	
Residual	0.0000	2	0.0000			
Lack of Fit	0.0000	1	0.0000	1.81	0.4066	not significant
Pure Error	0.0000	1	0.0000			
Cor Total	0.1456	5				

The Lack of Fit F-value of 1.81 implies that the Lack of Fit is insignificant relative to the pure error. There is a 40.66% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

The Predicted R^2 of 0.9905 is in reasonable agreement with the Adjusted R^2 of 0.9984; the difference is less than 0.2. Adequate Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Our ratio of 101.98 indicates an adequate signal. This model can be used to navigate the design space. Normal Plot of Residuals indicates whether the residuals follow a normal distribution, thus follow the straight line. A definitive pattern S-shaped curve indicates that the response may need further transformation. Figure 7 shows no extreme S-shaped scattered data. Thus, this plot indicates a good model.

The Residuals vs Predicted Plot tests the assumption of constant variance (Figure 11). The plot should be a random scatter (Constant Range of Residuals Across the Graph). Expanding variance (Megaphone Pattern) in this plot indicates the need for further transformation. Figure 12 shows no megaphone-shaped scattered data. Thus, this plot indicates a good model. Cook's Distance Plot is a measure of how much the entire regression function changes when the ith point is not included for fitting the model. It is the sum of differences in predictions at every point caused by leaving a point out for fitting the model. Figure 13 shows no data is plotted beyond the red line. Thus, this plot indicates a good model.

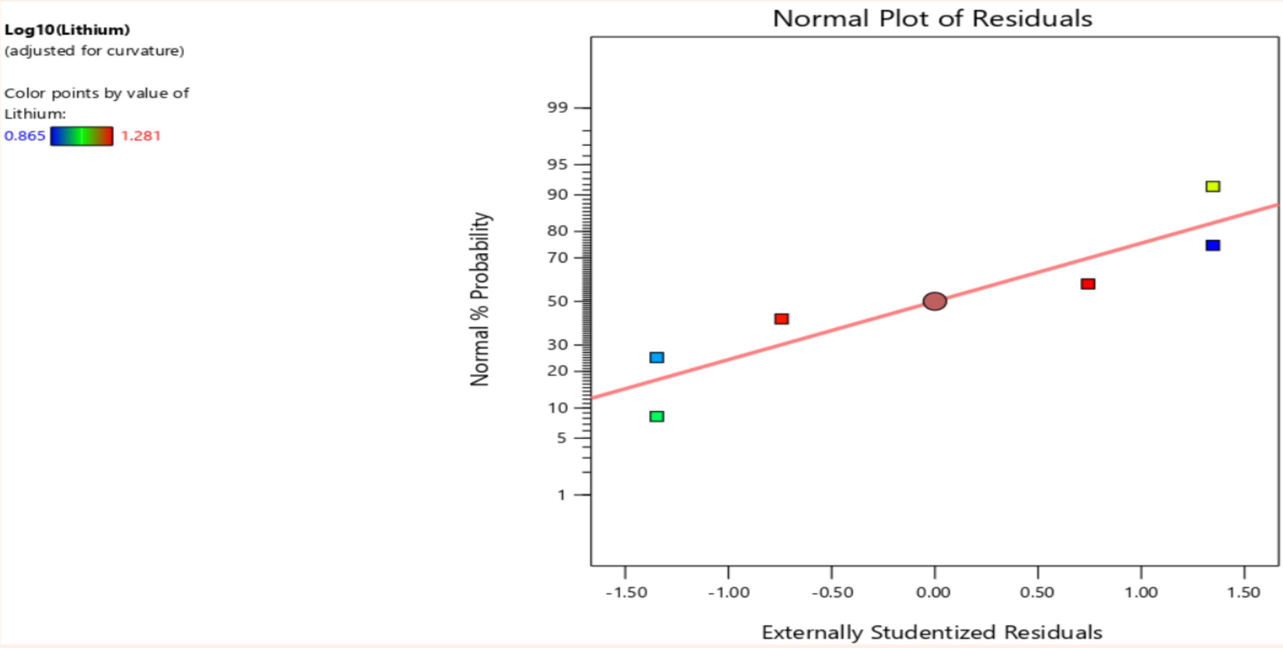

Figure 11: Normal plot of residuals lithium recovery by resin B.

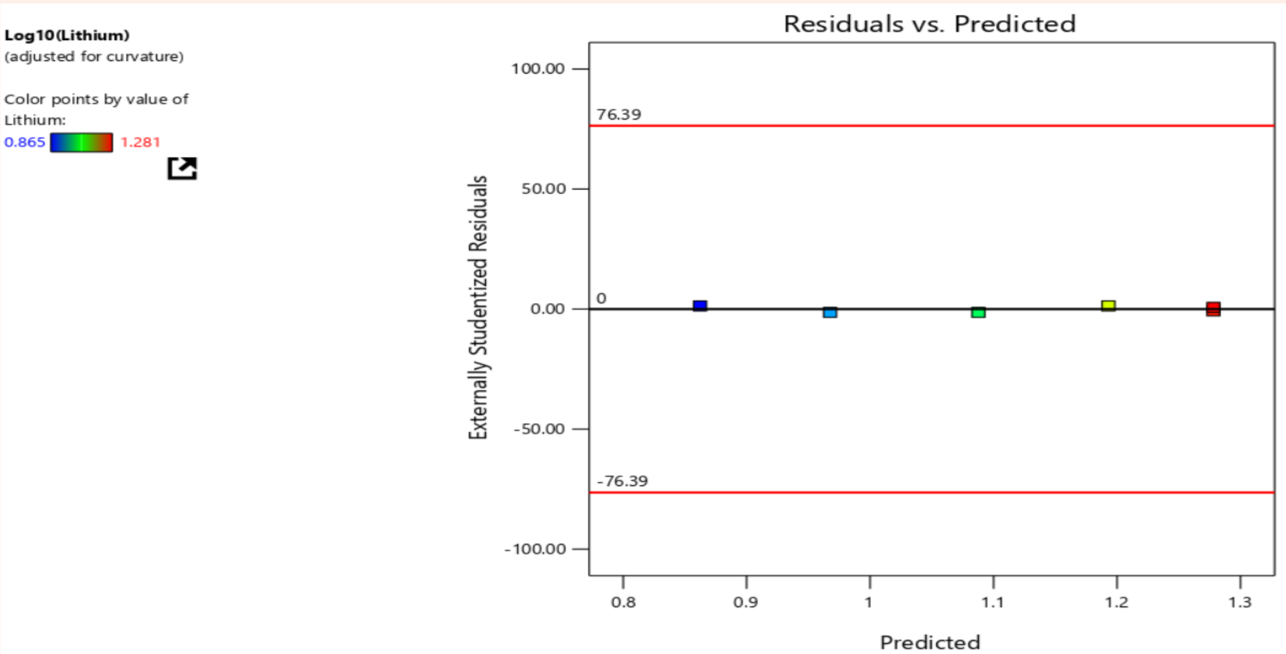

Figure 12: Residuals vs Predicted plot of lithium extraction by resin B.

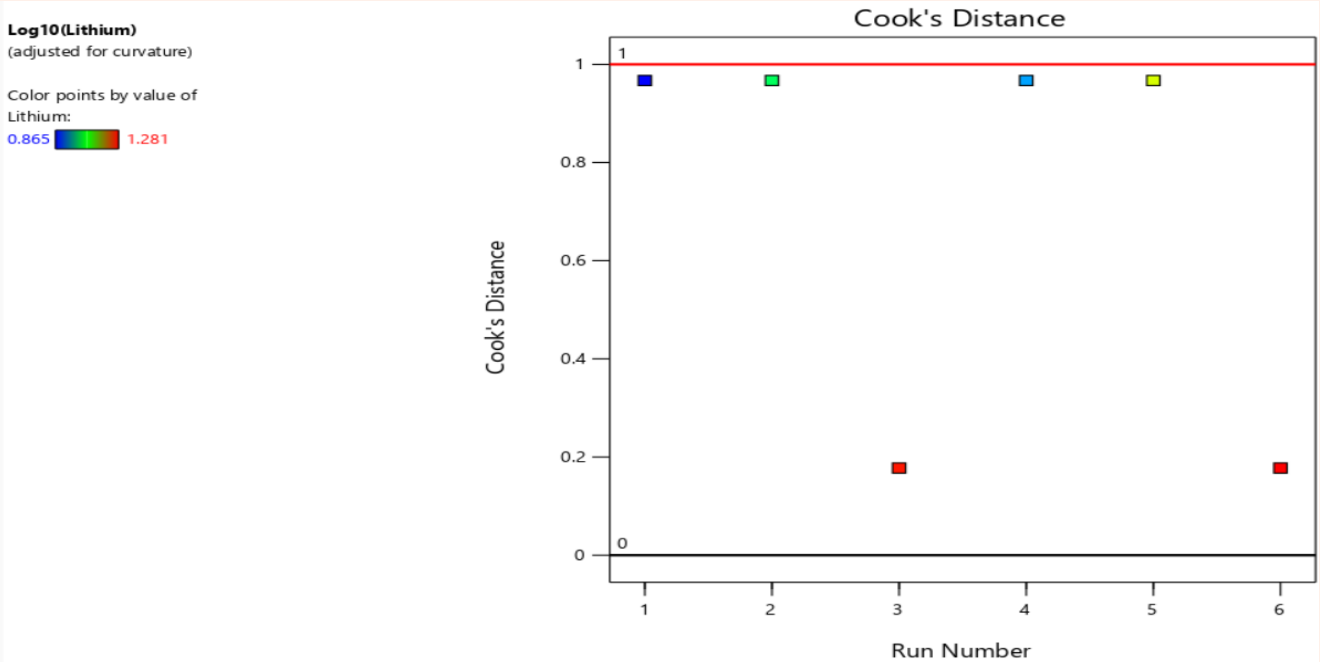

Figure 13: Cook's distance plot of lithium extraction by resin B.

The DFFITS vs Run Plot measures how much the prediction changes at the ith point when the ith point is not included for fitting the model. Figure 14 shows all data is plotted inside the boundary. Thus, this plot indicates a good model. We can interpret this model in 3D Surface Model Graph as illustrated by Figure 15. Based on this model, we can engineer lithium extraction optimization using the numerical optimization feature on Design-Expert. The outcome is a parameter setting recommendation to maximize lithium extraction (Figure 16). Figure 16 presents a set of parameters recommendation for lithium extraction by resin B optimization. It recommends "Time" set at 8 hours, "Temperature" at 55, and 0.2 grams of resin dose. The expected maximum lithium recovery by implementing these parameters is 19.1% (Based on the Experiment). The selectivity of each resin was also studied [31-34].

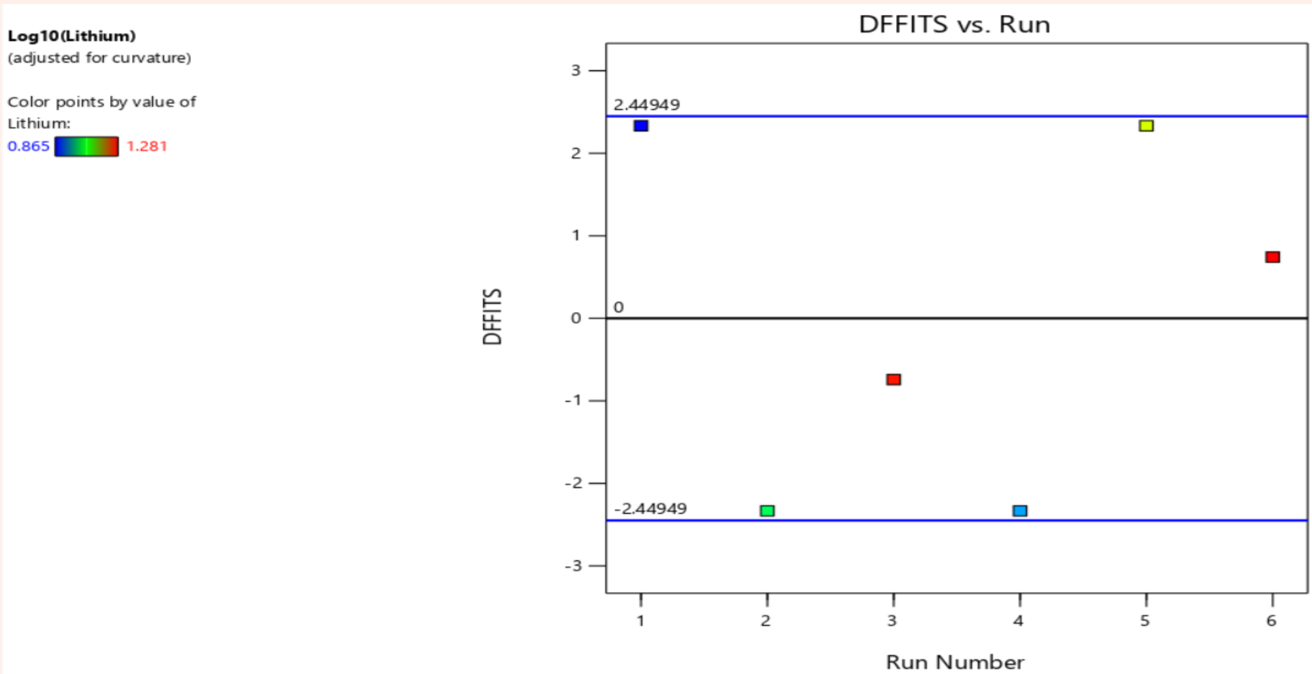

Figure 14: DFFITS vs Run plot of lithium extraction by resin B.

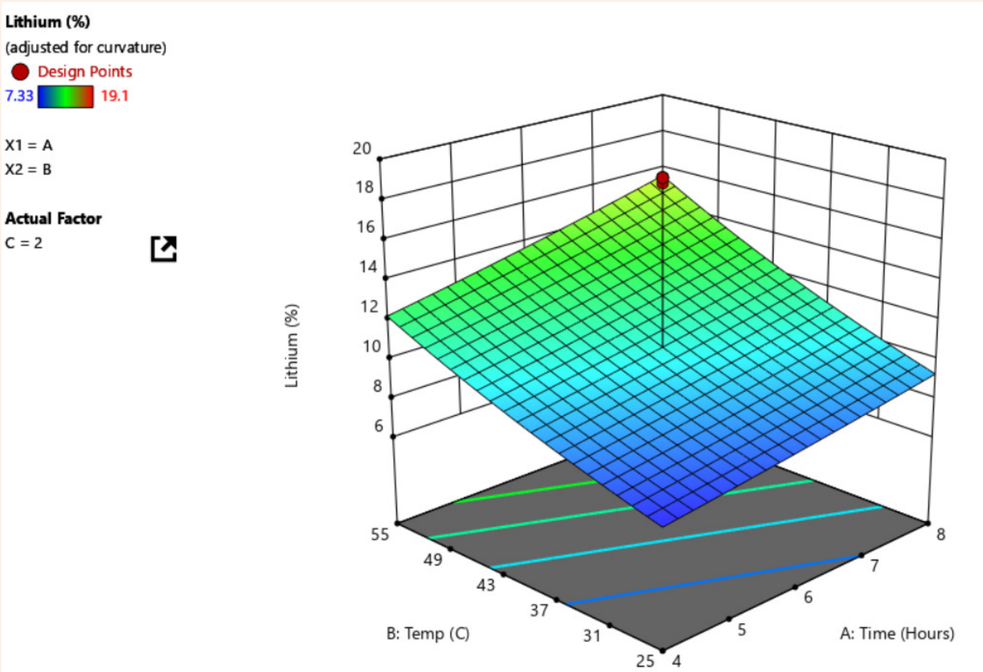

Figure 15: 3D surface model graph of lithium extraction by resin B.

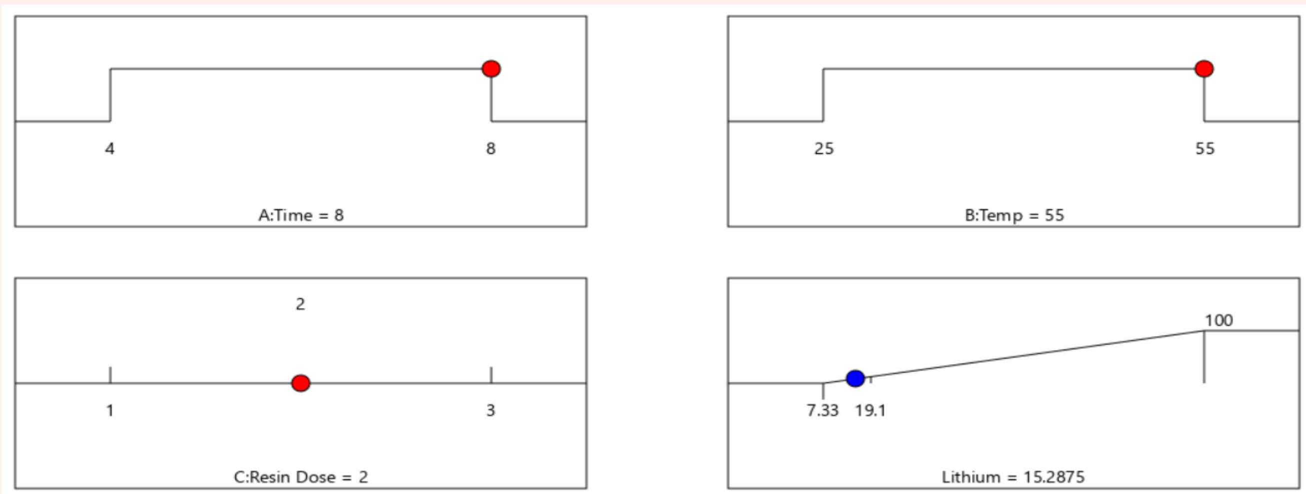

Figure 16: Set of parameters recommended for lithium extraction optimization (Resin B).

As seen at pH 3.5 initial solution (Tables 15 & 16), only manganese and iron were extracted by the resin. The resin's selectivity for this range of pH was specifically selective for Manganese. At pH 4.0 initial solution (Table 17), only manganese and iron were extracted by the resin. The resin's selectivity for this range of pH was specifically selective for Iron. At pH 5.0 initial solution (Table 18), only aluminum and iron were extracted by the resin. The resin's selectivity for aluminum was higher compared to iron. At pH 6.0 initial solution (Table 19), only aluminum and iron were extracted by the resin [35-40]. The resin's selectivity for aluminum was higher compared to iron. Table 20 shows a greater variety of elements that have been recovered by the resin. This case acted at pH 7 initial solution. Iron, aluminum, and manganese were consecutively the most selective for this pH range. Lithium was either in the 4th or the 5th position in terms of selectivity.

Table 15: Fit statistic of lithium recovery model (Resin B, Solution B, pH 6).

Std . Dev .	0.0050	R^2	0.9992
Mean	1.11	Adjusted R^2	0.9984
C.V. %	0.4494	Predicted R^2	0.9906
		Adeq Precision	101.9898

Table 16: Selectivity table of metals recovery by resin A on solution A at pH 3.5 initial solution.

pH 3.5							
Operational Condition	1st	2nd	3rd	4th	5th	6th	7th
STD 1 (4 hours ; 25 C ; Rsn lvl 3)	Mn						
STD 2 (8 hours ; 25 C ; Rsn lvl 1)	Mn	Fe					
STD 3 (4 hours ; 55 C ; Rsn lvl 1)	Mn	Fe					
STD 4 (8 hours ; 55 C ; Rsn lvl 3)	Mn						
STD 5 (6 hours ; 40 C ; Rsn lvl 2)	Mn						
STD 6 (6 hours ; 40 C ; Rsn lvl 2)	Mn						

Table 17: Selectivity table of metals recovery by resin A on solution A at pH 4 initial solution.

pH 4							
Operational Condition	1st	2nd	3rd	4th	5th	6th	7th
STD 1 (4 hours ; 25 C ; Rsn lvl 3)	Fe	AI					
STD 2 (8 hours ; 25 C ; Rsn lvl 1)	Fe	Al					
STD 3 (4 hours ; 55 C ; Rsn lv 1)	Fe	AI					
STD 4 (8 hours ; 55 C ; Rsn lvl 3)	Fe						
STD 5 (6 hours ; 40 C ; Rsn lvl 2)	Fe						
STD 6 (6 hours ; 40 C ; Rsn lvl 2)	Fe						

Table 18: Selectivity table of metals recovery by resin A on solution A at pH 5 initial solution.

pH 5							
Operational Condition	1st	2nd	3rd	4th	5th	6th	7th
STD 1 (4 hours ; 25 C ; Rsn lvl 3)	AI	Fe					
STD 2 (8 hours ; 25 C ; Rsn lvl 1)	AI	Fe					
STD 3 (4 hours ; 55 C ; Rsn lvl 1)	AI	Fe					
STD 4 (8 hours ; 55 C ; Rsn lvl 3)	AI	Fe					
STD 5 (6 hours ; 40 C ; Rsn lvl 2)	AI	Fe					
STD 6 (6 hours ; 40 C ; Rsn lvl 2)	AI	Fe					

Table 19: Selectivity table of metals recovery by resin A on solution A at pH 6 initial solution.

pH 6							
Operational Condition	1st	2nd	3rd	4th	5th	6th	7th
STD 1 (4 hours ; 25 C ; Rsn lvl 3)	AI	Fe					
STD 2 (8 hours ; 25 C ; Rsn lvl 1)	AI	Fe					
STD 3 (4 hours ; 55 C ; Rsn lvl 1)	AI	Fe					
STD 4 (8 hours ; 55 C ; Rsn lvl 3)	AI	Fe					
STD 5 (6 hours ; 40 C ; Rsn lvl 2)	AI	Fe					
STD 6 (6 hours ; 40 C ; Rsn lvl 2)	Al	Fe					

Table 20: Selectivity table of metals recovery by resin A on solution A at pH 7 initial solution.

pH 7							
Operational Condition	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**
STD 1 (4 hours ; 25 C ; Rsn lvl 3)	Fe	AI	Mn	K	Mg		
STD 2 (8 hours ; 25 C ; Rsn lvl 1)	Fe	Al	Mn	K	Li	Mg	
STD 3 (4 hours ; 55 C ; Rsn lv 1)	Fe	Al	Mn	Li	Mg	K	Ca
STD 4 (8 hours ; 55 C ; Rsn lvl 3)	Fe	AI	Mn	Li	K	Mg	
STD 5 (6 hours ; 40 C ; Rsn lvl 2)	Fe	AI	Mn	K	Mg	Li	
STD 6 (6 hours ; 40 C ; Rsn lvl 2)	Fe	AI	Mn	K	Li	Mg	

At pH 3.5 initial solution (Table 21), the resin's selectivity had several varieties. Potassium had the most chance to be extracted and was followed by iron. Elevated temperature operating conditions seemed favorable to extract iron. Aluminum and Calcium were most likely to be extracted in any operating condition, although those elements were not the most favorable. Lithium was not extracted at this range of head solution pH. At pH 4.0 initial solution (Table 22), Aluminum became the predominant element extracted by resin. Potassium came second best. Lithium got extracted in two operating conditions, STD 1 and STD 6. At pH 5.0 initial solution (Table 23) and specifically at low temperature condition, resin had a very high selectivity for lithium. At pH 6.0 initial solution (Table 24), resin showed the best capability to extract lithium compared to other initial solution's pH value. Lithium was extracted first over other elements in any condition [41-55]. At pH 7.0 initial solution (Table 25), Manganese, Potassium, and Calcium were consecutively the most compatible elements with the resin. Aluminum was extracted first over those elements only at low temperature-short time operating condition.

Table 21: Selectivity table of metals recovery by resin B on solution B at pH 3.5 initial solution.

pH 3.5							
Operational Condition	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**
STD 1 (4 hours ; 25 C ; Rsn lvl 3)	K	Fe	AI	Ca			
STD 2 (8 hours ; 25 C ; Rsn lvl 1)	Ca	AI	K				
STD 3 (4 hours ; 55 C ; Rsn lv 1)	Fe	Al	Ca				
STD 4 (8 hours ; 55 C ; Rsn lvl 3)	Fe	K	AI	Ca	Mg		
STD 5 (6 hours ; 40 C ; Rsn lvl 2)	K	AI	Ca	Mg			
STD 6 (6 hours ; 40 C ; Rsn lvl 2)	K	Ca	AI	Mg			

Table 22: Selectivity table of metals recovery by resin B on solution B at pH 4 initial solution.

pH 4							
Operational Condition	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**
STD 1 (4 hours ; 25 C ; Rsn lvl 3)	AI	Li	Mn				
STD 2 (8 hours ; 25 C ; Rsn lvl 1)							
STD 3 (4 hours ; 55 C ; Rsn lv 1)							
STD 4 (8 hours ; 55 C ; Rsn lvl 3)	AI	K	Mn				
STD 5 (6 hours ; 40 C ; Rsn lvl 2)	AI						
STD 6 (6 hours ; 40 C ; Rsn lvl 2)	AI	K	Li				

Table 23: Selectivity table of metals recovery by resin B on solution B at pH 5 initial solution.

pH 5							
Operational Condition	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**
STD 1 (4 hours ; 25 C ; Rsn lvl 3)	Li	Mn	K	Mg	Al	Ca	
STD 2 (8 hours ; 25 C ; Rsn lvl 1)	Li						
STD 3 (4 hours ; 55 C ; Rsn lvl 1)							
STD 4 (8 hours ; 55 C ; Rsn lvl 3)	AI						
STD 5 (6 hours ; 40 C ; Rsn lvl 2)							
STD 6 (6 hours ; 40 C ; Rsn lvl 2)	Al	K	Ca	Li			

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Table 24: Selectivity table of metals recovery by resin B on solution B at pH 6 initial solution.

pH 6							
Operational Condition	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**
STD 1 (4 hours ; 25 C ; Rsn lvl 3)	Li	AI					
STD 2 (8 hours ; 25 C ; Rsn lvl 1)	Li						
STD 3 (4 hours ; 55 C ; Rsn lvl 1)	Li						
STD 4 (8 hours ; 55 C ; Rsn lvl 3)	Li	Ca					
STD 5 (6 hours ; 40 C ; Rsn lvl 2)	Li						
STD 6 (6 hours ; 40 C ; Rsn lvl 2)	Li						

Table 25: Selectivity table of metals recovery by resin B on solution B at pH 7 initial solution.

pH 7							
Operational Condition	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**
STD 1 (4 hours ; 25 C ; Rsn lvl 3)	AI	Ca	K	Mn	Mg		
STD 2 (8 hours ; 25 C ; Rsn lvl 1)							
STD 3 (4 hours ; 55 C ; Rsn lvl 1)	Ca	Mn					
STD 4 (8 hours ; 55 C ; Rsn lvl 3)	Mn	K	Ca				
STD 5 (6 hours ; 40 C ; Rsn lvl 2)	Mn	K	Ca	Al	Mg		
STD 6 (6 hours ; 40 C ; Rsn lvl 2)	Mn	K	Ca				

Conclusion

The conclusions of this study can be summarized on several key points.

a. Lithium extraction by Resin A on Solution A only occurred at pH 7.0 initial solution.
b. Lithium extraction by Resin B on Solution B occurred at pH 4, 5, and 6 initial solutions. However, only the pH 6 condition produced extraction for all operating conditions.
c. Aside from its pH, Time and Temperature were the factors that significantly contributing to the level of lithium extraction from the solution.
d. Resin B is concluded to be better than Resin A practically, since it extracted lithium at lower pH. Hence, it has fewer consumption requirements of caustic during pre-treatment.

Recommendations

Below are the recommendations based on the results and conclusions.

a. Since the lithium extraction rate by these resins are heavily related to temperature, the extraction process is strongly indicated as chemical reaction rather than physical phenomena.
b. The experimentation did not consider the resin's attrition during the ion exchange process. It is highly recommended to consider that factor when it comes to industrial scale application.

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