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Modeling and Optimization of Manganese Carbonate Precipitation Using Response Surface Methodology and Central Composite Rotatable Design

Modelagem e Otimização da Precipitação de Carbonato de Manganês usando Metodologia de Superfície de Resposta e Projeto Rotativo de Composto Central

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Resumo

Uma solução de sulfato contendo 1773,965 mg/L Mn^{2+}, 3216,178 mg/L Mg^{2+} e 566,254 mg/L Ca^{2+} foi usada para realizar a recuperação máxima de manganês e a recuperação mínima de magnésio. A precipitação de carbonato foi usada devido à melhor seletividade do manganês sobre o magnésio e a recuperação de outras impurezas em comparação com a precipitação de hidróxido. Quatro fatores foram estudados: valor do pH da solução, tempo de contato, temperatura de reação e consumo de carbonato de sódio. Análise de variância (ANOVA) e metodologia de superfície de resposta (RSM) foram usadas para determinar o ótimo. Nas condições ótimas, as recuperações de manganês e magnésio foram as mais altas e as mais baixas, respectivamente, enquanto o pH, o tempo, a temperatura e o volume de Na_2CO_3 foram os mais baixos. Os valores dos quatro fatores foram encontrados da seguinte forma: 8,9293, 60,69 min, 77,95°F e 50,7650 mL, respectivamente. Além disso, as recuperações de manganês e magnésio foram de 99,9799% e 4,3045%, respectivamente. Os resultados mostram que a otimização usando RSM é eficaz na melhoria da precipitação de carbonato de manganês.

Abstract

A sulfate solution containing 1773.965 mg/L Mn^{2+}, 3216.178 mg/L Mg^{2+} and 566.254 mg/L Ca^{2+} was used to perform the maximum recovery of manganese and minimum recovery of magnesium. Carbonate precipitation was used due to the better selectivity for manganese over magnesium and other impurities recovery compared to hydroxide precipitation. Four factors were studied: solution pH value, contact time, reaction temperature and sodium carbonate consumption. Analysis of variance (ANOVA) and response surface methodology (RSM) were used to determine the optimum. Under the optimum conditions, the manganese and magnesium recoveries were the highest and the lowest respectively, while the pH, the time, the temperature and the volume of Na_2CO_3 were the lowest. The values of the four factors were found as followed: 8.9293, 60.69 min, 77.95°F, and 50.7650 mL respectively. Moreover, the recoveries of manganese and magnesium were 99.9799% and 4.3045% respectively. The results show that optimization using RSM is effective in improving carbonate precipitation of manganese.

Keywords: Carbonate precipitation. Manganese. Magnesium. Modeling. Response surface methodology.

1. Introduction

Research on the development of renewable or alternative resources has been carried out in order to reduce the consumption of fossil fuels for years and continues to be carried out. The electric vehicle battery manufacturing industry is developing rapidly and by 2040, the electric vehicle fleet could reach 15.6 million vehicles. Metals such as cobalt (Co), lithium (Li) and manganese (Mn) are the main constituent elements of these batteries, and their productions are increasingly important.

Manganese is the twelfth most abundant element in the earth's crust (0.096%), and appears mainly as pyrolusite (MnO_2), rhodochrosite ($MnCO_3$), rhodonite ($MnSiO_3$), manganite ($MnO(OH)$) and alabandite (MnS) (Zhang and Cheng, 2007 a).

Pereira et al. (2014) showed that manganese is used in the cell and battery manufacturing industry, the coloring of ceramics, the catalysis of certain organic reactions. The manganese used in batteries and accumulators has the oxide form, mainly manganese dioxide (MnO_2) obtained after calcination of manganese carbonate ($MnCO_3$) from the chemical precipitation of a sulfate solution.

Many authors have studied different ways of separation and recovery of Mn from solutions containing one or more metals such as copper (Cu), cobalt (Co), zinc (Zn), iron (Fe), and nickel (Ni) (Zhang et al., 2002; Zhang and Cheng, 2007 b; Bello-Teodoro, 2011). Some other authors have studied the separation of Mn from Ca and Mg by hydroxide precipitation, carbonate precipitation, or oxidative precipitation (Zhang and Cheng, 2007; Zhang et al., 2010; Zhang and Cheng, 2007 c). However, each way has presented advantages and disadvantages as shown in Table 1 (Pakarinen and Paatero, 2011; Lei et al., 2009).

Table 1 – Different ways of Mn recovery

Way	Advantages	Disadvantages
Hydroxide precipitation	Easy to co-precipitate Mn and Mg	Poor selectivity for Mn recovery
SO_2/O_2 (air) precipitation	High selectivity for Mn recovery	-Requires a very precise feed control; -Uses toxic and corrosive SO_2 gas
Carbonate precipitation	-Fast and effective for Mn recovery and iron separation from sulfate solutions; -Good filtration and leaching properties Low prices;	---

In this paper, Mn is precipitated as carbonate from a sulphate solution (mixture of manganese sulphate $MnSO_4$ and magnesium sulphate $MgSO_4$) obtained from the decobalting process in the production process of cobalt carbonate ($CoCO_3$). During the chemical precipitation of $MnCO_3$, it is generally very difficult to separate the Mg^{2+} and Ca^{2+} ions from the Mn^{2+} ions contained in sulphate solutions, due to their very similar chemical properties (Lin et al., 2016). Thus, to obtain a higher quality Mn precipitate from a sulphate solution, the Mg^{2+} concentration must be higher than that of Ca^{2+}. According to Haihe et al. (2021), the factors influencing the chemical precipitation reaction are the following: time, temperature, agitation, concentration and volume of the precipitating agent, purity and pH of the starting solution, nature and the concentration of metal cations in the solution, the presence of germination sites in the solution.

Four factors are taken into account in this paper (pH, time, temperature, and Na_2CO_3 consumption) to determine the optimum conditions for efficient and selective Mn recovery. Lin et al. (2016) studied the influence of pH (2 to 13) on the equilibrium ion concentrations of Mn^{2+}, Mg^{2+} and Ca^{2+} found as carbonates and hydroxides. They concluded that the precipitation potential of those ions in solution (at 77°F) evolves as follows: $MnCO_3 > CaCO_3 > MgCO_3 > Mn(OH)_2 >$

$Mg(OH)_2 > Ca(OH)_2$. This shows that carbonate precipitation is more convenient and selective for separating Mn from Mg and Ca.

There are several kinds of precipitating agents that are used depending on the type of metal to be precipitated. The most commonly used precipitating agents are calcium hydroxide ($Ca(OH)_2$), caustic soda (NaOH), sodium carbonate (Na_2CO_3), calcium carbonate ($CaCO_3$) and magnesium hydroxide (Mg $(OH)_2$); Lin et al. (2016) also used ammonium bicarbonate. Na_2CO_3 was used in this study to precipitate Mn ions for the preparation of $MnCO_3$ product and maintain calcium and magnesium ions in solution.

Generally, the precipitation of Mn^{2+} in a sulphate solution by the addition of carbonate ions takes place as shown in the following equation:

$$Mn^{2+} + CO_3^{2-} = MnCO_3 \tag{1}$$

On the other hand, increasing the pH by adding carbonate can also lead to the precipitation of a hydroxide (when the precipitation pH corresponding to this hydroxide is reached) depending on Equation (2). The precipitation of $MnCO_3$ in the presence of Ca and Mg is accompanied by co-precipitation of these two impurities, and this depends on several parameters such as temperature, pH, Mg/Ca ratio (Kamgaing, 2015).

$$Mn^{2+} + 2OH^{-} = Mn(OH)_2 \tag{2}$$

According to Shu et al. (2019), the precipitation yield increases with increasing pH but not indefinitely. Indeed, when the pH varies from 8.5 to 10.5, the precipitation yield of Mn varies from 91.55% to 99.98%. Over a pH value of 9.5, more impurities are precipitated with Mn and then the product is contaminated. On another hand, Pourmortazavi et al. (2012) studied statistical technique optimisation for Mn recovery in order to produce $MnCO_3$ nanoparticles.

This work aims to investigate the modeling of Mn and Mg recoveries by carbonate precipitation under some experimental variables such as the solution pH value, the time, the temperature and Na_2CO_3 consumption, on carbonate precipitation. After modeling, the optimum experimental conditions for maximizing manganese precipitation and minimizing co-precipitation magnesium are determined.

2. Methods

2.1 Characterisation of sulfate solution

A representative sample of sulfate solutions was used in this investigation. During 7 days, samples were taken at the outlet of pipe conducting sulfate solution from a hydrometallurgical process of a factory in the south of Lubumbashi region, the Democratic Republic of the Congo. A total of forty (40) liters of the sample was then constituted. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique was used to determine the element contents in the sample. Table 2 shows the result of the ICP analysis of the sample and those results revealed that the average concentration of Mn and Mg in the sample were 1773.965 mg/L and 3216.178 mg/L respectively. The analysis also revealed that the average pH of the solution was between 7.9 and 8.2.

Table 2– Contents of majors ions in manganese sulfate solution (mg/L)

Mn^{2+}	Mg^{2+}	Ca^{2+}	Co^{2+}	Cu^{2+}	Al^{3+}	Zn^{2+}	Fe^{3+}
1773.965	3216.178	566.254	0.00175	0.0022	0.0012	0.00293	0.0602

According to the results of Table 2, Mg^{2+} ions content is high due also to prior addition of magnesia during the de-coppering process. As Mn and Mg are likely to precipitate in the forms of manganese carbonate ($MnCO_3$) and magnesium carbonate ($MgCO_3$) respectively, this paper focuses on Mg to assess its degree of contamination in the final solution to be obtained.

2.2 Preparation of solutions

All the other chemicals used were of analytical grade. Na_2CO_3 (99,5%) was used as a precipitant agent. 50,25 g of this solution was diluted in 500 mL of distilled water to prepare 100 g/L of the solution, which was also used for pH adjustments. The further working solutions were made by dilution.

Standard nitric acid (HNO_3), perchloric acid ($HClO_4$) and hydrochloric acid (HCl) were used for the detection of the elements in the precipitates.

2.3 Precipitation experiments

Batch precipitation experiments were carried out in flasks of 5000 ml provided with a mechanical stirrer with agitating of 800 cycles per minute (rpm). A certain amount of Na_2CO_3 solution of 100 g/L was added to 1500 mL of sulfate solutions (the mixed solution of $MnSO_4$ and $MgSO_4$) until the required value of pH was reached flasks. Then the mixtures continued to be shaken at predetermined temperature and time. At the end of the reaction, the slurry was cooled to room temperature naturally for 2 hours and then filtrated. Then the filter cake was collected and washed with de-ionized water. $MnCO_3$ product was dried in a vacuum at 194°F for 2 h, weighed and analysed for the determination of the recoveries of Mn and Mg.

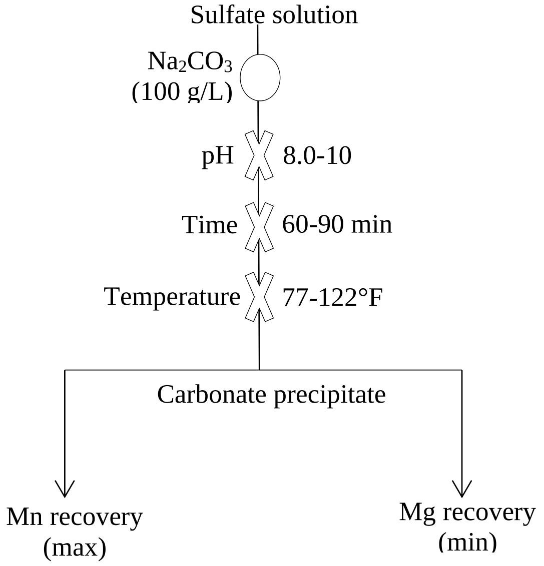


Figure 1 – Precipitation process experiments

The precipitation yield was determined using the following equations 3 and 4:

$$\eta(\%) = \frac{[Me]_{dep} - [Me]_{filt}}{[Me]_{dep} \times 100} \tag{3}$$

$$\eta(\%) = \frac{P_{prec} - T[Me]_{dep}}{V_{dep} \times 100} \tag{4}$$

where $[Me]_{dep}$ is the metal concentration in the starting solution, $[Me]_{filt}$ is the metal concentration in the filtrate, P_{prec} is the precipitate weight, $T[Me]_{dep}$ is the metal content in the precipitate, V_{dep} is volume of the starting solution.

The Mn and Mg contents in the solid products were detected by titration with standard HNO_3, $HClO_4$ and HCl solutions and analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

3. Experiment’s design and data analysis

Four factors (pH, time and temperature and Na_2CO_3 consumption) were considered, using the following ranges: pH from 8-10, time from 60-120 minutes, temperature from 77-122°F. As a certain amount of Na_2CO_3 was added to the solution progressively, Na_2CO_3 volume (mL) was considered without any fixed range. A total of 40 experiments with a central composite design were carried out. Minitab 16 and OriginPro software were used to design the experiments.

The first software was used to analyze the reliability of the results after comparison of the predicted and actual recoveries of Mn and Mg. Besides, the regression method was used to statistically analyse the results of experiments. Then, the resulting equation was used to calculate the predicted recoveries. The second software was used to produce three and two-dimensional contour plots of the obtained results in order to show the effect of different factors on the recoveries and the interaction between those factors.

MiniTab software was also used to predict the optimum values of the factors and then the resulting maximum recovery of Mn and minimum recovery of Mg, and analysis of variance (ANOVA) was used for statistical analysis of the model to assess the statistical parameters.

Montgomery (2001) and Myers and Montgomery (2002) showed that the response surface methodology (RSM), which is a statistical and mathematical technique for the modeling and optimization, could be used in most of the problems through the performing of the statistically designed experiments, the fitting of experimentally determined response data into a quadratic model followed by the estimation of the coefficients in a mathematical model, and the predicting of the response. RSM was also used for modeling and optimization studies (Mehrabani et al., 2010; Mark and Patrick, 2000).

Models (second-order model) used in RSM are built using central composite design (CCD). The advantage of the model used in RSM is the flexibility and the possibility to consider a wide variety of functional forms involving a good approximation to the true response surface. Then the estimation of parameters or factors is done using the method of least squares.

On another hand, Box and Wilson (1951) and Box and Hunter (1957) studied central composite rotatable design (CCRD) as an alternative to factorial design which has the advantages of giving almost as much information as a three-level factorial, using few tests compared to the full factorial design and has a good description of most of the steady-state process responses. Hence in this paper, CCRD was used to design the experiments.

Assuming that all variables are to be measurable for CCRD, the general equation form of the response surface can be expressed as follows:

$$y = f(x_1, x_2, x_3, \dots, x_i) \tag{5}$$

where y is the dependant variable and x_i the independent variables (factors).

Then a model was chosen after inserting the obtained results to OriginPro software.

The Fisher’s F-test analysis of variance (ANOVA) was used to evaluate the statistical significance of the effects and the interactions among the investigated factors. The results were conducted at 95% confidence intervals, so that the P-value higher than 0.05 indicates a non-significant factor or interaction by the difference between the average of the center points and the factorial points in the design space. The very low probability value (P-value) of F $((P_{Model}>F)<0.0001)$ indicates the model is highly significant.

The coefficient of determination, R^2, indicates how the variability in the response can be explained by the model. It also evaluates the fitness of the found modeling equation (Liu and Wang, 2007).

Joglekar and May (1987) suggested that for a good fit of a model, R^2 should be at least 0.80. On another hand, Murthy et al. (2000) showed that the coefficient of variation (CV) indicates the degree of precision with which the treatments are compared. The higher the CV, the greater the level of dispersion around the mean. The lower the value of the CV, the more precise the estimate.

4. Equations

40 sets of tests were designed: pH (x_1), time (x_2), temperature (x_3) and Na_2CO_3 consumption (x_4), with an appropriate combination. The variables, codes and symbols of full factorial design in actual values are presented in Table 3, while the results of experiments are presented in Table 4.

Table 3 – Variables, symbols, levels and codes used for factorial design

Variables	**pH**		**Time (minutes)**		**Temperature (°F)**	
Symbols	x_1		x_2		x_3	
	Level	Code	Level	Code	Level	Code
Variable code and level	8	1	60	1		
	8.5	2	80	2	77	1
	9	3	100	3	122	2
	9.5	4	120	4		

Na_2CO_3 consumption (x_4) has been calculated after the reaction for each chosen pH, time and temperature levels.

Table 4 – Full factorial design with variable values and results for both Mn and Mg recoveries symbols and levels use

Run N0	**Code level of variable**			**Na_2CO_3 consumption (mL)**	**Mn recovery (%)**	**Mg recovery (%)**
	x_1	x_2	x_3	x_4		
1	1	1	1	50.765	69.53	1.18
2	1	1	2	81.754	90.34	4.65
3	1	2	1	55.592	69.95	2.25
4	1	2	2	79.760	90.90	5.84
5	1	3	1	60.418	70.38	3.31
6	1	3	2	77.766	91.45	7.03
7	1	4	1	65.245	70.80	4.38
8	1	4	2	75.772	92.01	8.22
9	2	1	1	63.808	90.41	8.71
10	2	1	2	99.700	94.57	7.86
11	2	2	1	72.781	90.63	11.87
12	2	2	2	98.038	95.26	10.59
13	2	3	1	81.754	90.85	15.03
14	2	3	2	96.377	95.94	13.32
15	2	4	1	90.727	91.07	18.19

16	2	4	2	94.715	96.63	16.05
17	3	1	1	99.700	98.53	19.27
18	3	1	2	121.634	99.99	29.28
19	3	2	1	112.993	98.57	21.65
20	3	2	2	119.308	99.99	23.14
21	3	3	1	126.287	96.60	24.03
22	3	3	2	116.981	99.99	17.01
23	3	4	1	139.580	95.64	26.41
24	3	4	2	114.655	99.99	10.88
25	4	1	1	169.490	99.99	22.54
26	4	1	2	239.280	99.99	72.21
27	4	2	1	161.182	99.99	25.61
28	4	2	2	219.340	99.99	64.80
29	4	3	1	152.873	99.99	28.68
30	4	3	2	199.400	99.99	57.39
31	4	4	1	144.565	99.99	31.75
32	4	4	2	179.460	99.99	49.97
33	5	1	1	225.322	99.99	53.80
34	5	1	2	402.788	97.41	97.81
35	5	2	1	233.963	99.99	58.56
36	5	2	2	405.779	97.16	98.05
37	5	3	1	242.603	99.99	63.32
38	5	3	2	408.770	96.91	98.30
39	5	4	1	251.244	99.99	68.08
40	5	4	2	411.761	96.66	98.54

The mathematical model which represents second order polynomial is given by Equation 6,

$$y = f(x_1, x_2, x_3, x_4) \tag{6}$$

where y represents the response (Mn and Mg recoveries)

$\mathrm{x}_1, \mathrm{x}_2, \mathrm{x}_3$ and x_4 represent the pH, time, temperature and Na_2CO_3 consumption respectively.

4.1. Modeling equation of Mn recovery

From the results of table 4, the following equation was obtained by regression analysis for Mn recovery:

$$y_{Mn} = -2019 + 428.3x_1 + 0.381x_2 + 5.248x_3 - 2.035x_4 - 21.09x_1^2 + 0.000058x_2^2 - 0.000585x_4^2 - 0.0380x_1x_2 - 0.6226x_1x_3 + 0.1973x_1x_4 - 0.000404x_2x_3 + 0.000122x_2x_4 + 0.00368x_3x_4 \tag{7}$$

where y_{Mn} is the predicted Mn recovery;

$\mathrm{x}_1, \mathrm{x}_2, \mathrm{x}_3$ and x_4 are coded values for pH, time, temperature and Na_2CO_3 consumption respectively.

The above Equation 7 shows the most and considerable positive effect of the coefficient of x_1 for increasing recovery, compared to x_2 and x_3 variables. At the same time, the coefficient of x_4 has a negative effect on Mn recovery, which means that at low volumes of the precipitating agent, all CO_3^{2-} precipitate Mn^{2+} due to the high affinity between the two ions. But at high volumes of Na_2CO_3, the precipitation of impurities occurs, reducing the recovery yield of Mn in the solid precipitate. As the concentration of carbonate ions increases, impurities precipitate together with Mn.

The coefficients of the interactions x_1x_2 and x_1x_3 had a negative effect on recovery, while the coefficients of the interactions x_1x_4 had a very slight positive effect on recovery. The interactions x_2x_3, x_2x_4 and x_3x_4 have insignificant effects.

However, the effect of pH (x_1) and Na_2CO_3 consumption (x_4) were both significant while the influence of temperature (x_3) was highly significant (Table 5 and Figure 2). So that these factors have a direct relation with the recovery of Mn.

The probability value ($P_{Model}>F$) was found less than 0.0001 for pH-temperature interaction, indicating great significance.

Table 5 – Analysis of Variance for Mn recovery

Source	df	Sum of Square	Mean Square	F-Value	P-Value Prob>F	Remarks
Model	13	2947.07	226.698	78.13	<0.0001	HS
x_1	1	31.02	31.024	10.69	0.003	S
x_2	1	5.84	5.845	2.01	0.168	NS
x_3	1	48.69	48.695	16.78	<0.0001	HS
x_4	1	16.97	16.974	5.85	0.023	S
x_1^2	1	66.40	66.403	22.89	<0.0001	HS
x_2^2	1	0.02	0.021	0.01	0.932	NS
x_4^2	1	17.47	17.466	6.02	0.021	S
x_1x_2	1	2.80	2.799	0.96	0.335	NS
x_1x_3	1	134.74	134.736	46.44	<0.0001	HS
x_1x_4	1	18.70	18.702	6.45	0.017	S
x_2x_3	1	0.75	0.754	0.26	0.614	NS
x_2x_4	1	0.57	0.574	0.20	0.660	NS
x_3x_4	1	37.25	37.255	12.84	0.001	S
Error	26	75.44	2.901			
Total	39	3022.51				

F: Fishers' function, df: degrees of freedom, p-value: corresponding level of significance, NS: not significant; S: significant; HS: highly significant; CV=1.4584%; R^2=97.50%; Adj. R^2=96.26%, Pred. R^2=93.72%

According to Table 5, there was 97.50% of the variability in the response due to the high value of the determination coefficient R^2 and the adjusted determination coefficient (Adj. R^2= 96.26%) was also satisfactory and confirmed the significance of the model.

The precision and the reliability of the experiments were confirmed by the value of the coefficient of variation (CV=1.4584%).

4.2. Modeling equation for Mg recovery

The below model equation was obtained by regression analysis from results of the following Table 4.

$$y_{Mg} = -3604 + 834x_1 + 1.780x_2 + 6.86x_3 - 9.70x_4 - 47.61x_1^2 + 0.00076x_2^2 - 0.003739x_4^2 - 0.1566x_1x_2 - 0.870x_1x_3 + 1.052x_1x_4 - 0.00590x_2x_3 + 0.001212x_2x_4 + 0.01264x_3x_4 \quad (8)$$

where y_{Mg} is the predicted Mg recovery, x_1, x_2, x_3 and x_4 are coded values for pH, time, temperature and Na_2CO_3 consumption respectively.

According to Equation 8, the coefficients of pH (x_1), time (x_2) and temperature (x_3) variable had the positive effect of increasing recovery, while the coefficient of Na_2CO_3 consumption (x_4) had the negative effect of decreasing recovery. As observed for Mn recovery, at high volumes of Na_2CO_3, the precipitation of Mn and other impurities than Mg occurs, reducing the recovery yield of Mg in the solid precipitate.

Table 6 indicates the results of the analysis of variance for Mg recovery and according to that, the effect of pH (x_1), temperature (x_3) and Na_2CO_3 consumption (x_4) were highly significant (p-value less than 0.0001).

Table 6 – Analysis of Variance for Mg recovery

Source	df	Sum of Square	Mean Square	F-Value	P-Value Prob>F	Remarks
Model	13	34681.0	2667.77	215.05	<0.0001	HS
x_1	1	530.5	530.51	42.77	<0.0001	HS
x_2	1	166.0	166.05	13.39	0.001	S
x_3	1	468.3	468.31	37.75	<0.0001	HS
x_4	1	261.9	261.92	21.11	<0.0001	HS
x_1^2	1	338.4	338.38	27.28	<0.0001	HS
x_2^2	1	3.7	3.68	0.30	0.591	NS
x_4^2	1	714.2	714.25	57.58	<0.0001	HS
x_1x_2	1	47.5	47.54	3.83	0.061	NS
x_1x_3	1	263.3	263.31	21.23	<0.0001	HS
x_1x_4	1	531.8	531.81	42.87	<0.0001	HS
x_2x_3	1	161.1	161.10	12.99	0.001	S
x_2x_4	1	56.7	56.66	4.57	0.042	S
x_3x_4	1	439.6	439.59	35.44	<0.0001	HS
Error	26	322.5	12.41			
Total	39	35003.5				

F: Fishers' function, df: degrees of freedom, p-value: corresponding level of significance, NS: not significant; S: significant; HS: highly significant; CV=8.7432%; R^2=99.08%; Adj. R^2=98.62%, Pred. R^2=97.84%

The coefficients of the interactions x_1x_2, x_1x_3 and x_2x_3 had a negative effect on recovery, while the coefficients of the interactions x_2x_4 and x_3x_4 had a very slight positive effect on Mg recovery. According to the results of Table 6, the fit of the model was expressed by the coefficient of determination R^2 which was found to be 0.9908 and the reliability of the experiments was great due to the reasonable value of the coefficient of variation (CV=8.7432%). The confirmation is given in Figure 1b showing the dispersion around the mean. The small P-values ($P < 0.001$) associated to x_1x_3, x_1x_4 and x_3x_4 showed that their coefficients were highly significant.

Equations 7 and 8 were used to find predicted values of Mn and Mg recoveries respectively, and the results are presented in Table 7 and Figure 1.

Table 7 – Predicted values for Mn and Mg recoveries

Run N_0	Mn recovery (%)	Mg recovery (%)
1	71.20	0.00
2	88.12	3.25
3	71.32	1.84
4	89.23	4.03
5	71.49	4.36
6	90.36	5.28
7	71.69	7.56
8	91.53	7.02
9	89.53	10.93
10	97.11	15.93
11	89.10	12.69
12	97.72	14.84
13	88.66	14.89
14	98.37	14.25
15	88.21	17.53
16	99.05	14.17
17	98.05	13.95
18	98.95	23.20
19	97.42	17.34
20	99.07	20.13
21	96.69	20.67
22	99.22	17.52
23	95.87	23.93
24	99.40	15.37
25	99.98	27.91
26	100.89	71.45
27	100.84	29.88
28	100.46	66.57
29	101.63	31.55
30	99.51	58.35
31	102.34	32.90
32	98.04	46.80
33	100.02	53.32
34	97.04	97.39
35	99.82	57.57
36	97.00	97.47
37	99.61	62.29
38	97.01	98.24
39	99.41	67.48
40	97.07	99.70

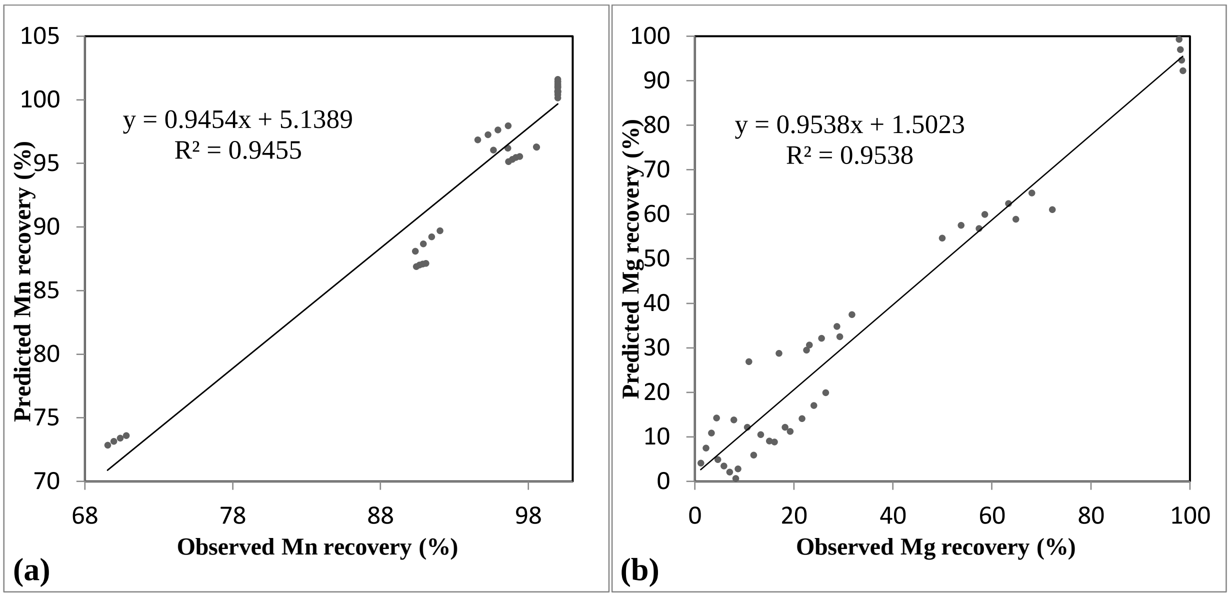


Figure 2 – Relationship between predicted and observed values for (a) Mn and (b) Mg recoveries

According to Figure 2, the predicted and experimental values (for both Mn and Mg recoveries) lie in the straight line, which shows that the model predicted values were reasonably close to the experimental values. Thus, the model is considered to be adequate for predicting within the range of variables employed. The results indicated a successful prediction of the correlation between the experimental and predicted values.

Figures 3 and 4 show the effects of each factor on Mn and Mg recoveries respectively, considering fitted means. It is obvious that the effects of pH, temperature and Na_2CO_3 consumption are more significant for the recoveries of both Mn and Mg.

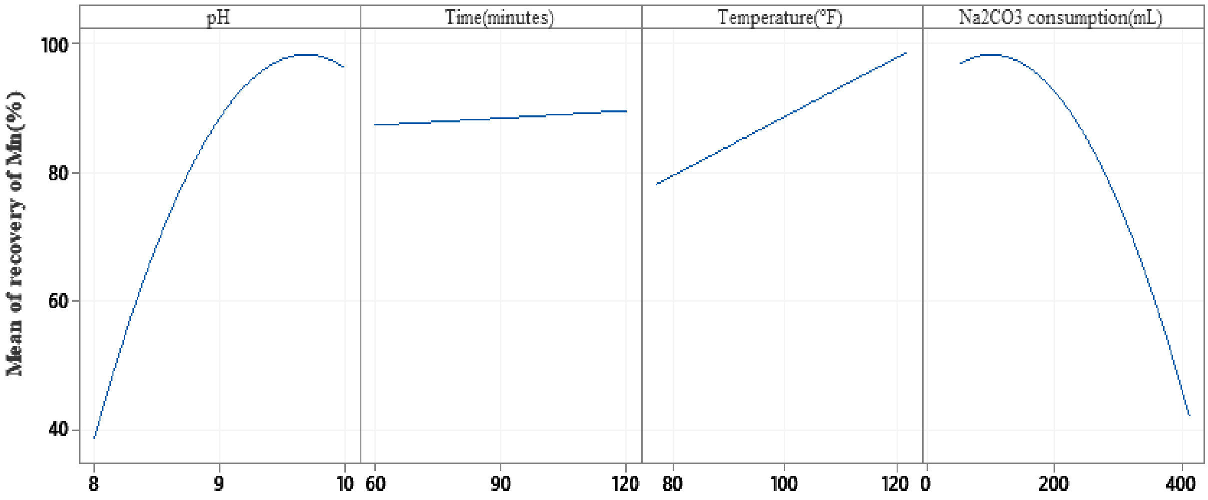


Figure 3 – Main effects plot for recovery of Mn (Fitted means)

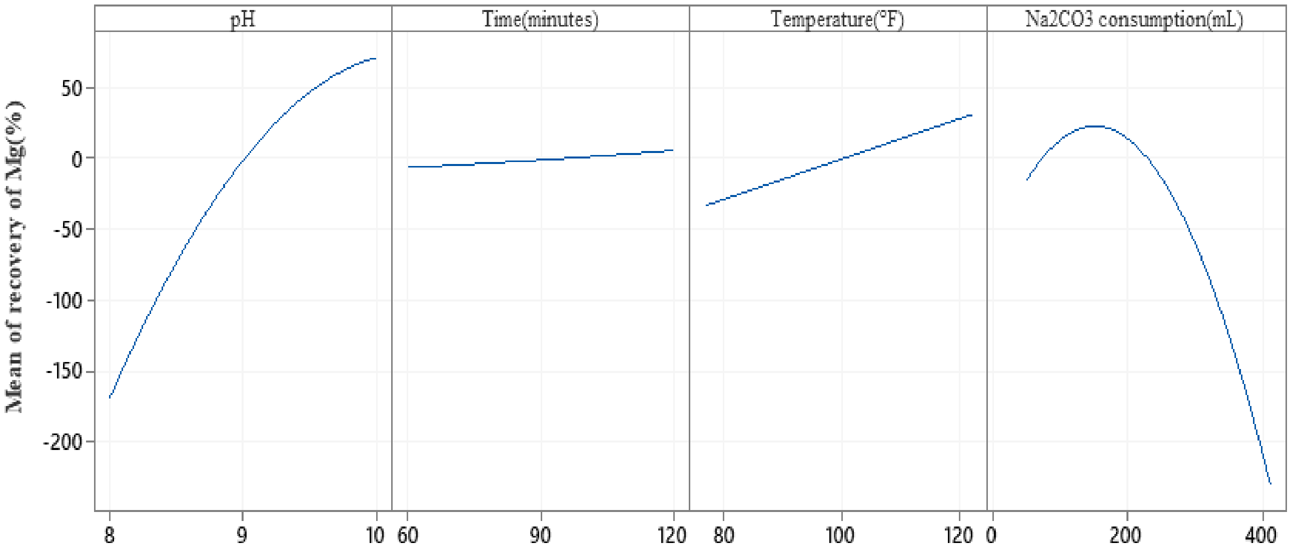


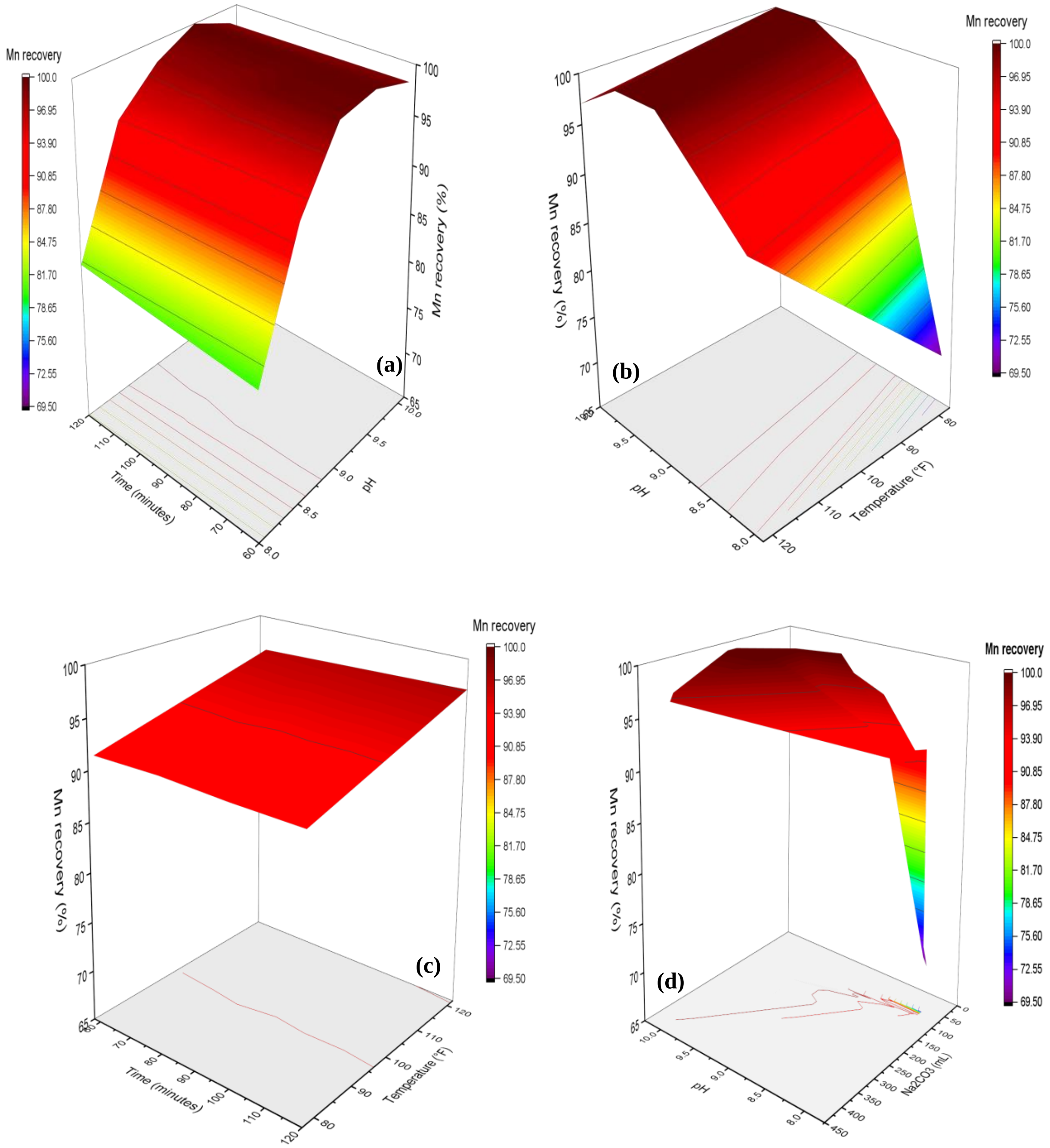
Figure 4 – Main effects plot for recovery of Mg (Fitted means)

4.3. Three dimensional (3D) response surface plot and two dimensional (2D) contour plots

Haider and Pakshirajan (2007) stated that the 3D response surface and the 2D contour plots are the graphical representations of the regression equation. Those plots were used in order to gain a better understanding of the interaction effects of factors (variables) on recovery, based on the model equations (Equations 7 and 8). For the representation of the plots, since each model has four variables, two variables were held constant at the center level.

3D response surface plots were constructed by OriginPro software and those plots are shown in Figure 5. The relationship between the variables and their influence on the response are investigated in this section. Figures 5 and 6 show the influence of pH, time, temperature and Na_2CO_3 consumption on the Mn and Mg recoveries respectively.

Note that the best situation to look for was to have maximum Mn recovery and minimum Mg recovery, using the factors at their minimum values.


Mn recovery
100.0
96.95
93.90
90.85
87.80
84.75
81.70
78.65
75.60
72.55
69.50
(a)
Mn recovery (%)
Time (minutes)
pH
(b)
Mn recovery (%)
pH
Temperature (°F)
(c)
Mn recovery (%)
Time (minutes)
Temperature (°F)
(d)
Mn recovery (%)
pH
Na2CO3 (mL)

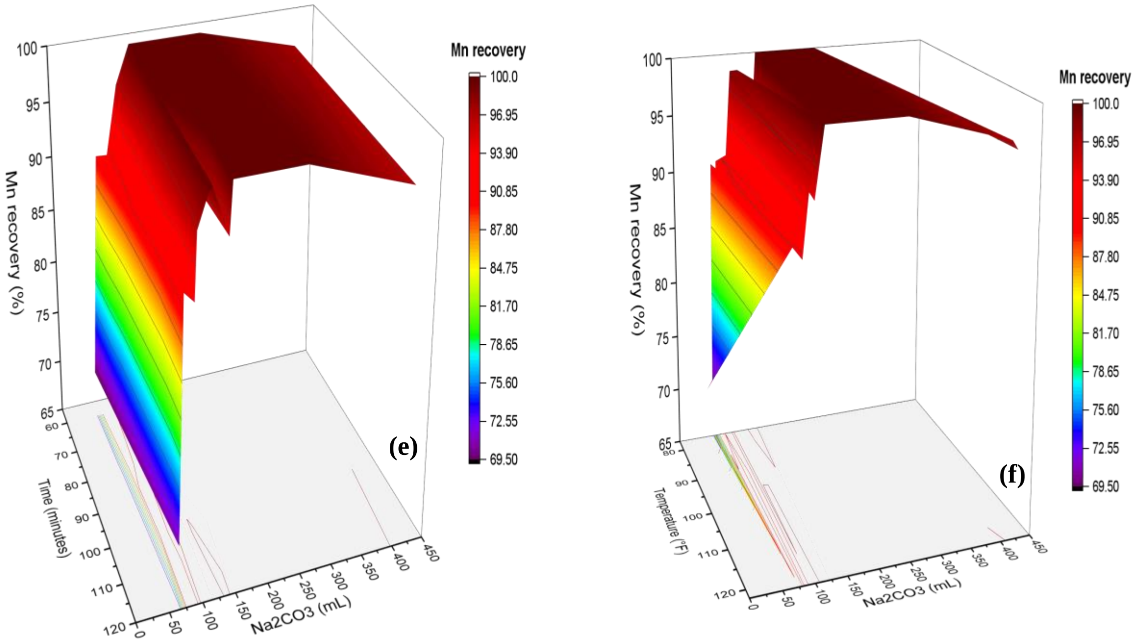
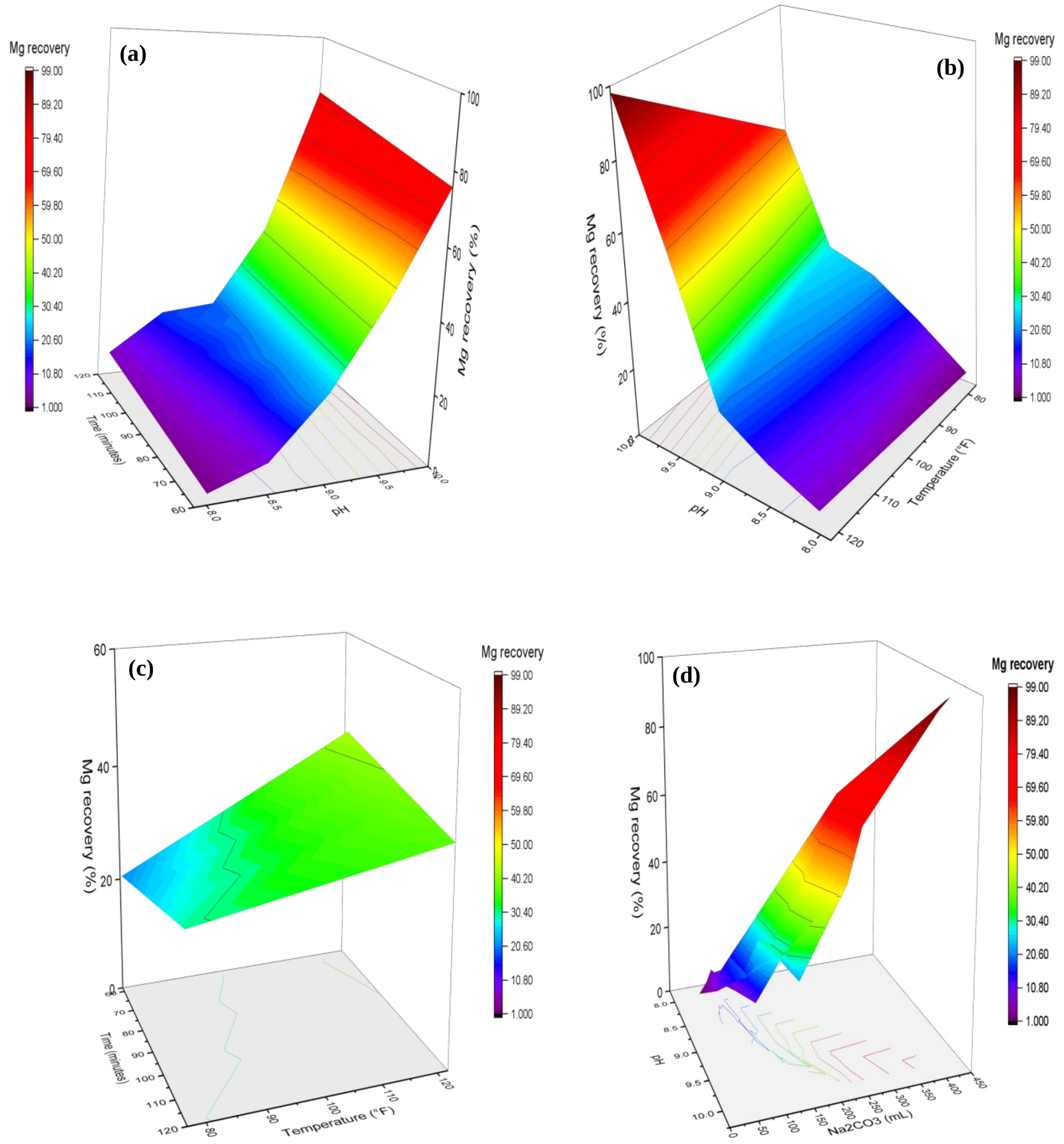


Figure 5 – Response surface plots showing the effects of two factors on Mn recovery (other variables are held at center level). (a) pH and time; (b) pH and temperature; (c) Time and temperature; (d) pH and Na_2CO_3 consumption; (e) Time and Na_2CO_3 consumption; (f) Time and Na_2CO_3 consumption

According to Figure 5, it is indicated that enhancement of pH increases the Mn recovery until a certain maximum value near 9.5 and then decreases slightly. The consumption of Na_2CO_3 is very variable and the curve is irregular because this solution was used as a supply of carbonate ions and also as a pH regulator. It is obvious that the pH of the solution and Na_2CO_3 (100 g / L) volume had a great effect on Mn recovery. The influence of time is less significant and approximately invariable. Regarding the recovery of Mn, the area whose yield is between 97% and 99.99% has a dark red color. In this zone, the pH varies between 9.3-9.8, the temperature is between 77°F and 122°F, the consumption of Na_2CO_3 is between 125-310 mL. However, the variation of the time has no impact but it is better to not exceed 85 min to be on the considered area.


(a)
Mg recovery
99.00
89.20
79.40
69.60
59.80
50.00
40.20
30.40
20.60
10.80
1.000
Time (minutes)
pH
Mg recovery (%)
(b)
Temperature (°F)
(c)
Temperature (°F)
(d)
Na2CO3 (mL)

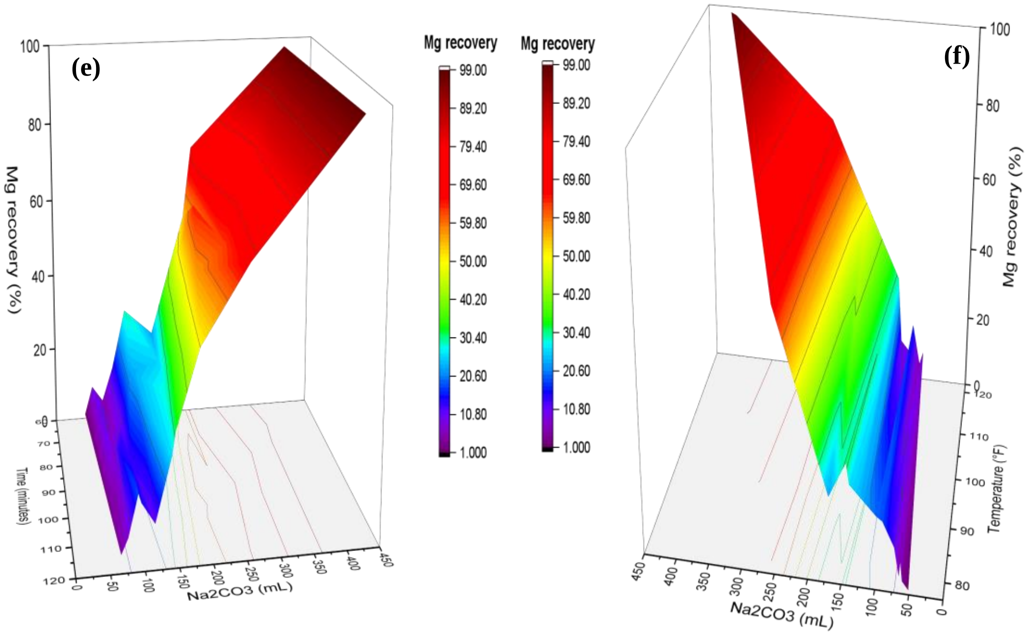


Figure 6 – Response surface plots showing the effects of two factors on Mn recovery (other variable is held at center level). (a) pH and time; (b) pH and temperature; (c) Time and temperature; (d) pH and Na_2CO_3 consumption; (e) Time and Na_2CO_3 consumption; (f) Time and Na_2CO_3 consumption

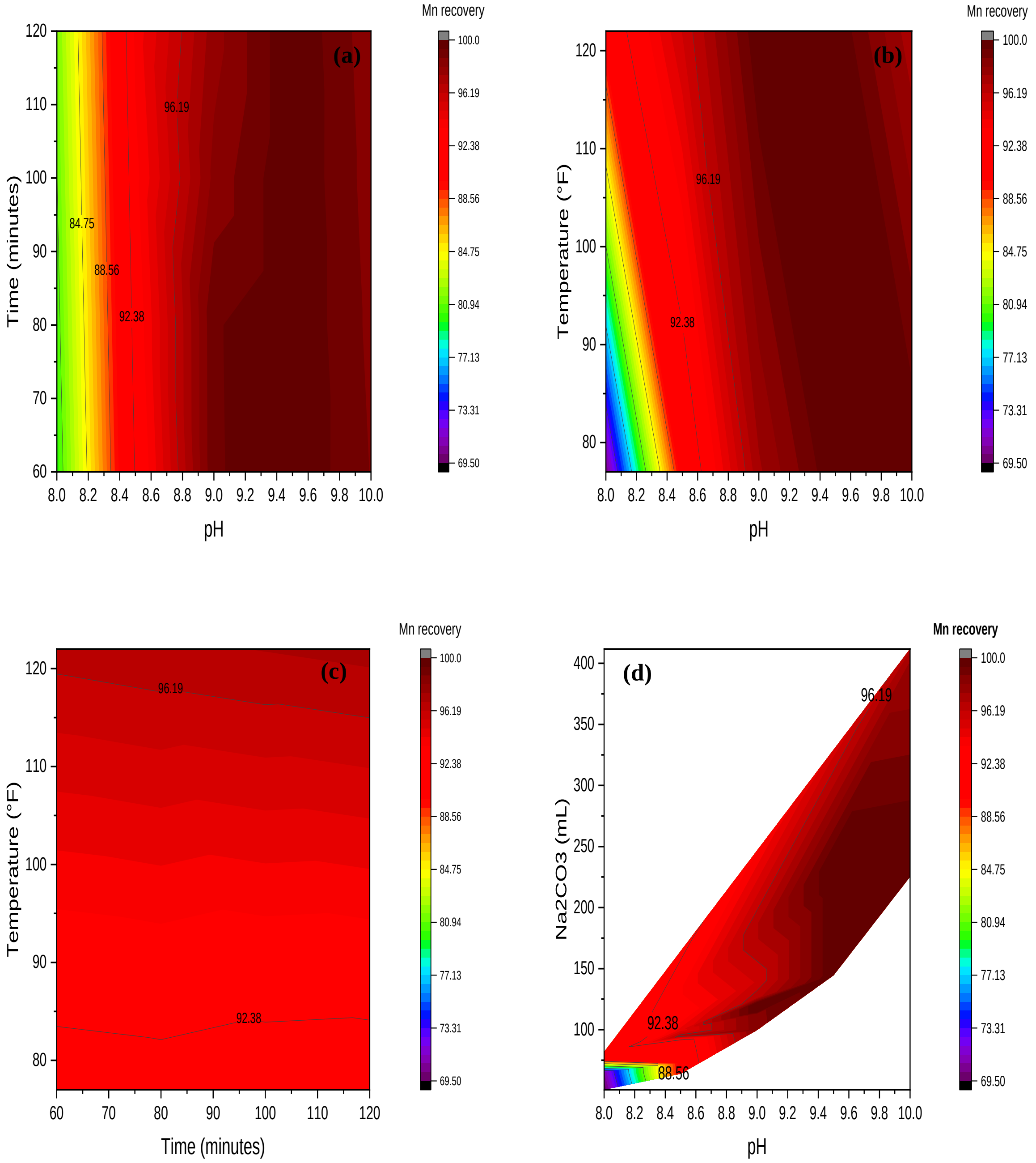
Figure 6 confirms the positive influence of enhancement of pH increasing the recovery and the influence of temperature on the Mn recovery is positively linear and the slope is higher than that of the time influence. Also, Na_2CO_3 volume shows a high influence on the Mn recovery.

Furthermore, Figure 6 indicates that enhancement of pH and temperature increases the Mg recovery to a certain maximum value. As seen for Mn recovery, Na_2CO_3 consumption is very variable and the curve is irregular because this solution was used as a supply of carbonate ions and also as a pH regulator. It is obvious that the pH of the solution and Na_2CO_3 (100 g/L) volume had a great effect on Mn recovery. The influence of time is less significant and approximately invariable. The influences of time and temperature have almost the same effects as for Mn recovery.

Results of Figure 6 concerning the recovery of Mg, the area whose yield is between 1% and 5% has a mauve color. In this zone, the pH varies between 8.0-8.3, the consumption of Na_2CO_3 is between 50-80 mL. However, the variations of both the temperature and the time have no impact but it is better to not exceed 90 min and 100°F.

In others words, pH, time and Na_2CO_3 volume have a significant influence on recoveries of both Mn and Mg. However, the temperature has an approximately invariable influence on the two recoveries.

The relationship between the variables and their influence on the response are investigated using 2D contour plots constructed by OriginPro software. Figures 7 and 8 show those plots. Note that Figures 7 and 8 (a, b, c, d, e, f) have been plotted according to Figures 5 and 6 (a, b, c, d, e, f) respectively.


(a)
Mn recovery
Time (minutes)
pH
84.75
88.56
92.38
96.19
100.0
80.94
77.13
73.31
69.50
(b)
Temperature (°F)
(c)
Time (minutes)
(d)
Na2CO3 (mL)

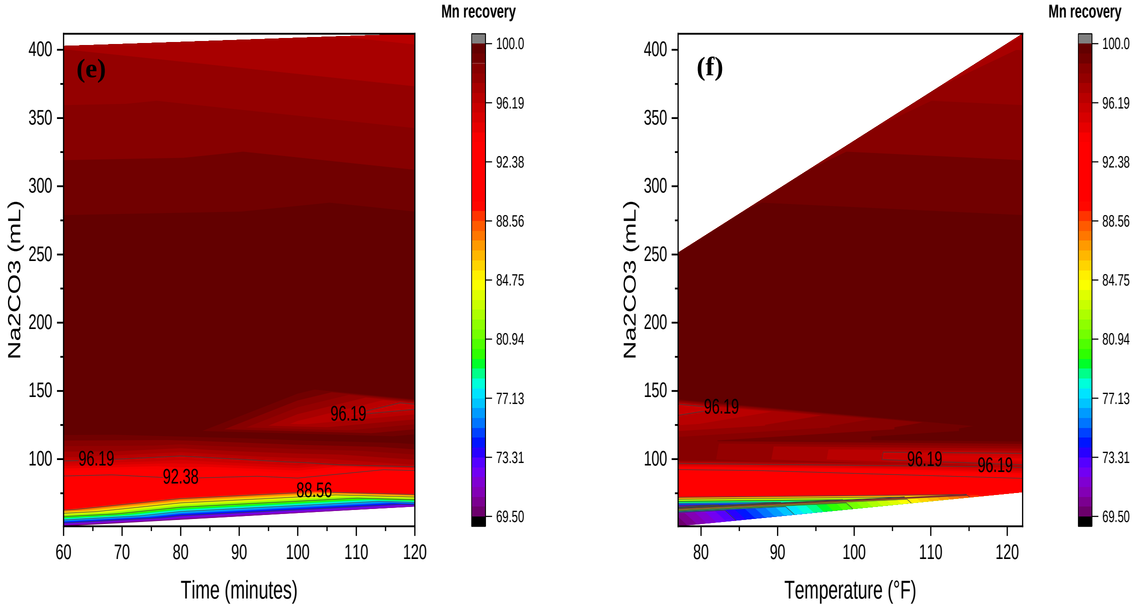
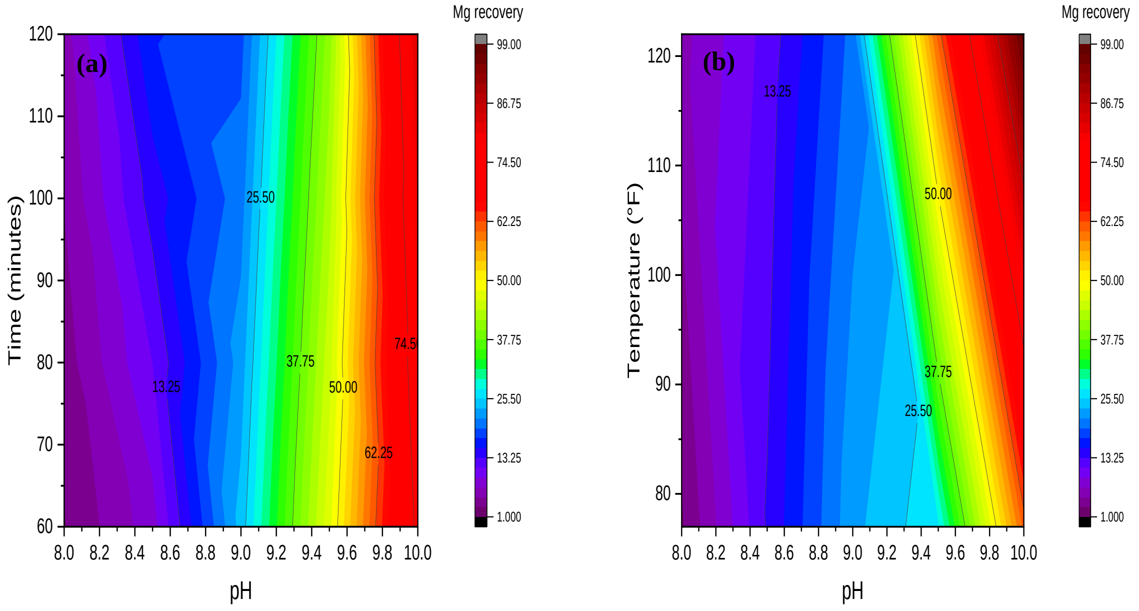


Figure 7 – Contour plots for Mn recovery

Considering the pH-time interaction, when the time is 60-80 min, the dark red area (97-99.99% Mn recovery) corresponds to that of pH equal to 9.1-9.75. Above 85 min of reaction, the pH range becomes 9.3-9.75. Regarding the pH-temperature interaction, the pH of the considered zone corresponds to 9.3-10 when the temperature is in the range of 77-96°F; above 96°F the pH range is reduced 9.3-9.7. In accordance with the pH-volume interaction of Na_2CO_3, the considered area is in the pH range of 9.3-10 with consumption of Na_2CO_3 equal to 125-31 mL. Moreover, the time-temperature-volume interactions of Na_2CO_3 show that the zone considered corresponds to the volume of 125-300 mL regardless of time and temperature.



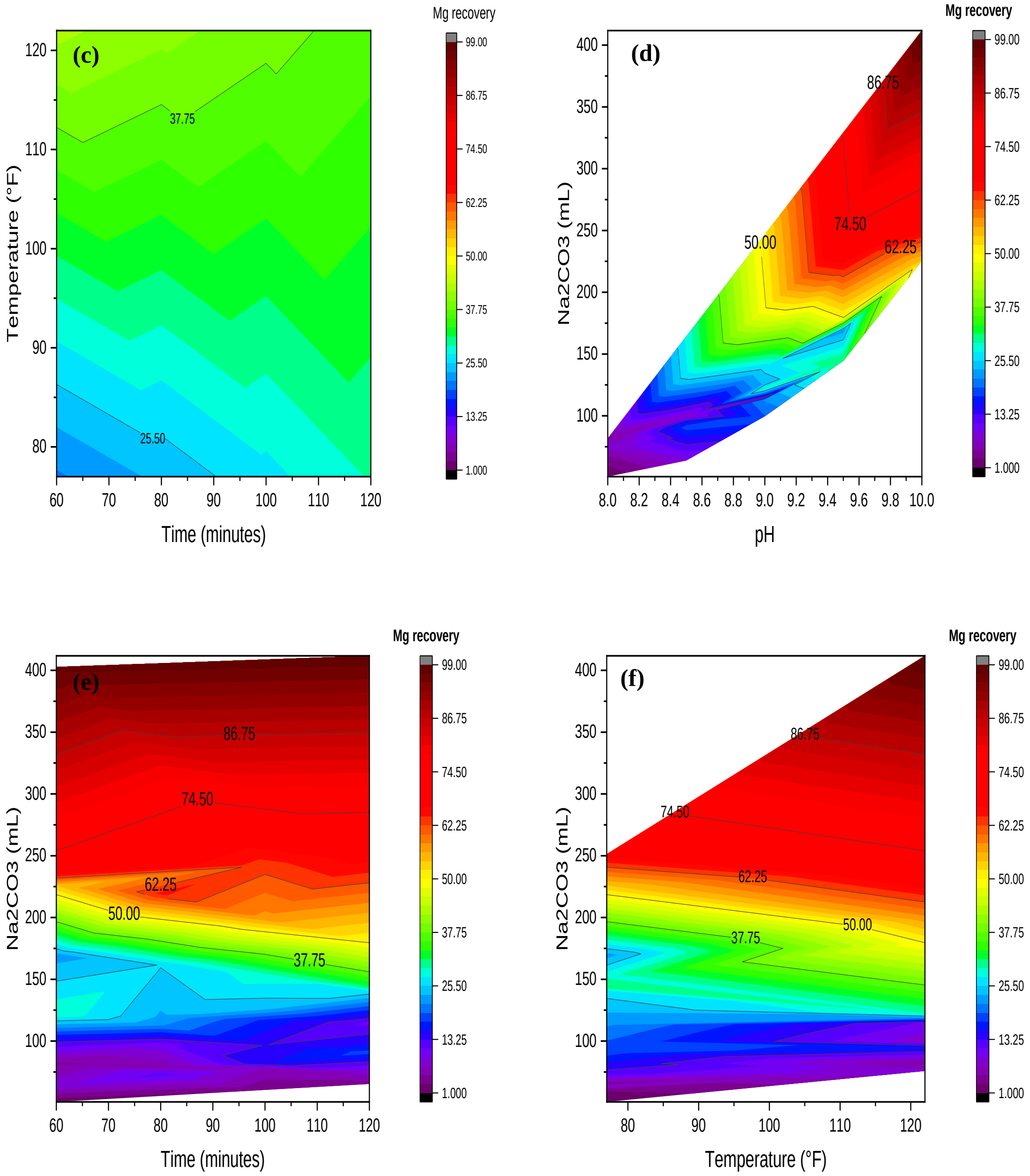


Figure 8 – Contour plots for Mg recovery

According to the pH-time interaction, the mauve color area (1-5% Mg recovery) corresponds to that of pH equal to 8.0-8.2 when the time is 60-90 min. The increase in the reaction time leads to a reduction in the concerned area and the pH is then reduced to 8.0.

For the pH-temperature interaction, the pH of the considered area corresponds to 8.0-8.1 and gradually decreases to the temperature of 100°F.

On another hand, with the pH-temperature-volume interactions of Na_2CO_3, the variation is quite irregular and when the consumption of Na_2CO_3 is 50-100 mL, the considered area is in the pH range of 8.0-8.1, but with the increase in time and temperature, the volume increases to 80 mL. In addition, the time-volume interaction of Na_2CO_3 shows that the considered area corresponds to the volume of 50-75 mL with a reaction time of 60-90 min, but the increasing of time involves the reduction of the volume of Na_2CO_3 up to 75 mL.

After observing the above plots, it is indicated that the increase of pH, temperature and volume of Na_2CO_3 involves the increasing of the precipitation yield of Mn and also Mg. Mn^{2+} ions are the first to precipitate until almost all of it is removed from the solution and thus its precipitation efficiency no longer changes. Subsequently, with the influence of the three factors mentioned, Mg^{2+} precipitates.

Mg_{2+} co-precipitation should be minimized by reducing pH, time, temperature and CO_3^{2-} ions input. So according to those results, the best ranges for pH, reaction time, temperature and volume of Na_2CO_3 are 8.0-9.3, 60-90 min, 77-100°F and 50-125 mL respectively.

4.4. Optimization

The main objective of this investigation was to find the optimum condition of the precipitation process with the highest Mn recovery, the lowest Mg recovery, the minimum pH, time, temperature and Na_2CO_3 consumption.

The desirable location, in which there are maximum and minimum variables in the design space, was found using the response surface methodology used by OriginPro software.

Table 8 shows the results of the precipitation process optimization (with two targets) and optimum levels of variables.

Table 8 – Optimisation and optimum levels of variables

No	Case	Target	pH	Time (minutes)	Temperature (°F)	Na_2CO_3 (mL)	Mn recovery (%)	Mg recovery (%)	Desirability
1	Mn recovery Variables Mg recovery	Maximum Minimum Maximum	9.9920	94.7749	122	404.343	97.2249	98.5312	0.9535
2	Mn recovery Variables Mg recovery	Maximum Minimum Minimum	8.9293	60.69	77.95	50.7650	99.9799	4.3045	0.9837

Note that the first target predicted conditions considering maximum levels of the Mn and Mg recoveries, and minimum values of variables as the optimization target. The results have shown that the Mn and Mg recoveries reached 97.2249 % and 98.5312% respectively; pH, time, temperature and Na_2CO_3 consumption (100 g/L) were 9.9920%, 94.7749 min, 122°F and 404.343 mL respectively. Besides, the desirability of this predicted condition achieved 0.9535. This target allowed us to understand at which conditions the impurities could contaminate the precipitate product.

The second target predicted conditions considered the maximum level of the Mn, minimum level of the Mg, and minimum values of variables as the optimization target. The results have shown that the Mn and Mg recoveries reached 99.9799% and 4.3045% respectively. The pH, the time, the temperature, the Na_2CO_3 consumption and the desirability were found 8.9293, 60.69 min, 77.95°F, 50.7650 mL and 0.9837 respectively.

It is obvious that the increasing of pH involves the precipitation of Mg which is an impurity for precipitation product. The desirability of the first condition was more and the Mn recovery was achieved more much, producing a precipitated compound rich in impurity (Mg).

Hence, the desirability of the second condition showed that the precipitated compound was contaminated by the high recovery of Mn at optimal conditions.

5. Conclusions

1) The mathematical equations for both Mn and Mg recoveries were achieved by using sets of experimental data and OriginPro software package.

2) The high correlation coefficients of the model equations for Mn recovery (R^2=0.9455) and Mg recovery (R^2=0.9538) show that the predicted values are in good agreement with the observed values.

3) In optimum conditions, the Mn and Mg recoveries of 99.9799% and 4.3045% were obtained respectively; also, the desirability of optimum condition was approximately 0.9837. As a result, the precipitation process can be a useful method for the recovery of Mn.

4) The values of pH, time, temperature and Na_2CO_3 consumption of 8.9293, 60.69 min, 77.95°F, 50.7650 mL respectively were obtained in optimum conditions,

5) The pH, the temperature and the Na_2CO_3 consumption had the most influence on the Mn recovery compared to the time.

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