Iranian Journal of Analytical Chemistry **مجله ایرانی شیمی تجزیه**
Volume 8, Issue 1, March 2021 (17-28) Origonal Research Article دوره۸، شماره ۱، فروردین ۱۴۰۰ (۲۸-۱۷)

Optimization of Nickel Removal Process From Zinc Sulfate Solution Using Central Composite Design of Experiments

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Received: 22 February 2021 **Accepted:** 3 March 2021
DOI: 10.30473/ijac.2021.57821.1181

Abstract
Nickel is one of the metallic impurities that should be removed from the electrolyte solution before the electrowinning of zinc. This study investigated the parameters affecting the process of nickel removal in an Iranian zinc smelter plant by the response surface methodology. According to the results of experiments, the optimum condition for removal of nickel was obtained at temperature of 85 °C, the residence time of 60 minutes, zinc powder of 2.5 g/l, mixing speed of 500 rpm, and pH of 5. With regards to the resulting model from the Design-Expert software, the significant parameters were concentration, residence time, and temperature, respectively.

Keywords
Removal of Nickel; Central Composite Design; Zinc Sulfate Solution; Optimization; Cementation.

1. INTRODUCTION

In recent years, the production and consumption of zinc have been rising due to its comprehensive applications in various industries. The major part of zinc is produced by hydrometallurgy in the world [1, 2]. For the production of high-quality zinc in this method, the electrolyte solution introduced into the electrowinning stage must be free of metallic impurities with a reduction potential higher than zinc [3-6]. Cobalt and nickel are the most harmful impurities for the zinc electrowinning. These impurities may reduce the purity of zinc sediment on the cathode, causing zinc to re-dissolve by forming Zn-Ni and Zn-Co galvanic cells. In addition, they increase the energy used to make zinc sheets due to the creation of overvoltage. Therefore, it is essential to properly treat the zinc-containing solution before the electrowinning [7-10]. In most of the world's zinc manufacturing units, cobalt and nickel removal is carried out using the cementation method at the hot purification stage[11, 12]. These two elements are eliminated during the hot purification stage by adding arsenic or antimony compounds and copper sulfate, together with zinc powder at temperatures above 85 °C [13, 14]. Zinc producers in Iran use the Anguran mine where, the concentration of impurities is more than the other reported feeds (Table 1) [15, 16]. For this reason, the simultaneous removal of cobalt and nickel in one step is difficult and, inevitably, cobalt must be first removed with a manganometric method by adding potassium permanganate and lime at 85 °C. In the next step, the concentration of nickel is then reached to the allowed amount for electrowinning by cementation with zinc powder [17, 18].

According to Dib et al. [19] investigations, the cementation of cobalt and nickel followed the first-order reaction, but the cementation reactions of nickel and cobalt were diffusion-controlled and chemically-controlled, respectively when, examining separately. The concentration of zinc sulfate had no measurable effect on nickel cementation but a negative effect on the cementation of cobalt. The lowest amounts of cobalt and nickel were obtained at 85 °C and 75 °C, respectively, and it was proved that the optimal amounts of nickel and cobalt would be obtained at a concentration of 200 mg/l of copper. Behnejadi et al. [20] investigated the removal of nickel and cobalt with arsenic trioxide additive. The minimum concentration of nickel was achieved at 90 °C, the residence time of 75 min, the concentration of zinc powder 4 g/l, and arsenic concentration of 0.2 g/l. The optimal conditions for the removal of cobalt were also

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*Corresponding Author: k.shayesteh@uma.ac.ir obtained at 85 °C, the residence time of 75 min, the concentration of 4 g/l, and arsenic concentration of 0.2 g/l. Boyanov et al. [21] studied the simultaneous removal of nickel and cobalt, concluding that the presence of copper ions has a more significant effect on nickel cementation than that of cobalt. From the view point of the stability of results over time, the best conditions were obtained at temperatures of 75-80 °C, 300 mg/l copper ion, and 18 % zinc powder. In previous research, Low removal of nickle is conducted by antimony trioxide and arsenic trioxide activator with copper sulfate in the temperature higher than 85 C. Krause et al.[22], Behnajady etal.[20] and Jari Nasi[23] used copper sulfate and arsenic trioxide activators to cementation of nickle and cobalt from zinc sulfate solution. Also Raghavan et al.[24], Boyan et al.[25], Toni et al.[26], Karlsson et al.[3]. Boyanov et al.[21] and Dib et al.[19, 27] employed antimony trioxide and copper for removal of nickle and cobalt from zinc sulfate solution. Vanderpas et al.[28] and Guler et al.[29] investigated the effect of potassium antimony tartrate and ammonium sulfate peroxide on the cobalt removal. In many researches, simultaneously removal of nickel and cobalt in the hot purification reactor using activator agents has been investigated. Hence, in this work removal of nickel in the cold purification reactor without using activator agents is considered. As well, due to low concentrations of nickel in the feed of (according to Table 1), researchers often focus on the removal of cobalt. Due to the lowering of qualified zinc mines and the increasing need for this metal in the world, the use of feed with higher metallic impurities will also be considered in the near future. Therefore, a high concentration of nickel should be considered in order to achieve high-purity zinc.

The purpose of this study is to investigate the removal of nickel by zinc powder and the determination of effective parameters. The parameters are optimized by designing the response surface experiments at an Iranian zinc smelter plant. Such parameters that seem to have a high impact on the removal process of nickel are the zinc powder concentration and processing temperature. These two parameters are also very cost effective. The time required for the reaction of nickel cementation, pH, and mixing speed is also expected to affect the performance of the cold purification reactor. Therefore, the optimization of these parameters by the surface response method is performed in this research.

Table 1. Amount of cobalt, nickel and cadmium impurities in the different feeds.

Reference	Year of publications	content of impurities (ppm)		
		Co	Ni	Cd
Present work	2019	110	167	600
Singh et al. [30]	1996	10-14	3-4	375-400
Polcaro et al. [31]	1995	10	-	-
Nelson [32]	1998	30	-	30
Lew [33]	1994	26	-	-
Raghavan et al. [24]	1999	5	4	360
Blaser et al. [34]	1983	5-25	-	-
Dib et al. [27]	2006	10	1.5	9.4
Lu et al. [35]	1997	30	-	-
Casarol et al. [36]	2005	50	50	50
Boyanov et al. [25]	2004	13.8	1.1	134
Bockman et al. [37]	2000	10	-	200
Van der pas [38]	1995	30	-	-
Guler et al. [29]	2016	4.4	12.3	13.3
Tozawa et al. [39]	1992	10	-	-
Xu et al. [40]	2006	3.9	1.6	9.4
Boyanov et al. [21]	2004	2.6-10	3.8	147.6
Kayin [41]	2003	75	-	-
Makhloufi et al. [19]	2007	10	1.5	-
Zaheri [42]	2011	15	-	-
Friedrich et al. [43]	2002	2.8	2.3	206
Krause et al. [22]	2015	39	-	266

2. EXPERIMENTAL

One of the goals in the design of experiments is to optimize the process and achieve the desired conditions. To this end, the response surface methodology is used in the statistical design of experiments. In the response surface method, response maps are in the form of either contour lines or three-dimensional views. They are just like diagrams, geologists work on which for topography with the difference that in theresponse surface method, parallel lines indicate the test response instead of height.

Designs performed in a two-level factorial method are not able to fit the surface by the response. To identify curvature and its form, there is a need to add some central points on the surface of factors that constitutes a basis for the design of response surface techniques. Of course, based on how these central points are added to the surface of factors, response surface methods are subdivided into some mostly used subcategories of the Box-Behnken and the central composite in designing the response of surface.

When the curvature between the levels of parameters is important, adding more points to the surfaces of the factors can lead to a precise determination of the behavior of response function. The central composite method is obtained by adding new points along the axis of space between the surfaces of the factors. Fig. 1 illustrates the two-factor and three-factor designing of this method.

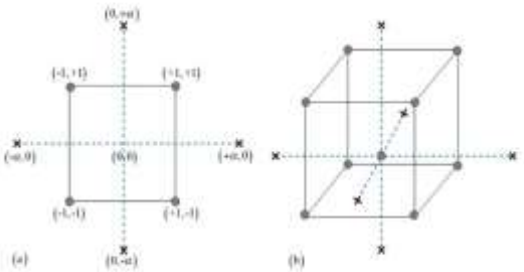


Fig. 1. Central composite method: (a) two-factor and (b) three-factor.

To increase the impact of the axial points, the points marked with the star in the figure, these points must be placed at a specific distance from the main points (factorial points). The ideal distance can be obtained by research, but this distance is very close to the square root of the number of factors. For example, for two-factor testing, the position of added axial points is 1.4 ($\sqrt{2}$) units far from the central points. Table 2 illustrates the variables and their levels by the central composite design method and specifies the type of points. Increasing the number of points increases the estimation power and defines the curvature properties better. In the central composite design method, each factor is varied in five levels: lower axial, lower factorial, central, upper factorial, and upper axial. It is noteworthy that this method is different from the five-level factorial method, because 25 (5^2) tests are required for two factors in the five-level method. However the central composite design method is a two-level factorial method in which the central and axial points are added so that the curvature behavior in the model can be well-defined. Similarly, if the factorial approach is to be used in this experiment to find the optimal point, the number of levels, 5, to the 5rd power (5 factors) is equal to 3125 tests. This number drops to 50 tests based on the response surface model, which is very important in terms of economic cost and reduced time of experiments.

Table 2. Independent variables and their levels for central composite design.

Code	Variable	Units	Type	Low actual	High actual	Low coded	High coded
A	Temperature	°C	Numeric	65	85	-1.000	1.000
B	pH		Numeric	3	5	-1.000	1.000
C	Time	min	Numeric	15	75	-1.000	1.000
D	Mixing speed	rpm	Numeric	300	700	-1.000	1.000
E	zinc powder Concentrati	g/l	Numeric	1	3	-1.000	1.000

The solution used in this work was the post-filtered solution of an Iranian zinc smelting plant. The chemical analysis of this solution is given in Table 3.

Table 3. Chemical analysis of the post-filtered solution.

Ion	Zn^{2+}	Co^{2+}	Ni^{2+}	Cd^{2+}	Fe^{2+}	Mn^{2+}	As^{3+}	Sb^{3+}
Concentration (mg/L)	85000	1.1	167	600	1	8	1<	1<

Distilled water was used for solubilization and dilution. Industrial-grade zinc powder was provided from the Zanjan powder production plant. Pure sulfuric acid and soda (Merck, Germany) were used to adjust the pH. Copper sulfate, zinc sulfate, nickel sulfate and cadmium sulfate were supplied by the Merck.

All experiments were carried out in a two-liter glass reactor. Optimal temperature conditions were achieved using a hot-plate-mixer (Heidloph MR 3001 K). The pH of the leached solution, and its temperature were adjusted by a pH-meter (WTW mul 9310). The amount of metallic was measured by an atomic absorption equipment (AA 240 Varian, Australia).

According to Table 4, fifty experiments were carried out to reach optimal response regions using Design-Expert software. One liter of the incoming solution for the cold purification stage of the zinc plant with an initial pH of 4.5 was poured into the glass reactor and the heated by heater to reach the desired temperature. Then, certain amounts of zinc powder were added to the solution and mixed on the mixer. After the mixing process, the mixture was filtered. Then, the sub-filter solution was sampled, and the impurities were measured by the atomic absorption equipment. It should be noted that the parameters studied in this study were temperature, time, amount of zinc dust, pH of the solution and mixing speed. Each test point in this article was the result of an average of 3 repetitions of the experiment. According to Eq. 1, the results are given in the form of removal percentage.

$$\text{Removal percent of nickel} = \frac{\text{Initial concentration of nickel} - \text{Secondary concentration of nickel}}{\text{Initial concentration of nickel}} \times 100 \quad (1)$$

3. RESULT AND DISCUSSION

The best statistical model was fitted by the software with the information obtained from the removal of nickel. Eq. 2 is a fitted polynomial model for nickel with a regression coefficient (R^2) of 0.9657. This value represents a proper fitting for the response data. Based on this model, the most effective parameters are the concentration of zinc dust, residence time, and temperature, respectively.

$$\text{Removal percentages of Ni} = -172.50 + 2.69A - 6.89B + 1.88C + 0.07D + 75.48E + 0.11AB - 9.12{*}10^{-3}AC - 1.63{*}10^{-4}AD - 0.37AE + 8.38{*}10^{-3}BC + 1.81{*}10^{-3}BD + 0.47BE - 2.47{*}10^{-4}CD - 0.18CE - 5.58{*}10^{-3}DE - 8.86{*}10^{-3}A2 - 0.18B2 - 5.03{*}10^{-3}C2 - 3.84{*}10^{-5}D2 - 6.53E^2 \quad (2)$$

Statistical evaluation of Equation 2 was performed by performing F-test and ANOVA analysis of variance and the result is presented in Table 5. ANOVA data confirms the accuracy of this quadratic model. With regards to the first-order model, it can be seen that the pvalue of the quadratic model is less than 0.0001, indicating that the model is significant (generally, p-values of model less than 0.05 indicate that the model is significant).

Table 4. Design of experiments by the central composite method.

Number of test	Residence time (min)	Amount of zinc powder (g/l)	pH	Mixing speed (rpm)	Temperature (°C)	Removal percentage of Ni (%)
1	60	2.5	4.5	400	80	99.06
2	15	2	4	500	75	77.53
3	30	1.5	4.5	400	70	75.23
4	45	2	5	500	75	91.58
5	30	2.5	3.5	400	70	89.10
6	30	1.5	3.5	400	80	80.06
7	60	2.5	3.5	600	70	94.94
8	30	2.5	3.5	400	80	93.64
9	45	2	4	500	75	92.53
10	45	2	4	700	75	90.35
11	60	1.5	4.5	600	80	91.70
12	60	2.5	4.5	600	80	98.17
13	30	2.5	3.5	600	70	89.64
14	45	2	4	500	75	92.35
15	30	1.5	3.5	600	80	83.64
16	45	1	4	500	75	69.94
17	45	2	4	500	75	92.18
18	60	2.5	3.5	400	70	94.58
19	75	2	4	500	75	95.41
20	60	2.5	4.5	600	70	95.82
21	30	1.5	4.5	600	70	75.76
22	30	1.5	3.5	400	70	74.00
23	60	2.5	4.5	400	70	94.47
24	30	2.5	4.5	600	80	97.53
25	30	2.5	4.5	400	80	94.88
26	45	2	4	500	75	92.53
27	60	1.5	4.5	600	70	85.82
28	45	2	4	500	75	92.05
29	60	1.5	3.5	400	80	89.29
30	30	2.5	4.5	600	70	92.53
31	30	1.5	4.5	400	80	84.00
32	30	1.5	4.5	600	80	85.17
33	45	2	4	500	75	92.06
34	45	2	4	500	75	92.23
35	60	1.5	4.5	400	80	90.70
36	45	2	4	500	75	92.47
37	45	2	4	500	85	97.29
38	60	1.5	3.5	600	70	85.06
39	60	1.5	4.5	400	70	83.82
40	60	1.5	3.5	600	80	90.74
41	60	2.5	3.5	600	80	92.29
42	30	2.5	4.5	400	80	91.00
43	60	2.5	35	400	80	97.29
44	45	3	4	500	75	99.00
45	30	1.5	3.5	600	70	74.94
46	45	2	4	300	75	88.58
47	45	2	3	500	75	90.06
48	30	2.5	3.5	600	80	96.53
49	45	2	4	500	65	82.94
50	60	1.5	3.5	400	70	83.11

The F-parameter is also a measure of the deviation of the data from the mean value. In general, for a model that successfully predicts test results, the F-value is typically high. The F for this model is 40.84 for nickel, which indicates that the model is completely meaningful.

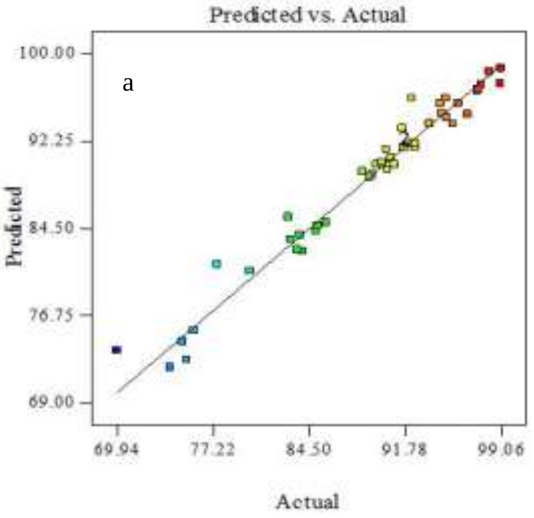
Furthermore, a great R2 of 0.9657 confirms the high accuracy of the established model (it is recommended to determine the regression coefficient of determination-R2 should be higher than 0.80). In addition, the predicted correlation coefficient (Pred-R2) and adjusted correlation coefficient (Adj-R2) are also within a reasonable range (if the difference between Pred-R2 and Adj-R2 values is less than 20%, the developed model can be considered valid).

Table 5. The results of the analysis of variance (ANOVA) table of the model fitted to the response data.

Source	Sum of Squares	Mean Square	F Value	P-Value
Model	2394.52	119.73	40.84	0.0001
A-T	320.85	320.85	109.44	0.0001
B-pH	22.67	22.67	7.73	0.0094
C-t	388.7	388.7	132.58	0.0001
D-Mix	9.32	9.32	3.18	0.0850
E-C	1402.23	1402.23	478.29	0.0001
AB	2.49	2.49	0.85	0.3640
AC	14.97	14.97	5.11	0.0315
AD	0.21	0.21	0.072	0.7896
AE	28.1	28.1	9.59	0.0043
BC	0.13	0.13	0.043	0.8369
BD	0.26	0.26	0.090	0.7661
BE	0.45	0.45	0.15	0.6971
CD	4.4	4.4	1.5	0.2302
CE	64.45	64.45	21.98	0.0001
DE	2.49	2.49	0.85	0.3640
A^2	1.57	1.57	0.54	0.4698
B^2	0.066	0.066	0.023	0.8817
C^2	41.07	41.07	14.01	0.0008
D^2	4.72	4.72	1.61	0.2144
E^2	85.33	85.33	29.11	0.0001
R-Squared	0.9657			
Adj R-Squared	0.9421			
Pred R-Square	0.8656			
Std. Dev.	1.71			
Mean	89.31			
C.V.%	1.92			

Fig. 2a shows the predicted data versus actual ones. If the points are located on a straight line, it can be assumed that the normal distribution of data is acceptable. The data obtained from the experiments are in harmony with the predicted data by the model. Therefore, the hypothesis of the normal distribution of data can be validated.

Fig. 2b also shows the predicted response values for each experiment by the model versus the residuals. It can be assumed that the points of distribution are random and the assumption of the equality of variances is confirmed.



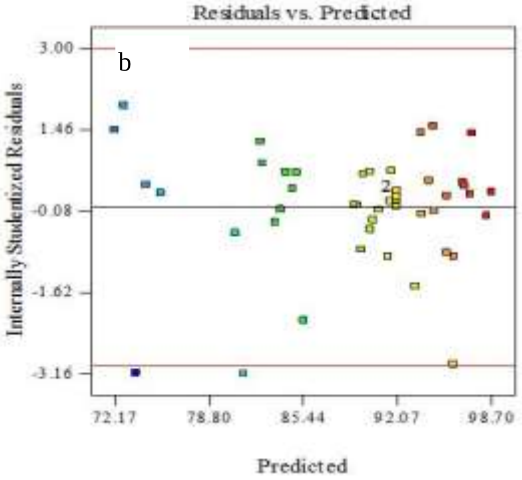


Fig. 2. (a) Predicted data versus actual ones and (b) residuals versus the predicted data.

The effect of temperature on nickel cementation by zinc powder is presented in Fig 3a. The rate of nickel cementation reaction has dramatically increased with increasing temperature, which significantly decreases the concentration of nickel ions in the solution. As the temperature increases, the kinetic energy of the electrolyte solution increases and more nickel ions can cross the energy barrier. As a result, the temperature rise would increase the speed of the cementation reaction of nickel using zinc powder. As well, the rise of temperature reduces the viscosity of the solution. In accordance with Stock's law, a decrease in the viscosity increases ionic mobility, which can be effective on the efficiency of the nickel reduction reaction.

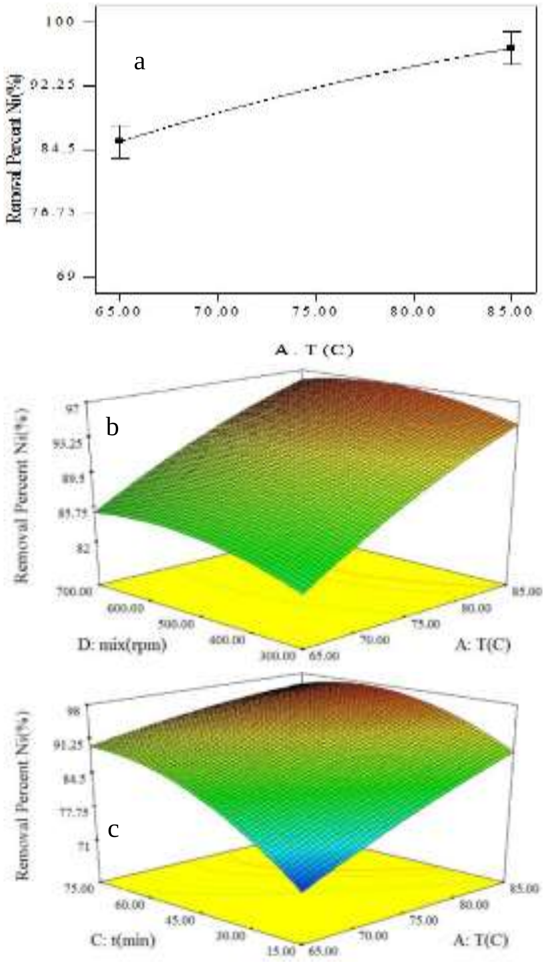


Fig. 3. (a) Effect of temperature on removal of nickel, (b) interaction between temperature and mixing speed and (c) interaction between temperature and time.

Fig. 3b illustrates the interaction of temperature with mixing speed on the reaction of nickel reduction. Nickel reduction is well-progressed at high temperatures, even at low mixing speeds. This can be attributed to a decrease in viscosity at high temperatures, which results in proper mixing.

Fig. 3c shows the interaction of temperature with residence time on the nickel cementation reaction. As can be seen, the efficiency of nickel removal reaction increases with the simultaneous increase in temperature and residence time. The desired removal rate can be achieved by increasing the temperature at a lower residence time or increasing the residence time at lower temperatures. During the purification stage, reducing the temperature can lower energy consumption, and reducing the residence time can also be effective in production capacity. Considering the importance of each of both parameters and according to the needs of the production unit, the favorable result can be maintained by increasing only one of these parameters.

Fig. 4a shows the amount of nickel removal by zinc powder as a function of pH. The nickel removal increases by increasing pH. The lower the pH, the higher the concentration of hydrogen ions in the solution, which can easily react with zinc powder and generate hydrogen gas due to its higher reduction potential than the nickel. Therefore, at lower pHs, the hydrogen reduction is more intense with the probability of forming a layer of hydrogen molecules at the surface of the powder. The presence of gas molecules on the surface of powders creates a resistance to the diffusion and reduction of nickel ions, which leads to a decrease in the overall rate of nickel cementation reaction.

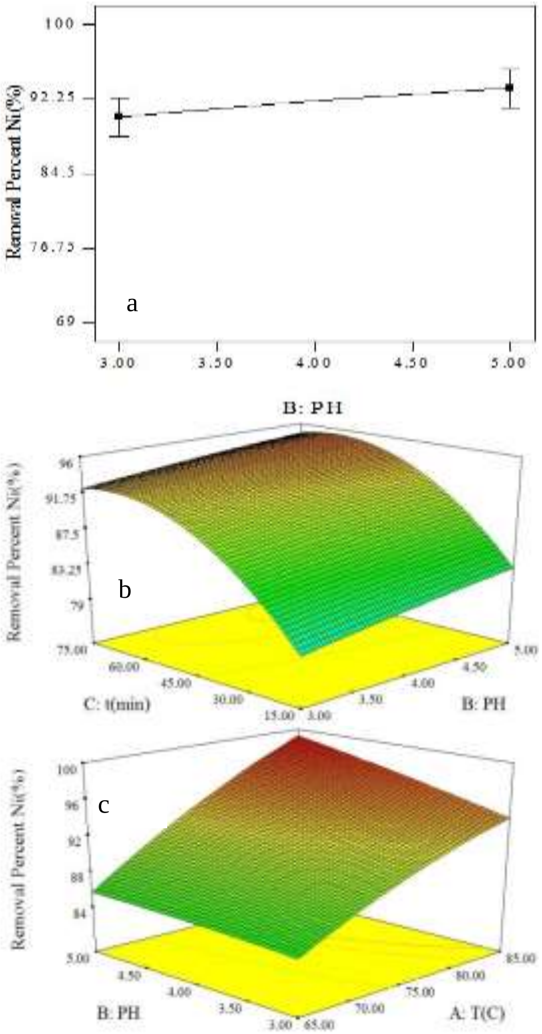


Fig. 4. (a) Effect of pH on removal of nickel, (b) interaction between time and pH and (c) interaction between temperature and pH.

The interaction of pH with residence time on the efficiency of nickel cementation with zinc powder is represented in Fig. 4b. As can be observed, the nickel removal increases by increasing the residence time at various pHs. Hydrogen gas molecules find more time to enter the solution over time. On the other hand, the concentration of hydrogen ions also decreases due to the reduction on the surface of zinc powder by increasing the residence time. It may result in a decrease in the concentration of hydrogen gas molecules at the surface of zinc powder as well as the resistance of the gas phase, which leads to the increase in nickel reduction.

The interaction of pH with temperature on the reduction of nickel is also demonstrated in Fig. 4c. The reduction of nickel by zinc powder increases with increasing the temperature at all pHs. In fact, the kinetic energy of hydrogen molecules increases with increasing the temperature, which increases the diffusion rate of hydrogen gas into the electrolyte solution. All of these levels lead to a decrease in gas resistance on the surface of zinc powder and an increase in the removal of nickel ions in solution.

The effect of residence time on the yield of nickel cementation reaction is presented in Fig. 5a. The efficiency of removal of nickel ions by zinc powder increases up to 60 minutes of residence time. At higher than 60 minutes, the nickel removal efficiency is constant, and more increase in time does not have much effect on the reduction of nickel. There is not enough time to complete the reaction of nickel cementation on zinc powder at low residence times. Increasing the residence time provides a sufficient opportunity for the ion exchange and substitution of nickel with zinc which, increases the efficiency of nickel removal. The reason for the decrease in the reaction rate after 45 minutes and its uniformity after 60 minutes can be related to the decrease in the concentration of zinc powder in the solution. In this case, the deposited layer on the surface of zinc powder is very high (after 60 minutes) as the electrons cannot longer be transferred from the surface of the zinc powder to the nickel ions.

Fig. 5b demonstrates the interaction of residence time with mixing speed on the efficiency of nickel reduction. Proper mixing leads to an increase in the reduction of nickel at all residence times. By an appropriate mixing speed, the probability of a collision of nickel ions and zinc powder particles can be increased, which can improve the nickel cementation reaction.

Fig. 5c, which shows the interaction of concentration of zinc powder with residence time, indicates that increasing the concentration of zinc powder at all residence times greatly reduces the concentration of nickel ions in the solution. Increasing the concentration of zinc powder leads to an increase in proper collisions and interaction of nickel ions with zinc powder particles by increasing the available surface for nickel reduction, which may cause a high percentage of removal even at low residence times. To achieve a certain concentration of nickel ions in the solution, increasing the residence time to 60 minutes can diminish the amount of zinc powder used. Also, when less reaction time is needed, it can be obtained by increasing zinc powder concentration.

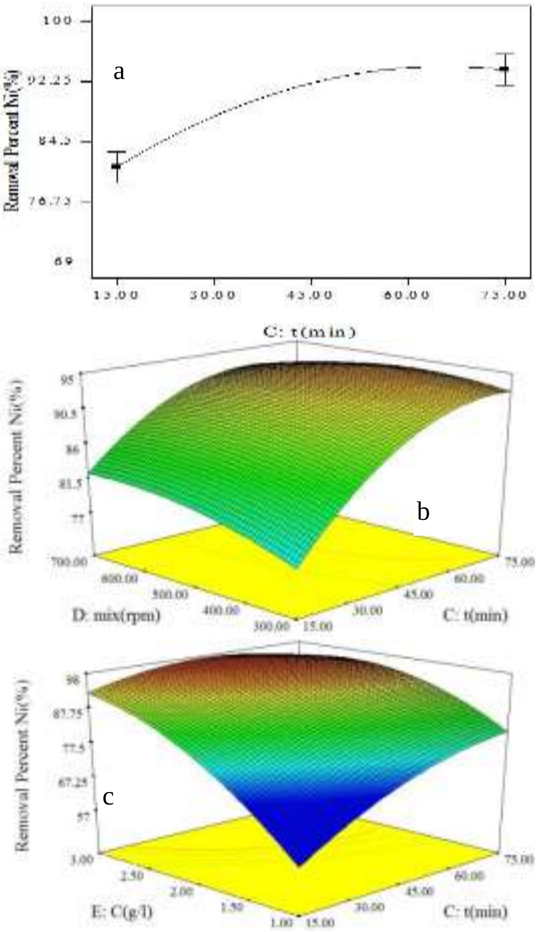


Fig. 5. (a) Effect of residence time on the removal of nickel, (b) interaction between residence time and mixing speed and (c) interaction between residence time and concentration of zinc dust.

The effect of the concentration of zinc powder on the nickel cementation reaction is illustrated in Fig. 6a. The progress of cementation by reduction of metallic ions on the zinc powder surface results in the deposition of metallic impurities in the solution. The higher the level of zinc powder available, the better the improvement of the cementation reaction of metallic impurities. According to Fig. 6a, the rate of reduction of nickel ions increases significantly with increasing the concentration of zinc powder reaching a uniformity in concentrations above 2.5 g/l. Actually, concentrations above 2.5 g/l have little effect on the rate of nickel reduction after 45 minutes. An adequate surface for the desired reduction of nickel is provided by 2.5 g/l zinc powder; hence, increasing the concentration of zinc powder cannot increase the reaction speed with regards to the constancy of other parameters. Any way increasing the concentration of zinc powder can affect other parameters and reduce their effectiveness. As shown in Fig. 6b, the interaction of temperature with the concentration of zinc powder indicates that the nickel reduction reaction can have an acceptable yield at all temperatures by increasing the concentration of zinc powder. Increasing the temperature reduces the consumption of zinc powder to achieve a constant concentration of nickel ions. An increase in the concentration of zinc powder can also reduce the temperature required to complete the reaction.

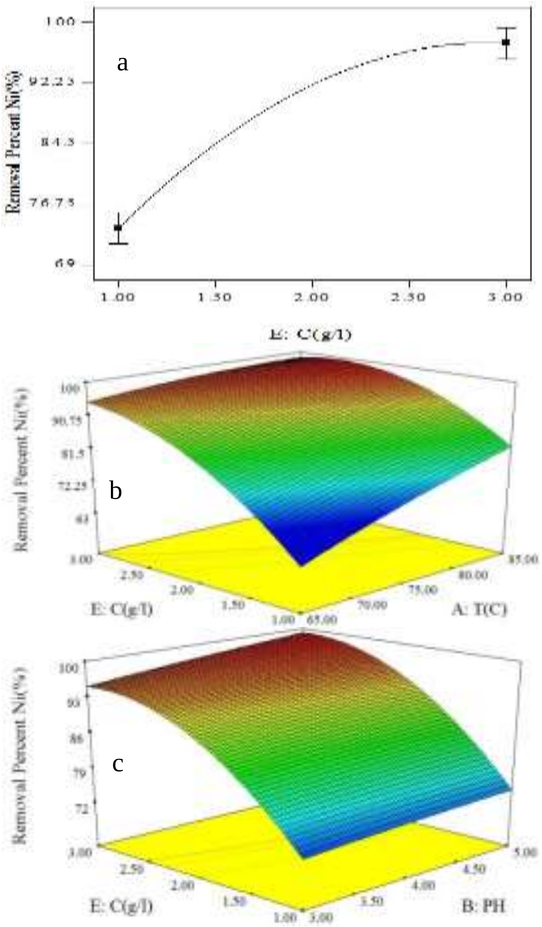


Fig. 6. (a) Effect of concentration of zinc powder on nickel cementation reaction, (b) interaction between temperature and concentration of zinc powder and (c) interaction between pH and concentration of zinc dust.

Fig. 6c shows the interaction of zinc powder concentration with pH. As seen, pH changes have almost little effect on the reduction of nickel. In fact, the large surface created causes the reaction of hydrogen ion reduction on the surface of the powder has no significant disturbance for the reduction of nickel. As well, increasing pH would be cost-effective by reducing the consumption of zinc powder. In point of fact, the desired concentration of nickel in the solution can be achieved at higher pHs with lower consumption of zinc powder.

Fig. 7a represents the effect of mixing speed on the removal of nickel by zinc powder. As can be seen, the rate of nickel ions removal from the zinc sulfate solution increases up to 500 rpm mixing speed but decreases gradually in mixing speeds above 500 rpm. The mixing speed can control the rate of heterogeneous chemical reactions. Increasing the mixing speed increases the amount of mass transfer and the number of effective collisions. From other perspectives, cementation reactions are heterogeneous electrochemical reactions, in which the cation reaches the solid surface and takes the electron from the anode makes the zinc cation releases in the solution. In such an electron interaction, the sedimentation of the intruder cation forms on the anode. The necessary condition for the cementations reaction is that the nickel ions must pass themselves to the active sites of zinc powder, and then overcome the energy barrier with sufficient energy and precipitate elementally by gaining electron from the zinc powder. The appropriate mixing speed increases the probability of colliding nickel ions with active sites of zinc, which increases the rate of nickel cementation reaction. Increasing the speed of mixing impurities in the leach solution with zinc powder increases the rate of cementation reaction of nickel. As well, proper mixing results in a uniform distribution of zinc powder particles in the solution and prevents them from depositing, which can have a significant impact on the efficiency and duration of the reaction.

The interaction of pH with mixing speed is demonstrated in Fig. 7b. Obviously, the best performance is obtained by mixing speed at 500 rpm and pH of 5. However, the effects of these parameters are lower than those of temperature, the concentration of zinc powder and residence.

Fig. 7c shows the interaction of mixing speed with the concentration of zinc powder. A high removal percentage occurs by increasing the concentrations of zinc powder in almost all mixing speeds, which indicates that nickel ions are more readily available to the surface of the powder in high concentrations of zinc dust. Much more increasing of the mixing speed makes the tangential velocity component around the shaft, which creates a vortex. In fact, based on the centrifugal force, the fluid tends to be thrown towards the reactor wall. As a result, fluid layers are adhere to the wall of the reactor, creating a gap between the mixing shaft and the fluid. With this action, more molecules of the air can enter the solution, which reduces the efficiency of the mixer. As well, due to the lack of use of the entire reactor space and the accumulation of fluid on the wall as well as the presence of a centrifugal force that is more effective on the solid, the zinc powder cannot be well-distributed. The higher diffusion of oxygen molecules into the solution can also reduce the rate of nickel cementitious reaction by forming zinc oxide and zinc hydroxide in the diffusion layer.

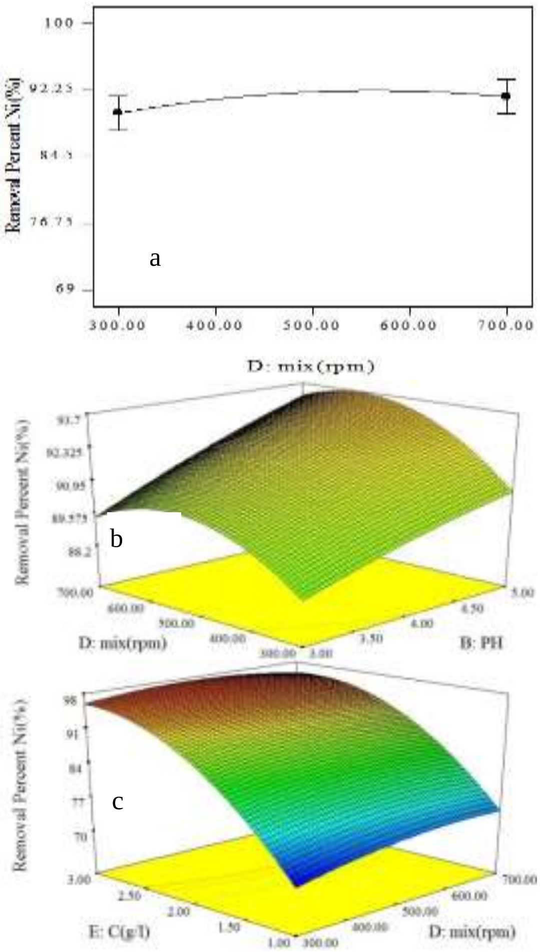


Fig. 7. (a) Effect of mixing speed on the removal of nickel, (b) interaction between mixing and pH and (c) interaction between mixing speed and concentration of zinc dust.

After analyzing the effects of important parameters in order to achieve the best processing conditions, optimization of parameters was performed using Design-Expert software. In fact, the goal of optimization is to achieve a removal percentage of 99.4 (Limit of smelting zinc plants in Iran) for nickel in economic conditions . According to Fig. 8, the optimum conditions can be obtained at a temperature of 84.83 °C, zinc powder concentration of 1.97 g/l, the pH of 4.99, mixing speed of 486.8 rpm and residence time of 56.39 min. According to optimal conditions, five experiments were performed (at temperature of 85 °C, 1.97 g/l of zinc dust, the residence time of 56 min, pH of 5 and mixing speed of 490 rpm). Average concentration of main impurities after purification process based on the proposed optimal conditions are Cd^{2+} = 0.4 mg/l, Ni^{2+} = 0.5 mg/l and Co^{2+} = 0.9 mg/l. As can be seen, the concentration of all impurities is below than 1 ppm, which is an excellent limit in Iran industries.

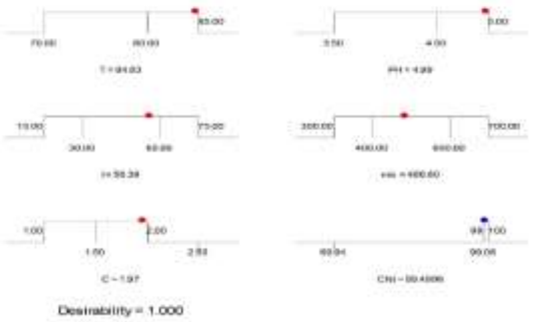


Fig. 8. Optimum conditions proposed by Design-Expert software

4. CONCLUSION

In this study, the effective factors on the nickel removal of in the leaced solution of an Iranian zinc smelter plant were investigated using the surface response method and the optimum conditions were determined. The results showed that the concentration of zinc powder, time, and temperature had the most effects on the removal of nickel .The Interaction of parameters showed that increasing the concentration of zinc powder can reduce the time and temperature of the complete reaction. It also neutralized the effect of pH change and mixing speed. Increasing the temperature, increased the nickel cementations reaction rate and the highest removal percentage was obtained at 85 °C. In low pHs, the efficiency of nickel removal was low and the consumption of powder was also increased because of the high concentration of hydrogen ions. also The best pH was found to be 5 for the optimum reaction of nickel cementation by zinc powder. In the first 60 minutes, the nickel cementations reaction rate increased, but residence times of higher than 60 minutes had a adverse effect on the removal efficiency of nickel. The best mixing speed was 500 rpm; however, the effect of this parameter was overall lower than the other parameters. The concentration of zinc powder up to 2.5 g/l increased the rate of nickel cementation reaction and had the most significant impact on the increase of the reaction efficiency compared to other parameters.

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بررسی و بهینه سازی پارامترهای موثر بر حذف نیکل از محلول سولفات روی با استفاده از طرح مرکب مرکزی

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تاریخ دریافت: ۰٤ اسفند ۱۳۹۹ تاریخ پذیرش: ۱۳ اسفند ۱۳۹۹

چکیده

نیکل یکی از ناخاصی های فلزی می باشد که قبل از الکترووینینگ روی باید از محلول الکترولیت حذف شود. در این پژوهش پارامترهای موثر بر فرایند حذف نیکل در کارخانه روی دندی توسط روش سطح پاسخ مورد بررسی قرار گرفت. نتایج آزمایشات نشان داد که بهینه ترین حالت برای حذف نیکل در دمای ۸۵ درجه سانتی گراد، زمان ماند ۶۰ دقیقه، ۲,۵ گرم بر لیتر غلظت پودر روی، اختلاط ۵۰۰ دور بر دقیقه و pH برابر ۵ حاصل شد. با توجه با مدل حاصله از نرم افزار دیزاین اکسپرت، بیشترین تاثیر گذاری به ترتیب متعلق به غلظت، زمان ماند و دما می باشد.

واژه‌های کلیدی

حذف نیکل؛ طراحی مرکب مرکزی؛ محلول سولفات روی؛ بهینه سازی؛ سمنتاسیون.