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## Optimization and Comparison of Ni and Cd Removal Using Zinc Powder with the Response Surface Methodology

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### ABSTRACT

*In an Iranian zinc smelter plant, nickel and cadmium are removed from the electrolyte solution at the cold purification stage with the help of zinc powder. This study tries to investigate the optimal conditions for the removal of these impurities through the response surface methodology by examining the effects of effective parameters on the process. The results of the experiments showed that cadmium was cemented by zinc powder much more conveniently than nickel. The interplay of parameters showed that increasing the concentration of zinc powder can reduce the time and temperature of the entire reaction. It also neutralized the effect of the changes of pH and mixing speed. The optimum conditions for the simultaneous removal of nickel and cadmium were obtained at 75 °C, the pH of 4.5, the residence time of 45 min, the mixing speed of 500 rpm, and 2 g/l of zinc powder. Under optimal conditions, more than 99 % of nickel and cadmium were removed from the electrolyte solution.*

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### 1. Introduction

The most important feature of zinc is its ability to prevent rusting by galvanization. A thin layer of zinc metal increases the life of the low-grade steels significantly by reducing corrosion. For this reason, it saves energy and additives used in the production of stainless steel [1, 2]. In an Iranian zinc smelter plant, the zinc metal is produced by the electrowinning of the zinc sulfate electrolyte solution [3, 4]. In order to accelerate the electrowinning process and produce high quality and high purity zinc ingots, the zinc

electrolyte should be very pure and the current density must be high. In the case of leaching the zinc-containing soil at a low pH, other impurities such as copper, cobalt, nickel, cadmium, iron, germanium, etc. are dissolved in the solution of electrolyte in addition to zinc [5-7]. All of the impurities should be removed from the process during the purification step. These impurities may result in the re-dissolution of zinc, perforating sheets, damages to the anode and cathode, increasing the energy consumption, and reducing the purity of zinc. Accordingly, the

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efficient treatment of the zinc sulfate electrolyte solution is very necessary and unavoidable for a successful electrowinning process [8-11]. In most of the zinc-producing plants in the world, cobalt and nickel are removed by cementation with zinc powder and additives such as arsenic trioxide and antimony trioxide during the hot purification process [12, 13]. Cadmium is also deposited from the electrolyte solution at the cold purification stage by zinc powder [14]. The primary feed of the Iranian zinc smelter plant is usually supplied from the Anguran mine, of which impurities are far higher than those of other zinc mines in the world as shown in Table 1. Therefore, in this unit, potassium permanganate is used to remove cobalt during the hot purification step. Also, nickel and cadmium are removed by the cementation with zinc powder at the cold purification stage [15, 16]. Due to the low level of impurities in the cold purification process, the focus of most research works in the world has been on the hot purification. Thus, the removal of nickel and cadmium in high concentrations and under special conditions has not been seriously addressed at the same time [17]. In previous researches, low removal of nickel has been conducted by antimony trioxide and arsenic trioxide activators with copper sulfate in the temperature higher than 85 °C. Krause et al. [18], Behnajady et al. [4] and Jari Nasi [19] used copper sulfate and arsenic trioxide activators for the cementation of nickel and cobalt from the zinc sulfate solution. Also Raghavan et al. [20], Boyan et al. [21], Toni et al. [22], Boyanov et al. [23] and Dib et al. [24, 25] employed antimony trioxide and copper for the removal of nickel and cobalt from the zinc sulfate solution. Vanderpas et al. [26] and Guler et al. [27] investigated the

effect of potassium antimony tartrate and ammonium sulfate peroxide on the cobalt removal. In many researches, the simultaneous removal of nickel and cobalt in the hot purification reactor using activator agents has been investigated. Hence, in this work the simultaneous removal of nickel and cadmium in the cold purification reactor without using activator agents is considered. Due to the declining of the zinc supply with high quality and the increasing need for this metal in the world, the use of feed with higher metal impurities will also be considered in the near future. Therefore, the process of cold purification will also be considered in order to achieve a higher purity of zinc.

Various factors such as temperature, pH, the concentration of zinc powder, the process time, and the mixing speed can be influential in the process of cementation [28]. Thermodynamically, pH and the solution temperature are critical parameters for determining the nature and stability of cementation products. The optimum acidity and temperature for the cementation process should be suitable for minimizing the hydrogen evolution reaction and the formation of basic zinc compounds such as zinc sulfate and zinc hydroxide [18, 20, 21]. The concentration of zinc powder and the time required to complete the cementation reaction are also two essential factors for determining the cost and efficiency of the zinc production process. In the low amounts of zinc powder and short reaction time, there is not sufficient surface and contact for the complete removal of impurities, and in higher amounts, the hydrogen evolution reaction is more likely to happen [18, 23]. As many researchers argued that the reaction of the nickel and cadmium cementation on the surface of zinc powder is controlled by

diffusion, mixing can also be one of the parameters that affect the kinetics of cementation reaction. Mixing can increase the speed of the cementitious reaction by

increasing the mass transfer and the number of effective collisions between the reactants or can reduce the efficiency of the reaction by creating the vortex [24, 25].

**Table 1**

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

Year of publications	Content of impurities (ppm)			References
	Co	Ni	Cd	
2016	4.4	12.3	13.3	Guler, et al [27]
2015	39	-	266	Krause, et al [18]
2011	15	-	-	Zaheri [29]
2007	10	1.5	-	Makhloufi, et al [25]
2006	3.9	1.6	9.4	Xu, et al [30]
2006	10	1.5	9.4	Dib, et al [24]
2005	50	50	50	Casaroli, et al [31]
2004	13.8	1.1	134	Boyanov, et al [23]
2004	2.6-10	3.8	147.6	Boyanov, et al [21]
2003	75	-	-	Kayin [32]
2002	2.8	2.3	206	Friedrich, et al [33]
2000	10	-	200	Bockman, et al [34]
1999	5	4	360	Raghavan, et al [20]
1998	30	-	30	Nelson [35]
1997	30	-	-	Lu, et al [36]
1996	10-14	3-4	375-400	Singh, et al [37]
1995	10	-	-	Polcaro, et al [38]
1995	30	-	-	Van der pas [39]
1994	26	-	-	Lew [40]
1992	10	-	-	Tozawa, et al [41]
1983	5-25	-	-	Blaser, et al [42]
2020	110	167	600	Present work

Each of these parameters can have a significant effect on the process of nickel and cadmium cementitious reactions. The research performed in this field has examined one factor in a time, and investigated one parameter after another independently. The simultaneous removal of both nickel and cadmium has not been investigated so far. Therefore, in order to better understand and optimize the process of cold purification in the zinc inpowderry of Iran, there was a need for researches having demonstrated the interplay of parameters in the removal of nickel and cadmium simultaneously. The

purpose of this study is to investigate the effective parameters of the process of the simultaneous removal of nickel and cadmium from the zinc sulfate electrolyte solution as well as finding the optimal conditions for removing these impurities using the response surface methodology. The response surface methodology is an attractive method for researchers due to its more complete responses, by performing a fewer number of experiments, as compared to the conventional factorial methods.

## 2. Design of experiments

One of the goals in designing the experiments is to optimize the process and achieve the desired conditions. To this end, the response surface methodology has been used in the statistical design of experiments. In the response surface method, there are response maps 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 the response surface method, parallel lines indicate the test response instead of height.

Designs that are created in a two-level factorial method are not able to fit the surface by the response. To identify the curvature and its form, there is a need for adding some central points to the surface of factors that constitutes the 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 most used subcategories of the Box-Behnken and the central composite in designing the response of surface.

### 3. Central composite method

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 the response function. The central composite method is obtained by adding new points

along the axis of space between the surfaces of the factors.

Table 2 illustrates the design of experiments 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: the 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. But the central composite design method is a two-level factorial method in which the central and axial points are added so that the behavior of the curvature in the model can be well-defined. Similarly, if the factorial approach was to be used in this experiment to find the optimal point, the number of levels, 5, to the 5<sup>th</sup> power (5 factors) was equal to 3125 tests. This number has dropped to 50 tests on the basis of the response surface model which would be very important in terms of the economical cost and the reduced time of experiments.

### 4. Materials and process

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

**Table 2**  
independent variables and their levels for the central composite design.

Factor	Name	Units	Type	Low actual	High actual	Low coded	High coded
T	Temperature	°C	Numeric	70	80.00	-1.000	1.000
pH	Acidity	-	Numeric	3.50	80.00	-1.000	1.000
t	time	Min	Numeric	30.00	60.00	-1.000	1.000
mix	Mixing speed	r/min	Numeric	400.00	600.00	-1.000	1.000
C	Concentration of zinc powder	g/l	Numeric	1.50	2.50	-1.000	1.000

**Table 3**

Chemical analysis of the post-filtered solution.

Ion	Zn <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cd <sup>2+</sup>	Fe <sup>2+</sup>	Mn <sup>2+</sup>	As <sup>3+</sup>	Sb <sup>3+</sup>
<b>Concentration (mg/l)</b>	85000	1.1	167	600	1	8	1<	1<

Distilled water was used for solubilization and dilution. In powder-grade zinc powder was provided from 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 used in this study were also supplied by Merck.

All experiments were carried out in a two-liter glass reactor. Optimal temperature conditions were achieved using a heater-mixer (Heidolph MR 3001 K). The pH of the make-up solution and its temperature were adjusted by a pH-meter (WTW mul 9310) and controlled during the experiments. The analysis and measurement of the amount of metallic ions in this study has been carried out by an atomic absorption equipment (AA 240 Varian, Australia).

According to Table 4, fifty experiments are

needed to reach the optimal response regions using the Design-Expert 7.0.0 software. One liter of the incoming solution to the cold purification stage of the zinc plant with an initial pH of 4.5 was poured into the glass reactor and heated by a heater to reach the desired temperature. Then, certain amounts of zinc powder were added to the solution and mixing was done by the mixer. After mixing process, the slurry was filtered. Then, the sub-filtered solution was sampled and the impurities were measured by the atomic absorption equipment. It should be noted that the parameters studied in this study have been temperature, time, the amount of zinc powder, the pH of solution and the mixing speed. Each test point in this article is the result of an average of 3 repetitions. Regarding the Eq. 1, The results are given in the form of the percentage of removal.

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

**Table 4**

Designing of experiments in a central composite method and its responses.

No.	Temperature (°C)	Residence time (min)	pH	Content of zinc powder (g/l)	Mixing speed (rpm)	Removal of Ni (%)	Removal of Cd (%)
1	80	60	4.5	2.5	400	99.06	99.87
2	75	15	4	2	500	77.53	92.57
3	70	30	4.5	1.5	400	75.23	92.54
4	75	45	5	2	500	91.58	98.67
5	70	30	3.5	2.5	400	89.1	95.83
6	80	30	3.5	1.5	400	80.06	93.75
7	70	60	3.5	2.5	600	94.94	97.03
8	80	30	3.5	2.5	400	93.64	97.46
9	75	45	4	2	500	92.53	98.96

10	75	45	4	2	700	90.35	96.94
11	80	60	4.5	1.5	600	91.7	97.2
12	80	60	4.5	2.5	600	98.17	99.95
13	70	30	3.5	2.5	600	89.64	96.26
14	75	45	4	2	500	92.35	98.97
15	80	30	3.5	1.5	600	83.64	93.93
16	75	45	4	1	500	69.94	93.42
17	75	45	4	2	500	92.18	99.05
18	70	60	3.5	2.5	400	94.58	96.76
19	75	75	4	2	500	95.41	98.15
20	70	60	4.5	2.5	600	95.82	98.25
21	70	30	4.5	1.5	600	75.76	92.97
22	70	30	3.5	1.5	400	74	91.75
23	70	60	4.5	2.5	400	94.47	97.82
24	80	30	4.5	2.5	600	97.53	98.28
25	80	30	4.5	2.5	400	94.88	98.05
26	75	45	4	2	500	92.53	98.96
27	70	60	4.5	1.5	600	85.82	95.38
28	75	45	4	2	500	92.05	98.97
29	80	60	3.5	1.5	400	89.29	96.3
30	70	30	4.5	2.5	600	92.53	96.87
31	80	30	4.5	1.5	400	84	94.47
32	80	30	4.5	1.5	600	85.17	94.63
33	75	45	4	2	500	92.06	98.96
34	75	45	4	2	500	92.23	99.03
35	80	60	4.5	1.5	400	90.7	97.1
36	75	45	4	2	500	92.47	98.96
37	85	45	4	2	500	97.29	99
38	70	60	3.5	1.5	600	85.06	94.37
39	70	60	4.5	1.5	400	83.82	94.91
40	80	60	3.5	1.5	600	90.74	96.7
41	80	60	3.5	2.5	600	92.29	99.67
42	80	30	4.5	2.5	400	91	96.52
43	80	60	3.5	2.5	400	97.29	99.61
44	75	45	4	3	500	99	99.99
45	70	30	3.5	1.5	600	74.94	92.13
46	75	45	4	2	300	88.58	97.19
47	75	45	3	2	500	90.06	97.95
48	80	30	3.5	2.5	600	96.53	97.83
49	65	45	4	2	500	82.94	94.64
50	70	60	3.5	1.5	400	83.11	93.84

## 5. Results and discussion

The best statistical models were fitted by the software with respect to the data obtained

from the removal of cadmium and nickel. Eqs 2 and 3 are fitted polynomial models for cadmium and nickel with a regression

coefficient ( $R^2$ ) of 0.9921 and 0.9657 respectively. These values represent a good fitting for the response data. Based on these

models, the most effective parameters are the concentration of zinc powder, residence time, and temperature respectively.

$$\text{Removal of Cd (\%)} = -114.5 + 3.74T + 9.92pH + 0.35t + 0.061\text{mix} + 15.88C - 0.037TpH + 1.88Tt - 1.068T\text{mix} - 0.01TC + 3.37pHt - 2.31pH\text{mix} - 0.16pHC - 3.96t\text{mix} - 0.032tC - 2.68\text{mix}C - 0.02T^2 - 0.77pH^2 - 4.14t^2 - 5.06\text{mix}^2 - 2.38C^2 \quad (2)$$

$$\text{Removal of Ni (\%)} = -172.5 + 2.69T - 6.89pH + 1.88t + 0.07\text{mix} + 75.48C + 0.11TpH - 9.12Tt - 1.63T\text{mix} - 0.37TC - 8.38pHt + 1.81pH\text{mix} + 0.47pHC - 2.47t\text{mix} - 0.19tC - 5.58\text{mix}C - 8.87T^2 - 0.18pH^2 - 5.03t^2 - 3.84\text{mix}^2 - 6.53C^2 \quad (3)$$

The statistical evaluation of Equations 2 and 3 was carried out by performing F-test and the ANOVA analysis of variance and the result is presented in Table 5. Enova data confirms the accuracy of this quadratic model. With regards to the first-order model, it can be seen that the p-value of the quadratic model is less than 0.0001, indicating that the model is significant (generally, p-values of the model less than 0.05 indicate that the model is significant). 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 and 182.41 for nickel and cadmium respectively, which indicates that the model is completely meaningful. Furthermore, a great  $R^2$  of 0.9921 and 0.9657 confirms the high accuracy of the established model (it is recommended to determine the regression coefficient of determination- $R^2$  which should be higher than 0.80). In addition, the predicted correlation coefficient (Pred- $R^2$ ) and adjusted correlation coefficient (Adj- $R^2$ ) are also within a reasonable range (if the difference between Pred- $R^2$  and Adj- $R^2$  values is less than 20 %, the developed model can be considered valid).

As shown in Figures 1a-1b, there is a close correlation between the predicted values by

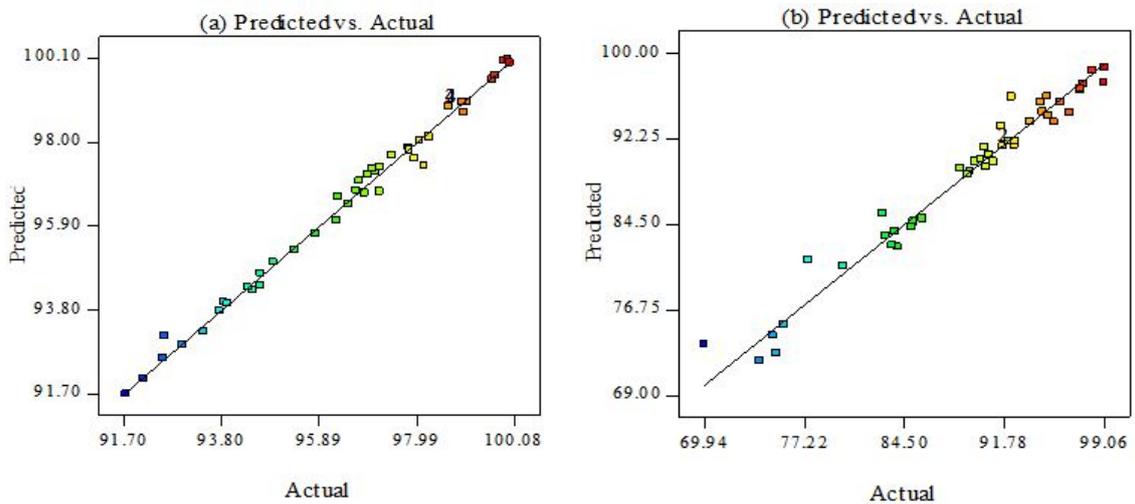
the software and the actual values, and these models are able to adequately cover these values.

Figures 2a-2b demonstrate the interaction between temperature and pH in the removal of cadmium and nickel respectively. Obviously, an increase in temperature at a constant pH would increase the yield of the removal of nickel and cadmium. As shown in Figure 2-a and Figure 2-b, the removal of nickel by the cementation with zinc powder is far more difficult than the removal of cadmium due to the higher hydration and activation energy. The best temperatures for the removal of cadmium and nickel are 80 °C and 85 °C respectively. The cementation reaction of cadmium is more favorable at the temperature range of 75 °C to near 85 °C and at the pH values greater than 3.5. As well, the reaction efficiency decreases at temperatures above 85 °C and at almost all pH values, which can be attributed to the higher activity of hydrogen ions at high temperatures. Hence, hydrogen ions can compete with cadmium ions to gain the electron faster causing the reduction reaction. The efficiency of the nickel cementation reaction is also advantageous at the temperature and pH values of above 80 °C and 4 respectively, having the best performance at 85 °C and the pH of 4.5.

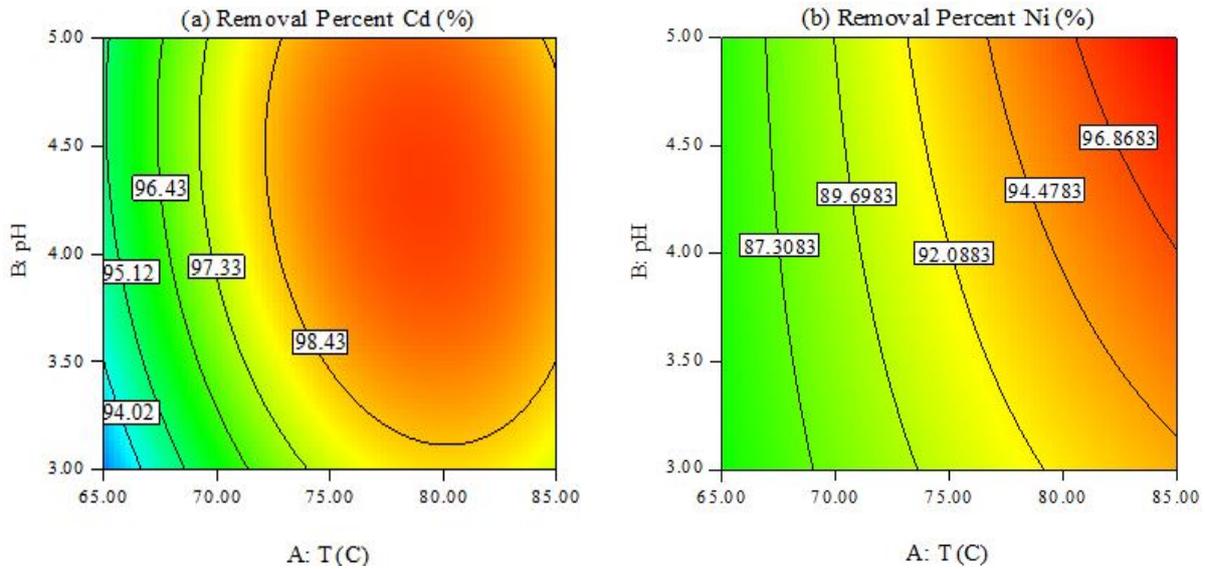
**Table 5**

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

Source	Ni		Cd	
	F Value	P-Value	F Value	P-Value
Model	40.84	0.0001	182.41	0.0001
A-T	109.44	0.0001	557.37	0.0001
B-pH	7.73	0.0094	58.48	0.0001
C-t	132.58	0.0001	624.58	0.0001
D-Mix	3.18	0.0850	6.56	0.0159
E-C	478.29	0.0001	1551.95	0.0001
AB	0.85	0.3640	3.84	0.0598
AC	5.11	0.0315	8.73	0.0062
AD	0.072	0.7896	1.26	0.2718
AE	9.59	0.0043	0.28	0.5997
BC	0.043	0.8369	0.28	0.5997
BD	0.090	0.7661	0.059	0.8102
BE	0.15	0.6971	0.69	0.4122
CD	1.5	0.2302	0.015	0.9018
CE	21.98	0.0001	25.91	0.0001
DE	0.85	0.3640	0.079	0.7802
A <sup>2</sup>	0.54	0.4698	141.33	0.0001
B <sup>2</sup>	0.023	0.8817	16.42	0.0003
C <sup>2</sup>	14.01	0.0008	381.81	0.0001
D <sup>2</sup>	1.61	0.2144	112.44	0.0001
E <sup>2</sup>	29.11	0.0001	156.02	0.0001
R-Squared	0.9657		0.9921	
Adj R-Squared	0.9421		0.9867	
Pred R-Square	0.8656		0.9686	
Std. Dev.	1.71		0.27	
Mean	89.31		96.77	
C.V. %	1.92		0.28	



**Figure 1.** Comparison between actual values and predicted values for: (a) cadmium, (b) nickel.



**Figure 2.** Interaction between temperature and pH on: (a) cadmium, (b) nickel.

Figure 3a and Figure 3b show the impact of temperature and time on cadmium and nickel cementation reactions. As it can be seen, no proper removal is performed at any temperature prior to 40 min. As shown in Figure 3a, the best conditions for the removal of cadmium are obtained at a temperature range of 75 to 85 °C and a the residence time of between 40 and 60 min while these conditions are achieved for nickel at temperatures of higher than 80 °C and the residence time of 60 min. At lower temperatures, the amount of the removal of nickel and cadmium increases with increasing the time, and the best performance occurs at the time of 75 min, while the reaction efficiency decreases at 60 minutes at higher temperatures. For the removal of nickel, the increase in temperature leads to a reduction in the residence time and a favorable result is obtained in less than 45 min with a temperature risen to 85 °C. The discharge potentials, a potential that is required to start an electrochemical reaction, of zinc, cadmium, copper, silver, mercury, chlorine, bromine, and iodine ions equal to the predicted turning potentials. Nickel, cobalt,

and iron ions act abnormally and their discharge potentials increase. It has been empirically proved that the higher the temperature, the lower the difference between the discharge potential and the turning potential. It means that the discharge potential decreases with increasing temperature causing the easier reduction of nickel. As shown in Figure 3a and Figure 3b, the removal efficiencies of cadmium and nickel have been 91 % and 76 %, respectively, at 65 °C after 15 min. This difference in efficiency under the same conditions is actually due to the higher discharge potential of nickel compared with that of cadmium.

Figure 4a and Figure 4b present the interaction between temperature and the mixing speed on the removal of cadmium and nickel respectively. As it can be deduced, the best condition for the removal of cadmium is 400 to 600 rpm and at the temperature range of 75 to 85 °C. The effect of the mixing speed on the removal of nickel is relatively less than that of cadmium. The removal efficiency of nickel is relatively uniform with no striking increase with a mixing speed of 300 rpm to 700 rpm at a constant temperature of at

almost all values. Generally, it still has a relatively better performance when mixing at 500 rpm. Since the cadmium cementation reaction has better efficiency than that of nickel at lower temperatures and the mixing

effect is more influential, it can be concluded that the cementation reaction of cadmium has been controlled through diffusion and mass transfer but the cementation reaction of nickel is controlled by the chemical reaction.

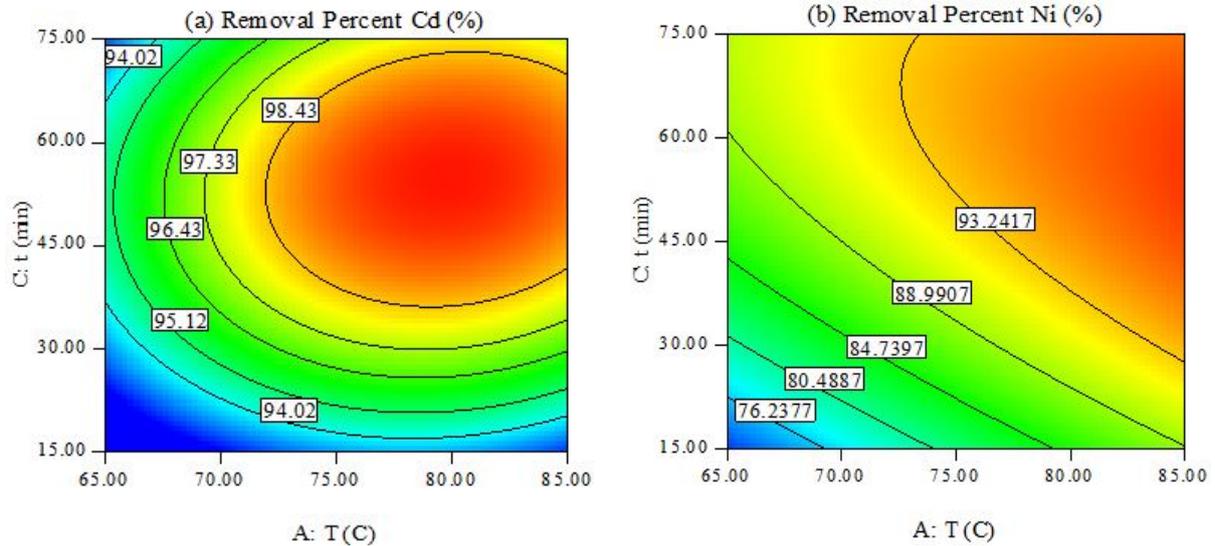


Figure 3. The interaction between temperature and time on: (a) cadmium, (b) nickel.

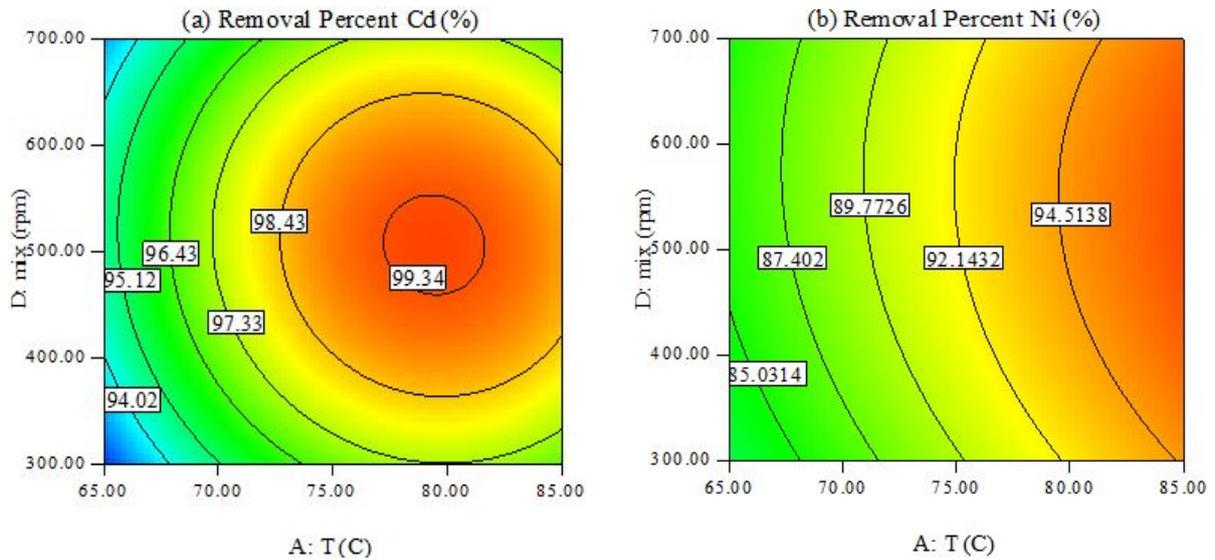


Figure 4. The interaction between temperature and mixing speed on: (a) cadmium, (b) nickel.

The interplay of temperature and the concentration of zinc powder in the removal of cadmium and nickel are shown in Figure 5a and Figure 5b. According to these figures, the removal percentage of nickel and cadmium at the lowest temperature and concentration of zinc powder are close to

70 % and above 90 % respectively, which indicates the lower activation energy of cadmium than nickel. To reach a constant concentration in the cementation reaction of nickel and cadmium, it is observed that the amount of zinc powder decreases with increasing temperature. As well, the

efficiency of the removal of these impurities from the solution intensely increases with increasing the zinc powder concentration at a constant temperature. Regarding this fact, it is possible to decrease the amount of zinc powder by increasing the temperature, which

ultimately reduces the production costs of zinc ingots. On the other hand, a favorable removal can be achieved by increasing the amount of zinc powder in plants which are not able to provide high temperatures for any reason.

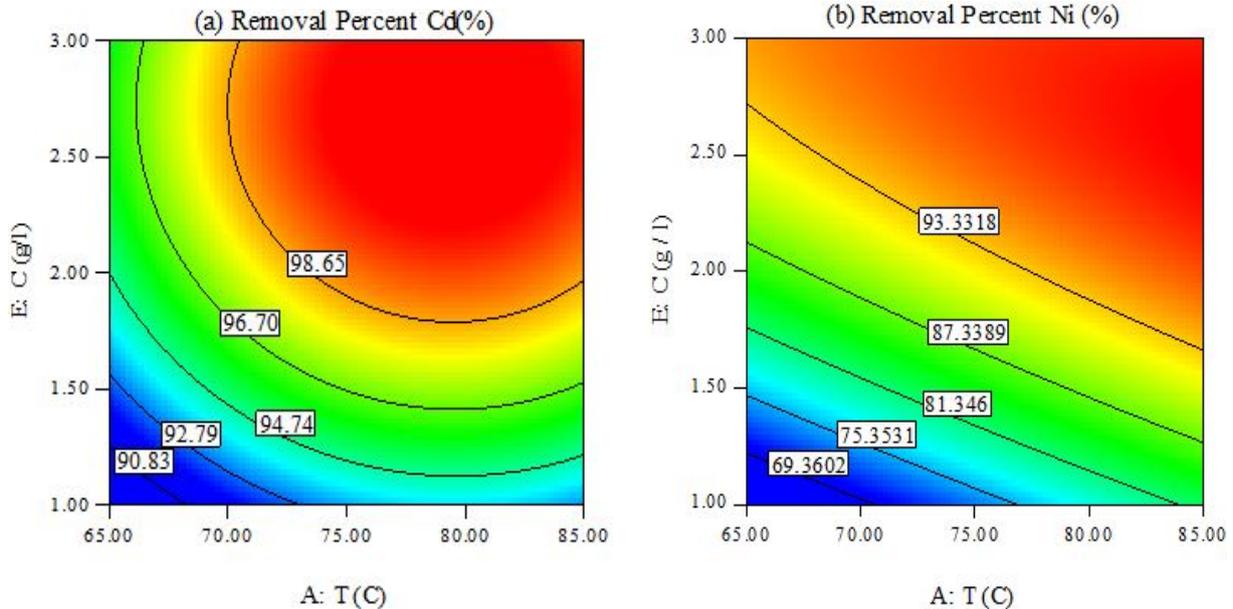


Figure 5. Interaction between temperature and concentration of zinc powder on: (a) cadmium, (b) nickel.

Figure 6a and Figure 6b have provided the interaction between pH and the residence time in the removal efficiency of cadmium and nickel. The removal efficiency of nickel and cadmium increases clearly with increasing the pH at a constant residence time. Due to the increase in hydrogen ions in the solution at low pHs, nickel and cadmium deposits are more likely to dissolve raising the probability of their presence as ions in the solution. Therefore, the removal efficiency may ultimately be reduced due to the residual values of nickel and cadmium in the solution after the time of reaction. The pH values greater than 5 are not usually suitable for the cementation reaction of nickel and cadmium because of the formation of zinc oxide and hydroxide. The best range of pH values for the optimum performance of nickel and cadmium

cementation reactions is 4 to 5, as shown in Figure 6a and Figure 6b.

The interaction between pH and the mixing speed for cadmium and nickel cementation reactions are illustrated in Figure 7a and Figure 7b. As it can be overall understood, changes in pH and the mixing speed have less effects on the removal of cadmium and nickel compared to the temperature, concentration of zinc powder, and residence time. Since the cementation reaction of cadmium with zinc powder is easier, the removal of cadmium at the pH values higher than 4 and the mixing speed of 500 rpm is closer to the maximum amount. However, regarding the reaction conditions for the cementation of nickel, the pH and mixing changes have little effects on the reaction efficiency.

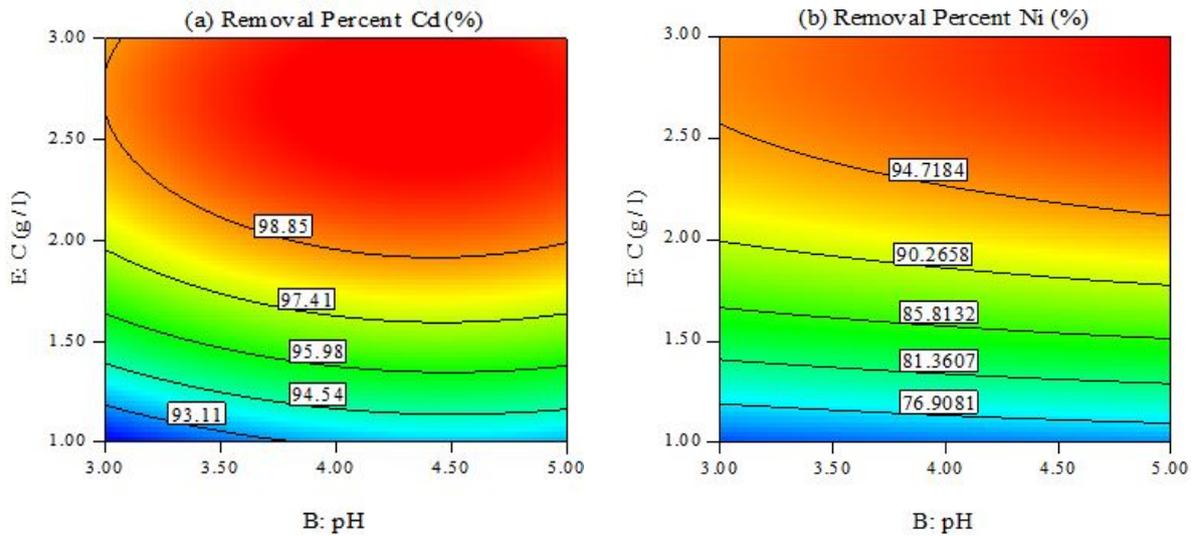


Figure 6. Interaction between time and pH on: (a) cadmium, (b) nickel.

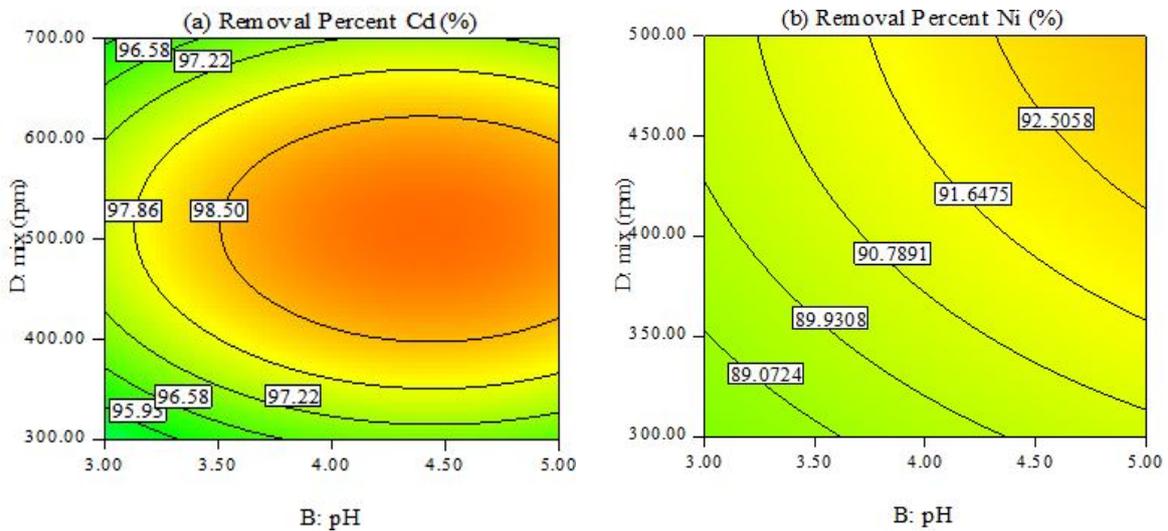


Figure 7. Interaction between mixing speed and pH on: (a) cadmium, (b) nickel.

The interplay of pH and the concentrations of zinc powder in the cementation reaction of cadmium and nickel are represented in Figure 8a and Figure 8b. The changes in pH have no significant effect on the removal efficiency at pH values of greater than 3.5 and different concentrations of zinc powder, as shown in Figure 8a. According to Figure 8b, changes in pH do not have much effect on the removal process in the low concentrations of zinc powder. At the concentrations of higher than 2 g/l, the cementation efficiency of nickel increases by increasing the pH, so that the nickel removal will get close to its highest

value at the pH of 5 even with the values of below 2.5 g/l of zinc powder. In fact, zinc powder can be prevented being consumed by hydrogen ions with the help of controlling pH in values of higher than 4.5. The diminishing amount of zinc powder can also help in lowering the costs.

The interplay of the residence time and the mixing speed for the cadmium and nickel cementation reaction are shown in Figure 9a and Figure 9b respectively. The yield of the cadmium and nickel cementation reaction increases in a constant mixing speed with increasing the residence time up to 60 min.

Anyway, the efficiency decreases at residence times of more than 60 min due to the reduction of hydrogen ions by zinc powder leading to an increased pH which causes the formation of zinc hydroxide and oxide by deactivating part of zinc powder. The best condition for the removal of nickel and cadmium is the mixing speed of 400 to 600

rpm and the residence time of 60 min. Also, increasing the mixing rate in a constant time would cause an increase in the efficiency of the removal at first, which would then be reduced in a mixing speed more than 600 rpm. The impacts of the residence time and mixing speed on the removal of nickel and cadmium by zinc powder are almost similar.

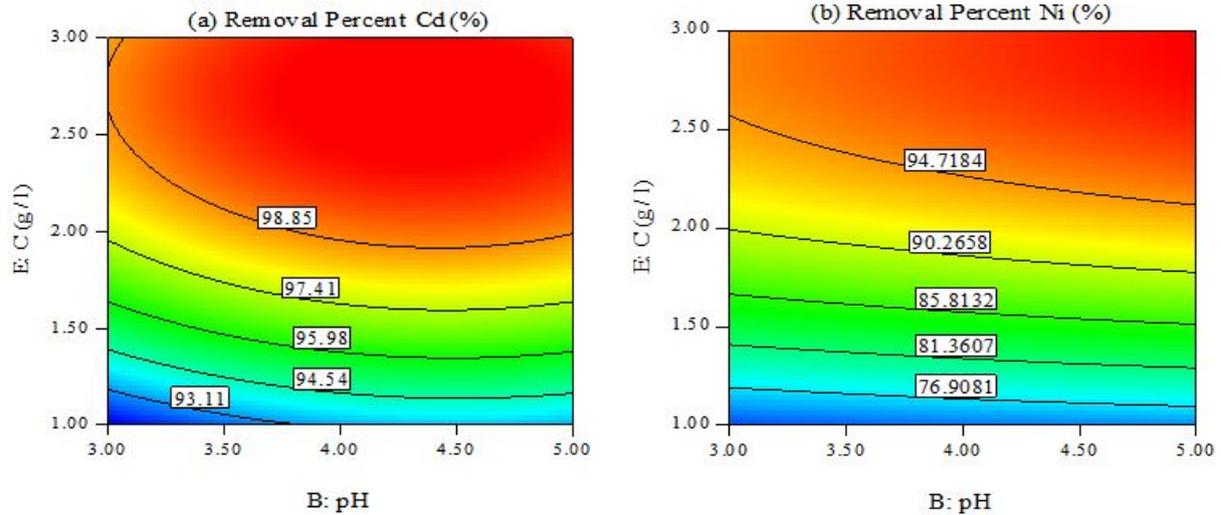


Figure 8. Interaction between pH and the concentration of zinc powder on: (a) cadmium, (b) nickel.

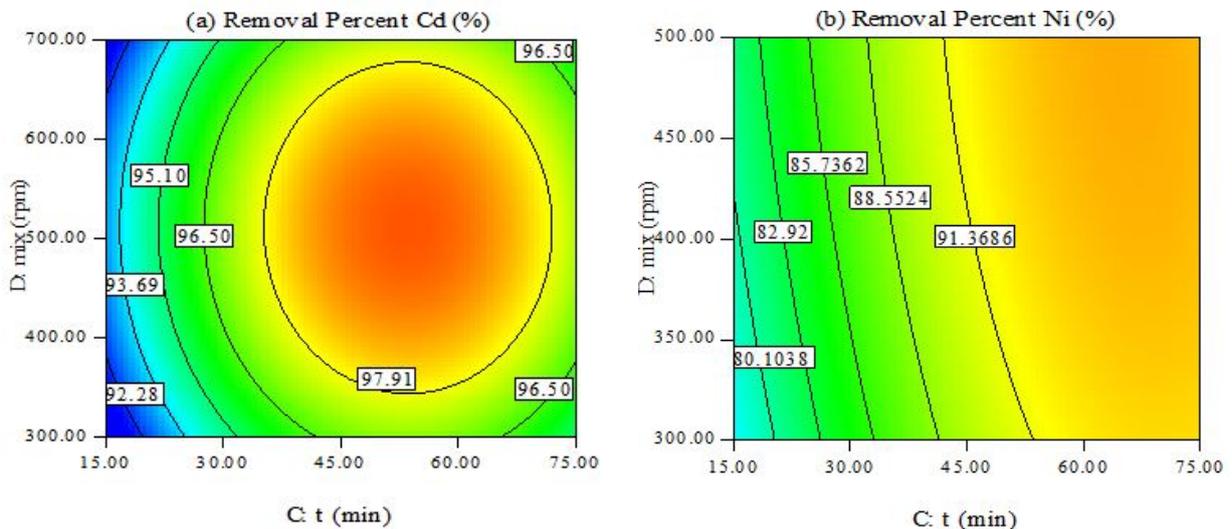


Figure 9. Interaction between time and mixing speed on: (a) cadmium, (b) nickel.

Figure 10a and Figure 10b show the interaction between the residence time and the concentration of zinc powder on removal of cadmium and nickel respectively. Obviously, the efficiency of the removal of cadmium and

nickel is greatly increased with increasing the concentration of zinc powder and the residence time, but there is a decreasing trend in the removal of nickel and cadmium at the residence times of more than 60 min. It has

also been observed that the removal would be more favorable by increasing the amount of zinc powder at a less residence time. In fact, in case of prioritizing the time, production units can reduce the duration of the reaction by increasing the amount of zinc powder, or if the time is not raised, they can decrease the zinc powder consumption by increasing the residence time to lower the production cost of ingots.

Figure 11a and Figure 11b show the interaction between the mixing speed and the

concentration of zinc powder in the cementation reaction of cadmium and nickel. According to these figures, the best mixing performance is 400 to 600 rpm in a constant concentration of zinc powder. The efficiency of nickel and cadmium cementation reactions would decrease in the mixing speeds of less than 400 rpm due to the reduction of mass transfer and the number of effective collisions between the reactants, as well as in mixing speeds above 600 rpm due to the formation of vortex flows.

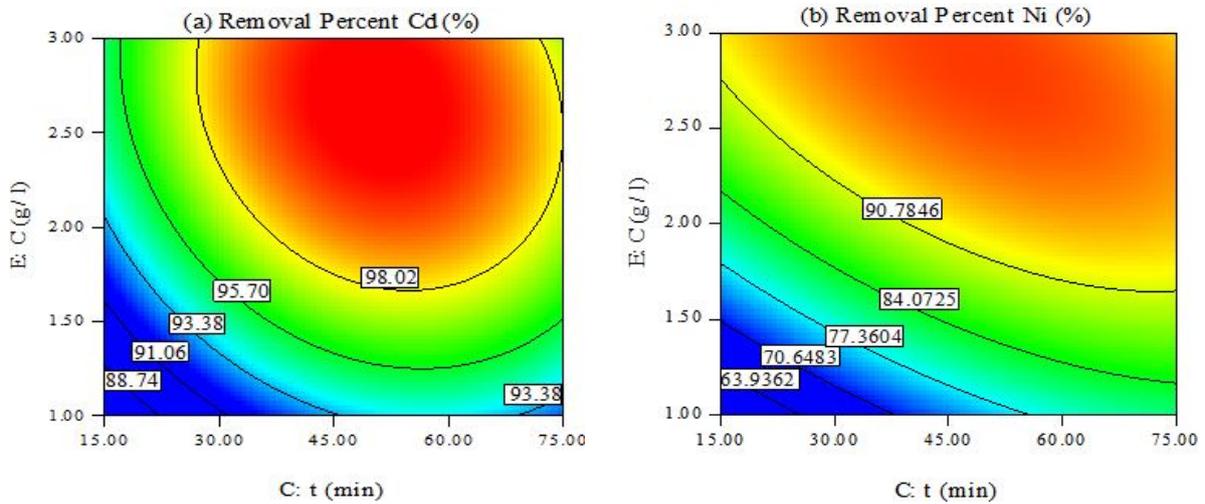


Figure 10. Interaction between time and the concentration of zinc powder on: (a) cadmium, (b) nickel.

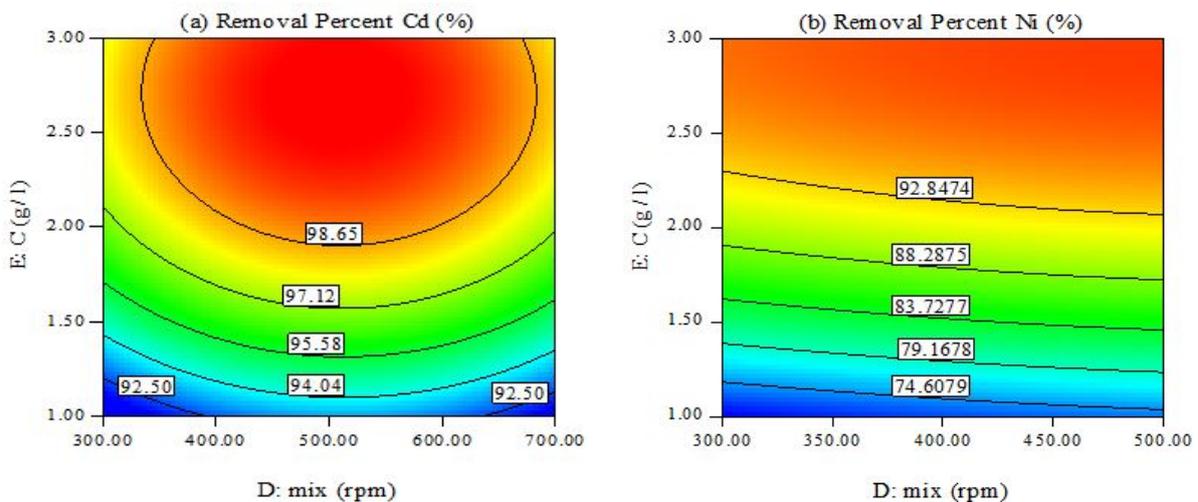


Figure 11. Interaction between the mixing speed and the concentration of zinc powder on: (a) cadmium, (b) nickel.

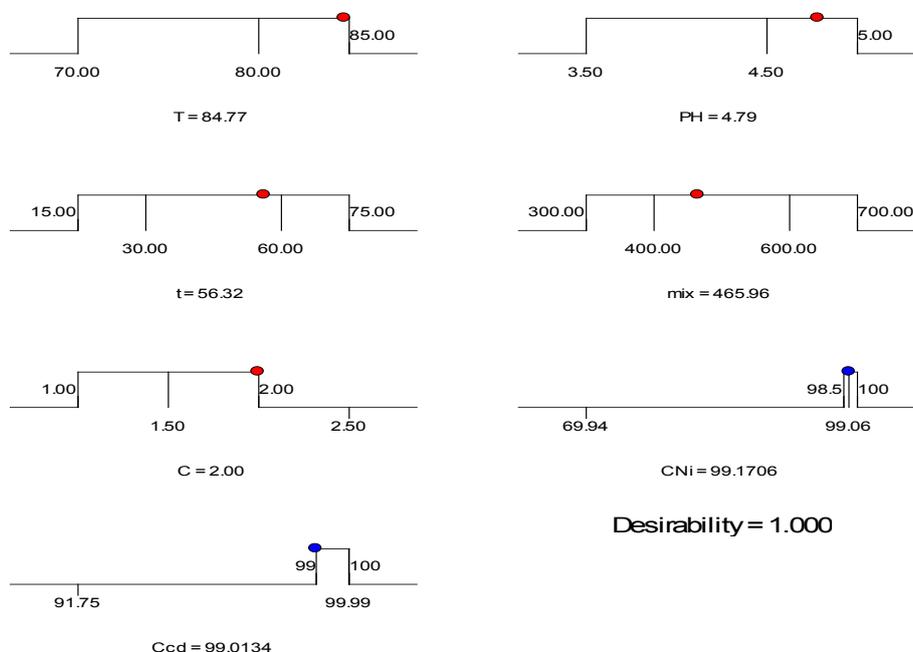
## 6. Optimization

Investigation of the effects of important

parameters for obtaining the best conditions using Design Expert leads to the optimization

of parameters. In fact, the purpose of optimization is to reach the removal of more than 99 % for nickel and 99.1 % for cadmium. According to Figure 12, the

optimized condition is obtained at 84.77 °C of temperature, 2 g/l of zinc powder, the pH of 4.79, the mixing speed of 465.96 rpm and the residence time of 56.32 min.



**Figure 12.** Optimum conditions obtained by the Design Expert software.

## 7. Conclusions

In this study, the effective factors of the simultaneous removal of nickel and cadmium in the leached solution from 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 were the most effective parameters in the simultaneous removal of nickel and cadmium. Also, studying the interactions between the parameters showed that by increasing the amount of zinc powder, the temperature and the residence time could be reduced. Also, in high concentrations of powder, changes in the mixing speed and pH had no significant effect on the efficiency of the process. Finally, the optimization was performed by the surface response method

and the best conditions for the simultaneous removal of nickel and cadmium were obtained at the 85 °C temperature, the pH of 4.8, the 56 min residence time, the 466 rpm mixing speed, and the 2 g/l concentration of zinc powder.

## References

- [1] Carrillo-Abad, J., Garcia-Gabaldon, M., Ortiz-Gandara, I., Bringas, E., Miren Urtiaga, A., Inmaculada Ortiz, I. and Perez-Herranz, V., "Selective recovery of zinc from spent pickling baths by the combination of membrane-based solvent extraction and electrowinning technologies", *Separation and Purification Technology*, **151**, 232 (2015).
- [2] Carrillo-Abad, J., García-Gabaldón, M.

- and Pérez-Herranz, V., “pH effect on zinc recovery from the spent pickling baths of hot dip galvanizing industries”, *Separation and Purification Technology*, **177**, 21 (2017).
- [3] Behnajady, B., Balesini, A. and Moghaddam, J., “A new approach to the optimisation of zinc electrolyte cold purification process by Taguchi’s method”, *Canadian Metallurgical Quarterly*, **53** (3), 333 (2014).
- [4] Behnajady, B. and Moghaddam, J., “Statistical evaluation and optimization of zinc electrolyte hot purification process by Taguchi method”, *Journal of Central South University*, **22** (6), 2066 (2015).
- [5] Zhang, B., Yang, C., Zhu, H., Li, Y. and Gui, W., “Kinetic modeling and parameter estimation for competing reactions in copper removal process from zinc sulfate solution”, *Industrial & Engineering Chemistry Research*, **52** (48), 17074 (2013).
- [6] Kilicarslan, A. and Saridede, M. N., “Treatment of industrial brass wastes for the recovery of copper and zinc”, *Separation Science and Technology*, **50** (2), 286 (2015).
- [7] Bayat, S., Aghazadeh, S. and Noaparast, M., “Germanium separation and purification by leaching and precipitation”, *Journal of Central South University*, **23** (9), 2214 (2016).
- [8] Hossain, M. R., Julie, K. and Decker, S., “Separation of cadmium from cobalt electrolyte solution by solvent extraction method using modified D2EHPA”, *Separation Science and Technology*, **46** (11), 1822 (2011).
- [9] Karbasi, M., Keshavarz Alamdari, E. and Amirkhani Dehkordi, E., “Electrochemical and anodic behaviors of MnO<sub>2</sub>/Pb nanocomposite in zinc electrowinning”, *Journal of Applied Electrochemistry*, **48** (3), 379 (2018).
- [10] Su, C., Zhang, W. and Ghali, E., “Electrochemical investigation of electrolyte composition and electrolysis parameters during zinc electrowinning”, *Journal of Applied Electrochemistry*, **47** (8), 941 (2017).
- [11] Wang, G. -W., Yang, Ch. and Zhu, H. - Q., “Reagent optimization for on-line simultaneous polarographic determination of trace amounts of Cu<sup>2+</sup>, Cd<sup>2+</sup> and Co<sup>2+</sup> in the presence of an extremely large excess of Zn<sup>2+</sup>”, *Journal of Central South University*, **23** (9), 2199 (2016).
- [12] Larosa, C., Salerno, M., Nann, P. and Reverberi, A., “Cobalt cementation in an ethanol-water system: Kinetics and morphology of metal aggregates”, *Industrial & Engineering Chemistry Research*, **51** (51), 16564 (2012).
- [13] Zeng, G., Zou, J., Peng, Q., Wen, H. and Xie, Y., “Reaction mechanism of cobalt cementation from high cobalt zinc sulphate solution by zinc dust”, *Canadian Metallurgical Quarterly*, **50** (1), 91 (2011).
- [14] Safarzadeh, M. S. and Moradkhani, D., “The effect of heat treatment on selective separation of nickel from Cd–Ni zinc plant residues”, *Separation and Purification Technology*, **73** (2), 339 (2010).
- [15] Fattahi, A., Rashchi, F. and Abkhoshk, E., “Reductive leaching of zinc, cobalt and manganese from zinc plant residue”, *Hydrometallurgy*, **161**, 185 (2016).
- [16] Safarzadeh, M. S., Dhawan, N., Birinci, M. and Moradkhani, D., “Reductive

- leaching of cobalt from zinc plant purification residues”, *Hydrometallurgy*, **106** (1-2), 51 (2011).
- [17] Shayesteh, K., Abbasi, P., VahidFard, V. and Shahedi, M., “Simultaneous removal of nickel and cadmium during the cold purification of zinc sulfate solution”, *Arabian Journal for Science and Engineering*, **1** (2020).
- [18] Krause, B. and Sandenbergh, R., “Optimization of cobalt removal from an aqueous sulfate zinc leach solution for zinc electrowinning”, *Hydrometallurgy*, **155**, 132 (2015).
- [19] Nāsi, J., “Statistical analysis of cobalt removal from zinc electrolyte using the arsenic-activated process”, *Hydrometallurgy*, **73** (1), 123 (2004).
- [20] Raghavan, R., Mohanan, P. and Verma, S., “Modified zinc sulphate solution purification technique to obtain low levels of cobalt for the zinc electrowinning process”, *Hydrometallurgy*, **51** (2), 187 (1999).
- [21] Boyanov, B. S., Konareva, V. V. and Kolev, N. K., “Purification of zinc sulfate solutions from cobalt and nickel through activated cementation”, *Hydrometallurgy*, **73** (1), 163 (2004).
- [22] Karlsson, T., Cao, Y., Colombus, Y. and Steenari, B., “Investigation of the kinetics and the morphology of cementation products formed during purification of a synthetic zinc sulfate electrolyte”, *Hydrometallurgy*, **181**, 169 (2018).
- [23] Boyanov, B., Konareva, V. and Kolev, N., “Removal of cobalt and nickel from zinc sulphate solutions using activated cementation”, *Journal of Mining and Metallurgy, Section B: Metallurgy*, **40** (1), 41 (2004).
- [24] Dib, A. and Makhloufi, L., “Mass transfer correlation of simultaneous removal by cementation of nickel and cobalt from sulphate industrial solution containing copper: Part II: Onto zinc powder”, *Chemical Engineering Journal*, **123** (1), 53 (2006).
- [25] Dib, A. and Makhloufi, L., “Mass transfer correlation of simultaneous removal by cementation of nickel and cobalt from sulfate industrial solution containing copper: Part I: Onto rotating zinc electrode disc”, *Chemical Engineering Journal*, **130** (1), 39 (2007).
- [26] Van der Pas, V. and Dreisinger, D., “A fundamental study of cobalt cementation by zinc dust in the presence of copper and antimony additives”, *Hydrometallurgy*, **43** (1-3), 187 (1996).
- [27] Güler, E. and Seyrankaya, A., “Precipitation of impurity ions from zinc leach solutions with high iron contents-A special emphasis on cobalt precipitation”, *Hydrometallurgy*, **164**, 118 (2016).
- [28] Nelson, A., Wang, W., Demopoulos, G. and Houlachi, G., “The removal of cobalt from zinc electrolyte by cementation: A critical review”, *Mineral Processing and Extractive Metallurgy Review*, **20** (4-6) 325 (2000).
- [29] Zaheri, Sh., “High temperature and high pressure cobalt cementation onto zinc dust”, M. Sc. Thesis, University of British Columbia, (2015).
- [30] Xu, R., Ma, K. and Guo, Z., “Activation mechanism of  $Sb_2O_3$  during removal of cobalt from zinc sulphate solution”, *Hydrometallurgy*, **82** (3), 150 (2006).
- [31] Casaroli, S., Cohen, B., Tong, A., Linkson, P. and Petrie, J., “Cementation for metal removal in zinc electrowinning circuits”, *Minerals Engineering*, **18** (13),

- 1282 (2005).
- [32] Kayin, P. B., "Removal of cobalt from zinc sulfate solution by cementation prior to zinc electrowinning", M. Sc. Thesis, Middle East Technical University, (2003).
- [33] Friedrich, B., Kruger, J. and Mendez-Bernal, G., "Alternative solution purification in the hydrometallurgical zinc production", *Metallurgija*, **8** (2), 85 (2002).
- [34] Bøckman, O., Østvold, T., Voyiatzis, G. and Papatheodorou, G., "Raman spectroscopy of cemented cobalt on zinc substrates", *Hydrometallurgy*, **55** (1), 93 (2000).
- [35] Nelson, A., "Novel activators in cobalt removal from zinc electrolyte by cementation.", M. Sc. Thesis, McGill University, Montreal, (1998).
- [36] Lu, J., Dreisinger, D. and Cooper, W., "Cobalt precipitation by reduction with sodium borohydride", *Hydrometallurgy*, **45** (3), 305 (1997).
- [37] Singh, V., "Technological innovation in the zinc electrolyte purification process of a hydrometallurgical zinc plant through reduction in zinc dust consumption", *Hydrometallurgy*, **40** (1-2), 247 (1996).
- [38] Polcaro, A. M., Palmas, S. and Dernini, S., "Kinetics of cobalt cementation on zinc powder", *Industrial & Engineering Chemistry Research*, **34** (9), 3090 (1995).
- [39] Van der Pas, V., "A fundamental study of cobalt cementation with zinc dust in the presence of copper and antimony additives", M. Sc. Thesis, University of British Columbia, (1995).
- [40] Lew, R. W., "The removal of cobalt from zinc sulphate electrolytes using the copper-antimony process", M. Sc. Thesis, University of British Columbia, (1994).
- [41] Tozawa, K., Nishimura, T., Akahori, M. and Malaga, A., "Comparison between purification processes for zinc leach solutions with arsenic and antimony trioxides", *Hydrometallurgy*, **30** (1-3), 445 (1992).
- [42] Blaser, M. S. and O'Keefe, T. J., "Screening design test for cobalt cementation from zinc electrolyte", *Metallurgical and Materials Transactions B*, **14** (3), 495 (1983).