



## Using Taguchi Method to Optimize Recovery of Bismuth by Electrolysis

Rasoul Khayyam Nekouei<sup>a,\*</sup>, Amir Peyman Soleymani<sup>b</sup>, Saeed Akhavan<sup>b</sup>, Ali Ashrafi NasrAbadi<sup>c</sup>  
and Alireza Aghababaei Samani<sup>b</sup>

<sup>a</sup> School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, Tehran, Iran

<sup>b</sup> Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran

<sup>c</sup> Department of Materials Science Engineering, Sharif University of Technology, Tehran Iran

### Abstract

This paper presents a methodology, based on the taguchi parameter design approach, for the optimization of process parameters for bismuth recovery from aqueous solutions. The process parameters considered are  $[Bi^{3+}]$ ,  $[NaCl]$ , temperature, and cathodic current density. In addition, cell voltage and current efficiency as two responses have been considered. An orthogonal array L9, the signal-to-noise (S/N) ratio, and the analysis of variance were used to analyze the effect of selected process parameters and their levels. From a metallurgical point of view, the separation and recovery of bismuth from a bismuth glance concentrate through leaching, purification and electrowinning of chloride solutions were carried out. The optimum conditions for the selected parameter values were found as  $[Bi^{3+}]$  (75 g/L),  $[NaCl]$  (25 g/L), temperature (65°C) and current density (100 A/m<sup>2</sup>). Finally, a mathematical model has been proposed and the results of a confirmatory run are reported to verify the results, which indicate that this methodology is more efficient in optimizing the process parameters.

**Keyword:** Bismuth; Electrowinning; Taguchi method; ANOVA; S/N ratio

### 1. Introduction

Only a small fraction of bismuth is produced from the primary processing of bismuth minerals. The majority of bismuth is obtained as a by-product in other metallurgical processes (e.g., during the extraction of copper, silver, tin, lead and gold) where bismuth usually shows the electrorefining sludge or acidic liquors. During extracting these metals, leaching by  $H_2SO_4$ , HCl or  $H_2SiF_6$  is usually carried out,

and highly acidic solutions containing base metals and bismuth are obtained. Generally, bismuth can be recovered from these spent solutions by hydrolysis.

Few authors have reported these paration of bismuth from leach solutions by electrowinning. Chen et al [1] recover the bismuth from copper smelter by a hydrometallurgical process in  $H_2SO_4$ -NaCl solution. Their total recovery of bismuth was 90% and the purity was up to above 90%. Zertoubi, et al [2] concluded that niobium electrode appeared to be suitable for bismuth recovery in acidic

\*Corresponding Author

E-mail address: [r.nekouei@ut.ac.ir](mailto:r.nekouei@ut.ac.ir)

media, but the electrochemical redissolution of the deposited bismuth prevented achieving greater than 50% recovery, even in the case of an oxide-free niobium electrode. Reyes-Aguilera, et al [3] also noted some other methods for bismuth recovery. Fisher, et al [4]; Szymanowski [5,6]; Kim, et al [7]; Dreisinger, et al [8,9] and Wang, et al [10] proposed the separation of bismuth from copper through ion exchange and solvent extraction. Other authors [11, 12, 13, 14] have proposed the extraction of  $\text{Bi}^{3+}$  from acid or highly acidic solutions of HCl, HBr,  $\text{HNO}_3$  and/or  $\text{H}_2\text{SO}_4$  using Cyanex 925, Cyanex 921, 2-bromo-alkanoic acid and Cyanex 302 as the extractant. While Reyes-Aguilera, et al [4] proposed using supported liquid membranes (SLM) for the recovery of bismuth from aqueous solutions.

The design of experiment (DOE) and statistical techniques are widely used to optimize process parameters [15, 16]. Often the results which have been obtained from the traditional approach of studying "one factor at a time" were only valid for fixed experimental [17].

The Taguchi technique provides an efficient and systematic method to optimize the performance designs, quality, and cost [18, 19]. The method uses a limited number of experiments in the experimental design. Another important point is that many different variables can be examined simultaneously [18, 20].

In this study, a model based on a L9 orthogonal array of Taguchi design was created to optimize the process parameters and another metallurgical process is proposed for the separation and recovery of bismuth from bismuth glance (bismuthinite,  $\text{Bi}_2\text{S}_3$ ) concentrate by leaching and electrowinning from chloride solution. The main aim in this investigation is optimizing process parameters for achieving maximum current efficiency and minimum cell voltage in electrowinning of bismuth.

## 2. Experimental Details

### 2.1. Materials

The bismuth concentrate obtained for this study was characterized physically and chemically. The as-receive concentrate was ground and dry screened to 100% passing 100 mesh (the exact mesh size was  $147\mu\text{m}$ ) and all samples were leached without further grinding. Chemical analysis of the concentrate was carried out by atomic adsorption spectroscopy (AAS). The results are presented in Table 1. X-ray diffraction analysis indicated that bismuth was present mainly as bismuthinite ( $\text{Bi}_2\text{S}_3$ ) (>95%) and a small portion was present as bismite ( $\text{Bi}_2\text{O}_3$ ) (<5%). Optical microscopy mineralogical analysis identified the presence of minor quantities of quartz ( $\text{SiO}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), pyrite ( $\text{FeS}_2$ ), limonite ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ), and wustite ( $\text{FeO}$ ). Pyrite ( $\text{FeS}_2$ ) was the predominant iron mineral present.

**Table 1.** Chemical composition of bismuth glance concentrat(%)

Bi	Pb	Fe	Cu	S	$\text{SiO}_2$
14.7	0.8	26.3	1.2	32.5	13.1

### 2.2. Metallurgical Experiment method

The schematic procedure for leaching, purification and recovery of bismuth from the bismuth glance concentrate by electrowinning is presented in Fig. 1. Leaching was carried out in 250 ml glass flasks with magnetic stirring at 250 rpm. The temperature of the system was controlled within  $2^\circ\text{C}$ . At the end of each experiment, the insoluble leach residue was filtered and washed with 1 M HCl and distilled water. The recovered bismuth was calculated by mass balance using the analysis of the concentrate and the leach residue.

The leaching solution was recycled to leach fresh concentrate until the bismuth concentration in solution was enriched to more than 70 g/L (by reaction 1).



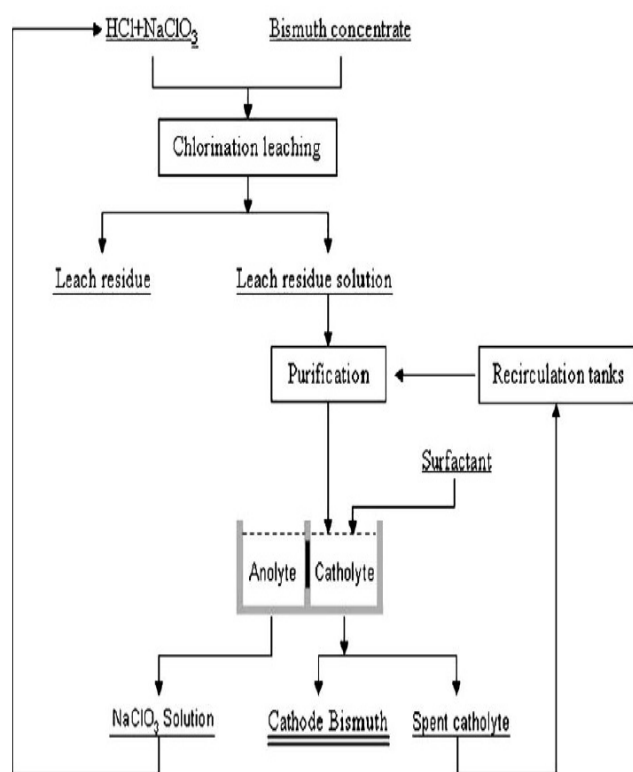


Fig. 1. Schematic representation of the experimental procedure

In the purification procedure, a weighed amount of active bismuth powder was added to the stirred solution (according to reaction 2 and 3) to reduce  $\text{Fe}^{3+}$  and displace  $\text{Cu}^{2+}$ . Then a quantity of ammoniumsulfide was added dropwise to precipitate remaining copper (reaction 4). After filtration, the degree of purification was calculated from analysis of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  concentrations by AAS.



In the electrowinning tests, a two-compartment acrylic cell (dimensions  $85 \times 75 \times 150$  mm) was used, which was separated by a widely-used commercial anion exchange membrane. The membrane was fitted between 2-mm-thick rubber seals in a  $50 \times 40$  mm acrylic window and the distance from the anode and cathode to the membrane was 2.5 cm. The cathode was made of 99.99% titanium plate with a nominal surface area of  $12.00 \text{ cm}^2$  and the anode was

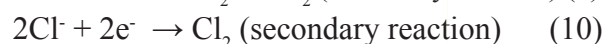
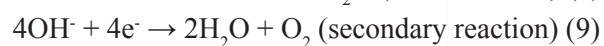
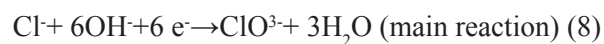
a graphite plate with the same surface area. Duration of Electrowinning was 24 hours. The Cell voltage was read according to the rectifier displayer and Current efficiency was determined by comparing the theoretical and experimental weight as shown.

$$\text{Current efficiency (\%)} = \left( \frac{\text{experimental weight}}{\text{theoretical weight}} \right) \times 100 \quad (5)$$

The composition of the catholyte was 70 g/L  $\text{Bi}^{3+}$  (as bismuth chloride), 25 g/L NaCl, and 4.5 mole/L HCl. The composition of the anolyte was initially 20 g/L sodium hydroxide. Both electrolytes were circulated to separate tanks by means of two independent peristaltic. The cathodic reactions are:



At the anode, the following reactions are possible, but no oxygen or chlorine was detected under tests condition:



### 2.3. Plan of Taguchi's orthogonal arrays and analysis of variance

As shown in Table 2, after the initial trial and error tests and analysis of the results were completed, the following four parameters were selected: [Bi], [NaCl], temperature of electrolyte and cathodic current density, each at three levels. Two responses (cathodic current efficiency and cell voltage) were chosen for optimization. The factors and levels used to design an orthogonal array  $\text{L}_9 (3^4)$  for the experiments are shown in Table 3. Each of the nine Taguchi-designed experiments was conducted two times and the mean values were reported.

The analysis of variance (ANOVA), predicted for a 95% confidence level, was performed

**Table 2.** Selected parameters and levels

Level	A: Bismuth Concentration (g/l)	B: NaCl Concentration (g/l)	C: Temperature (°C)	D: Cathod current density (A/m <sup>2</sup> )
1	25	5	25	100
2	50	15	45	200
3	75	25	65	300

**Table 3.** An L9 (3<sup>4</sup>) Taguchi orthogonal array

Standard Number of Experiment	Level of A	Level of B	Level of C	Level of D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

on the experimental results. A mathematical model of each response was developed by multiple linear regression analysis [21]. The software used for mathematical calculations (ANOVA and modeling) were Design-Expert 7.0.0 and WinRobust 1.02. Finally, confirmation experiments were carried out with optimal process parameters to verify the predicted results [21].

#### 2.4. Taguchi design of orthogonal array and signal-to-noise analysis

There are several S/N ratios available depending on the type of characteristics being optimized: lower is the best (LB), nominal is the best (NB), and higher is the best (HB) [22]. The greater the S/N ratio, the smaller the variance of the parameter being considered around its desired value and the better is the performance characteristics [23]. In the present study, there are two responses with two types of characteristics. Because it is the intent to maximize the cathodic current efficiency, the S/N ratio for HB characteristics was selected; because it is the intent to minimize the cell voltage, the S/N ratio for LB characteristics

was selected. These S/N ratios are calculated as follows:

$$(S/N)_{HB} = -10 \log \left( \frac{1}{n} \sum_{i=1}^n \frac{1}{k^2} \right) \quad (11)$$

$$(S/N)_{LB} = -10 \log \left( \frac{1}{n} \sum_{i=1}^n k^2 \right) \quad (12)$$

Where n is the repetition number of each experiment under the same condition for design parameters (here n equals 2), and k is the response of an individual measurement at the i'th test. After calculating and plotting the mean S/N ratios (the S/N unit is dB) at each level for various factors the optimal level among all levels of the factors, can be determined. Process parameter settings with the highest S/N ratio always yield the optimum quality with minimum variance [21].

### 3. Results and discussions

#### 3.1. Metallurgical Results and Discussions

##### 3.1.1. Leaching results

During preliminary experiments, various leaching conditions were examined and the most suitable condition for bismuth extraction was obtained in the temperature range of 60 to 85°C over two hours with 150 g/L HCl using a solid-liquid ratio of 1:4 by mass. As shown in Table 4, the recovery of bismuth in the leach

solution was substantially higher than the other metals. Through calculations and analysis of  $\text{Bi}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cu}^{2+}$  in the leach solutions and in the leach residue, it was found that more than 99.5% Bi was leached from the bismuth glance concentrate. This procedure yielded a bismuth enriched solution consisting of 73.5 g/L  $\text{Bi}^{3+}$  contaminated with about 3 g/L iron and <1 g/L copper and lead.

### 3.1.2. Purification results and discussions

The major aim of purification was to produce a pure electrolyte for electrowinning. The most suitable purification conditions were obtained in the temperature range of 30 to 45°C with the addition of 1.4 times of the stoichiometric quantity of bismuth powder and stirring for two hours. This was followed by the addition of 1.2 times of the stoichiometric quantity of ammonium sulfide for sulfide precipitation over 30 min. Under these conditions, the bismuth concentration increased slightly while iron (III), copper and lead were substantially lower as shown in Table 4. The reduction of copper and lead was >99.8% with little loss of bismuth.

### 3.1.3. The effect of each parameter in electrowinning

#### 3.1.3.1. Bismuth concentration

The best level for this parameter was 75 g/l Bismuth. The current efficiency increases with increasing bismuth concentration. Bismuth deposits were easily detached from the cathode during electrolysis. At low bismuth concentrations, the rate of hydrogen evolution reaction was increased at the cathode surface which results in lower current efficiencies and brittle bismuth deposits via the mechanism of hydrogen embrittlement.

#### 3.1.3.2. NaCl Concentration

The best level for this parameter was 25 g/l NaCl in the catholyte. The purpose of incorporating sodium chloride into the electrolyte was to enhance the formation of  $\text{BiCl}_4^-$  species and to improve the conductivity of the solution during bismuth electrowinning. The current efficiency increases and the cell voltage decreases with NaCl addition up to 25 g/L. This may be explained by increasing  $\text{BiCl}_4^-$  species and lower cathodic over potential required obtaining the desired current density. The decreased overpotential results in lower hydrogen evolution and higher efficiency for bismuth deposition.

#### 3.1.3.3. Temperature

The best level for this parameter was 65°C. When the temperature increased from 25 to 65°C, the current efficiency increased and the cell voltage decreased. Furthermore, the bismuth deposit formed at temperatures below 45°C was non-uniform and non-adherent, whilst higher temperatures improved both the quality and adherence of the bismuth deposit. The higher current efficiency and deposit quality is obviously due to increased bismuth ion mobility at higher temperatures and less hydrogen production [2].

#### 3.1.3.4. Cathodic current density

The best level for this parameter was 100 A/m<sup>2</sup>. The effect of cathodic current density on the current efficiency, cell voltage and resultant sodium chlorate concentration in the anolyte was conducted by varying the cathode current density from 100 A/m<sup>2</sup> to 300 A/m<sup>2</sup>. The current efficiency remained constant around 97% to 98%, while cell voltage increased steadily with cathode current density. At the

**Table 4.** Leaching and purification analysis under optimized condition

Elements	$\text{Bi}^{3+}$	$\text{Pb}^{2+}$	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$	$\text{Cu}^{2+}$
Leach (g/l)	73.5	0.3	2.4	0.5	0.5
Purification (g/l)	74.7	< 0.005	2.9	< 0.005	< 0.005

**Table 5.** The responses and S/N ratio values (According to experimental results).

Experiment	A: Bismuth Concentration (g/lit)	B: NaCl Concentration (g/lit)	C: Temperature (°C)	D: Cathode current density (A/m <sup>2</sup> )	Current Efficiency (%)	S/N Ratio (dB)	Cell Voltage (V)	S/N Ratio (dB)
1	25	5	25	100	82	-8.94	2.8	38.28
2	25	15	45	200	87	-8.30	2.6	38.79
3	25	25	65	300	87	-8.94	2.8	38.79
4	50	5	45	300	90	-10.10	3.2	39.08
5	50	15	65	100	92	-7.23	2.3	39.28
6	50	25	25	200	90	-8.94	2.8	39.08
7	75	5	65	200	95	-8.94	2.8	39.55
8	75	15	25	300	96	-10.10	3.2	39.65
9	75	25	45	100	96	-6.84	2.2	39.65

same time, the quality of the deposit also changed. The deposit was loose and non-adherent at low cathode current density, but as the current density increased from 100 A/m<sup>2</sup> to 300 A/m<sup>2</sup>, the bismuth coverage of the cathode increased and the deposit was more adherent. However, the higher current density required an increase in the cathodic voltage, which resulted in increased hydrogen evolution. This made the deposit at the edges increasingly powdery and dendritic.

As the cathode current density increased, the electro-synthesized sodium chlorate concentration increased smoothly. It appears that the steady increase of cathode current density causes a greater rate of penetration of chloride ions through the membrane into the anode compartment and causes the following anodic reaction:



### 3.2. Taguchi Results and discussions

#### 3.2.1. The analysis of the S/N ratios

Table 5 shows the results of cell voltage, cathodic current efficiency and the various S/N ratios after conducting the experimentation and applying Taguchi analysis to the results. To

obtain optimal condition, the LB performance characteristics were taken for cell voltage and the HB performance characteristics were taken for the current efficiency. The average S/N ratios of both parameters are shown in Figure 2. The response of each factor to its individual level was calculated by averaging the S/N ratios of all experiments at each level for each factor. In order to evaluate the influence of each factor on each response, the S/N ratio for each factor should be calculated (as shown in Figure2) [24]. For example, the mean S/N ratio for NaCl concentration at level 1 can be calculated by averaging the S/N ratios for the experiments 1, 4 and 7. The mean S/N ratio for each factor at different levels is calculated similarly. Analysis of the influence of each factor on each response has been performed with S/N response table using WinRobust version 1.02. Table 5 shows the experimental layout and their results with calculated S/N ratios for responses. Figure 2 shows the S/N ratio at each level of the factor and how it is changed when settings of each factor are changed from level 1 to 3. As previously discussed; the higher this difference, the more influential the factor [21].

Optimal testing conditions of these factors can

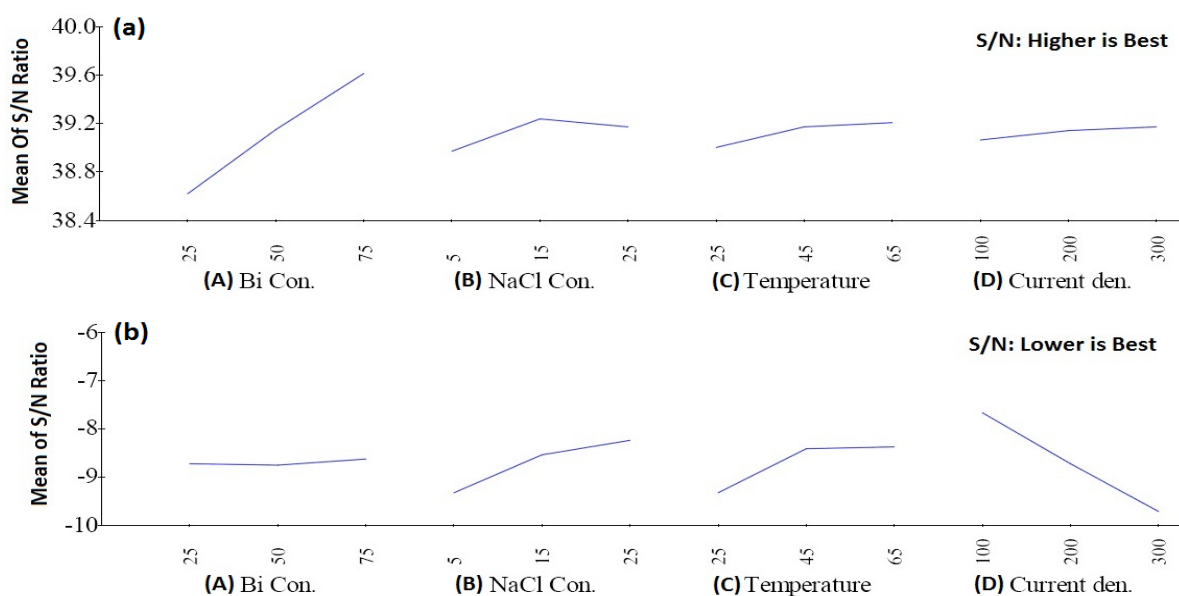


Fig 2. The mean S/N ratio diagram for (a) current efficiency; (b) cell voltage

be very easily determined from these graphs. It can be seen in Fig. 2 (a) that the optimum condition for current efficiency becomes  $A_3B_2C_3D_3$  for main factors. It is evident that bismuth concentration had the greatest effect on process optimization and after that B, C and D. It can be seen in Fig.2 (b) that the optimum condition is  $A_1B_1C_1D_4$  for the main factor. It is evident that current density had the greatest effect on influencing the optimal testing condition and after that C, B and A respectively.

### 3.2.2. ANOVA

The ANOVA results for two responses are illustrated in Tables 5 and 6. The fit summary output indicates that the models developed are statistically significant for the prediction of the responses; therefore they will be used for further analysis. The P-value demonstrates the significance level. From table 5, it can be seen that current efficiency, B, C, D and errors effects are 19.15, 17.02, 63.83 and 0.24% respectively. From Table 6 it can be seen that cell voltage, A, B, C, and errors effects are 88.90, 6.41, 3.82 and 0.87% respectively. On the other hand, the analysis of variance tables show that A (i.e., the Bi concentration)

within the range evaluated had low effect on the cell voltage. Thus, in this simulation it is realized as error. Accordingly, D (i.e., the current density) within the range evaluated (100 to 300 A/m<sup>2</sup>) had low effect on the current efficiency and was realized as error.

According to statistical tables, the critical value of the model's F-value is 19.33 at (6, 2) and 19 at (2, 2) for the tabulated factors at 95% confidence interval. The first number in parenthesis is parameter or model degrees of freedom and second number is the residual degrees of freedom. To categorize parameter or model as a significant value, calculated F-value must be more than its value in the statistical tables.

### 3.2.3. Proposal Model

By considering the values of cell voltage and current efficiency as outputs and the factors as inputs, it is possible to attain a model equation expressing the relationship between the outputs and inputs. The correlations between the main factors and the responses were obtained by multiple linear regressions. When a regression analysis was performed, utilizing the least squares method to the experimental data in order to obtain the coefficients of

**Table 6.** ANOVA Results for current efficiency

Source	Sum of Square	df	Variance	F Value ( $F_{\alpha} = 5\%$ )	Contribution P (%)	P-Value Prob> F	
Model	178.67	6	29.78	38.29	99.13	0.0257	significant
A	160.22	2	80.11	103.00	88.90	0.0096	
B	11.56	2	5.78	7.43	6.41	0.1186	
C	6.89	2	3.44	4.43	3.82	0.1842	
Error	1.56	2	0.78		0.87		
Total	180.22	8			100		

**Table 7.** ANOVA results for cell voltage

Source	Sum of Square	df	Variance	F Value ( $F_{\alpha} = 5\%$ )	Contribution P (%)	P-Value Prob> F	
Model	0.94	6	0.16	141.00	99.76	0.0071	significant
B	0.18	2	0.088	79.00	19.15	0.0125	
C	0.16	2	0.081	73.00	17.02	0.0135	
D	0.60	2	0.30	271.00	63.83	0.0037	
Error	$2.222 * 10^{-3}$	2	$1.111 * 10^{-3}$		0.24		
Total	0.94	8			100		

this equation, the following equation was established for cell voltage:

$$\text{Cell Voltage} = +2.74444 - 0.16667 * B - 0.15000 * C + 0.31667 * D \quad (14)$$

And for current efficiency:

$$\text{Current Efficiency} = +76.22222 + 5.16667 * A + 1.00000 * B + 1.00000 * C \quad (15)$$

As explained, A and D have a low effect on cell voltage and current efficiency, respectively. So, from a statistical point of view, using these parameters in models can strongly decrease the accuracy of the model.

The values of responses can be calculated by substituting the actual values of the variables for any experimental condition in equation 13 and 14. figure 3 also shows a comparison of the model predictions with experimental results of the responses. As shown in these figures; the fits between experimental and predicted responses values are very good. These facts suggest reasonably good reliability of the equation to predict responses within the selected experimental conditions. However, some differences were observed. There is no doubt that the data gathered through the

experiments possess some errors, and this fact influences the models obtained.

According to the tables of ANOVA and P-value, the presented model is significant. The 2.57% deviation for cell voltage and 0.71% deviation for current efficiency show that current efficiency model is stronger.

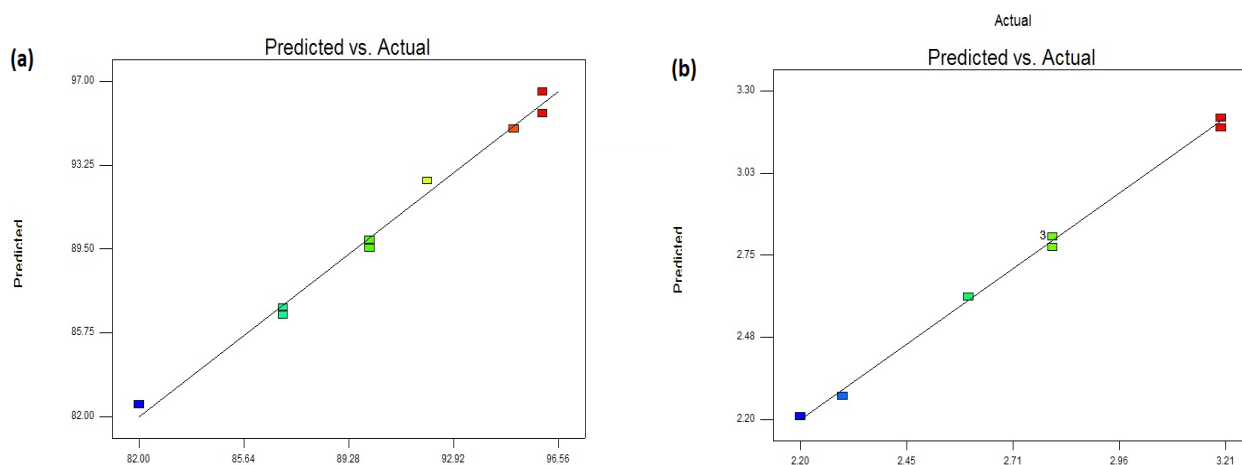
### 3.2.4 Confirmation experiment

The confirmation experiments are the final step in verifying the conclusions from the previous round of experimentation. If the results of the confirmation runs are not consistent with the expected conclusions, a new Taguchi method design is required [22]. If the predicted results are confirmed, the suggested optimum working conditions would be adopted [21]. By using the Design-Expert 7 software, the confirmation experiment was performed by setting the experimental condition of the four factors  $A_3B_3C_3D_1$  as shown in Table 8. The confirmation test results were compared with the predicted performance. The obtained cell voltage is 2.2 and its S/N ratio is -6.85 dB; the obtained current efficiency is 98% and



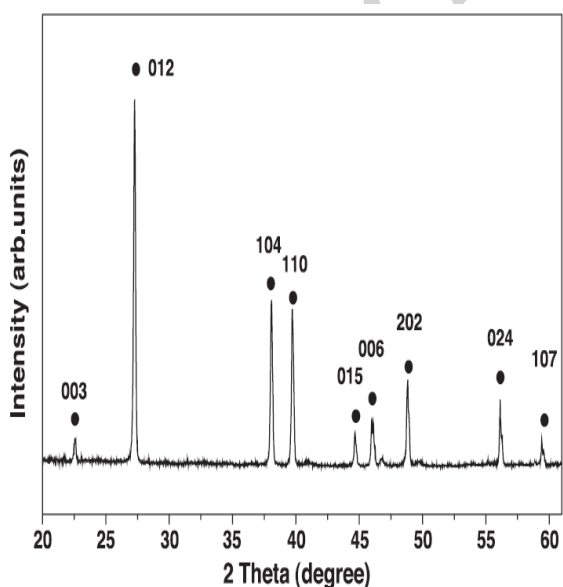
**Table 8.** Optimal combination of parameters and estimated Current efficiency and cathodic voltage

Type of test	A: Bismuth Concentration (g/l)	B: NaCl Concentration (g/l)	C: Temperature (°C)	C: Cathod current density (A/m <sup>2</sup> )	Current efficiency (%)	Cathodic voltage (V)
Taguchi ethod Anticipation	75	25	65	100	97.72	2.11
Experimental	75	25	65	100	98	2.2

**Fig 3.** Actual results of (a) current efficiency; (b) cell voltage; against predicted

its S/N ratio is 39.82 dB. These results show that both cell voltage and current efficiency are improved by using the optimal condition determined by the approach presented in this study. Fig. 4 shows the XRD pattern of the

deposits prepared from the confirmation test. This clearly indicates that the as-prepared deposits are pure bismuth, and bismuth oxide and other impurities was not detected (JCPDC card No. 026-0214).

**Fig. 4.** XRD pattern of bismuth deposits in confirmation test

#### 4. Conclusion

1. In this study, Taguchi's design of experiment (L9) was employed to optimize the cell voltage and current efficiency. The factors considered were Bi concentration, NaCl concentration, temperature and cathode current density. The DOE conclusions drawn from this study are summarized as follows:

- Among the four factors and three levels testing, it was concluded that Bi concentration had the most significant effect on the current efficiency, and the current density had the most significant effect on the cell voltage.

- The optimum conditions within the selected parameter values were found as the third level of Bi concentration (75 g/L), the third level of

NaCl concentration (25 g/L), the third level of temperature (65 g/L) and first level of current density (100 A/m<sup>2</sup>).

-The confirmation test was carried out at optimum working conditions. Cell voltage was 2.2 volts and current efficiency was 98% by setting the control factors. Predicted and observed values are in very good agreement with each other.

2. A comprehensive procedure was developed for the separation and recovery of bismuth from bismuth sulfide concentrate containing mainly pyrite and minor quantities of copper, lead and silica. All the process conditions, including HCl leaching; purification and electrowinning of bismuth, were optimized. Selective leaching of bismuth from pyrite was achieved using chlorate ion as oxidant and copper and lead impurities were removed by cementation and sulfide precipitation. By using an electrolytic cell fitted with an anion exchange membrane separator, pure bismuth plate (99.98%) was obtained from the purified leach liquor catholyte with 98% current efficiency.

## References

- [1] Y. Chen, T. Liao, G. Li, B. Chen, X. Shi, *Miner. Eng.* 39. (2012) 23.
- [2] M. Zertoubi, M. Chatelut, O. Vittori, *Hydrometallurgy*. 34. (1993) 109.
- [3] J.A. Reyes-Aguilera, M.P. Gonzalez, R. Navarro, T.I Saucedo, M. Avila-Rodriguez, *J. Membrane Sci.* 310. (2008) 13.
- [4] B.M. Fisher, R.C. Hills, F.J. Touro, Process for the manufacture of electrolytic copper, US Patent 3. 1975.
- [5] J. Szymanowski, *Pol. J. Appl. Chem.* 40. (1996) 3.
- [6] J. Szymanowski, *Miner. Process.Extr.Metall. Rev.* 18.(1998) 389.
- [7] D.K. Kim, T.A. Leese, M.N. Neild, B.R. Saito, S.K. Young, C.J. Weidner, *EPD Congress 1998. Proc. TMS Annual Meeting, San Antonio, 1998(TMS, United States, 1998) p.301.*
- [8] D.B. Dreisinger, B.J.Y. Leong, B.R. Saito, P.J. West-Sells, *Hydrometallurgy fundamentals, Littleton, Colorado, 1993 (SME, United States, 1993) p. 801.*
- [9] D.B. Dreisinger, B.J.Y. Leong, B.J. Bailint, M.H. Beyad, *Proceedings of International Solvent Extraction Conference, London, 1993 (Elsevier Applied Science, United Kingdom, 1993) p. 271.*
- [10] C. Wang, K. Jiang, D. Liu, H. Wang, *Cape Town. (2002) 1039.*
- [11] M. Cox, D.S. Flett, T. Velea, C. Vasiliu, *International Solvent Extraction Conference, Cape Town, 2002(Springer, South Africa, 2002) p.995.*
- [12] J.N. Iyer, P.M. Dhadke, *Ind. J. Chem. Technol.* 10. (2003) 665.
- [13] K.A. Ali, A.K. Vanjara, *Ind. J. Chem. Technol.* 8. (2001) 239.
- [14] Y. Moriya, M. Sugai, S. Nakata, N. Ogawa, *Anal. Sci.* 17.(2001) 297.
- [15] E.M. Anawa, A.G. Olabi, *Opt. Laser Technol.* 40. (2008) 379.
- [16] H. Oktem,, T. Erzurumlu, M. Col, *Int. J. Adv. Manuf. Technol.* 28. (2006) 694.
- [17] G Coman, G. Bahrim, *Ann. Microbial.* 10. (2010) 12.
- [18] W. Ahmed, E. Ahmed, C. Maryam, M.J. Jackson, A.A. Ogwa, N. Ali, V.F. Neto, J. Gracio, *J. Mater. Eng. Perform.* 15. (2006) 236.
- [19] A. Kamyabi-Gol, M. Sheikh-Amiri, *J. Iron Steel Res. Int.* 17. (2010) 45.
- [20] S. Kimar, P.S. Satsangi, D.R. Prajapati, *Int. J. Adv. Manuf. Technol.* 25. (2010) 48.
- [21] R. Surace, L.A. Ciro De Filippis, A. Ludovico, A., G. Boghetich, *Int. J. Mater. Form.* 3. (2010) 1.
- [22] M. Aliofkhazraei, *Russ. J. Non-ferr. Met.* 50. (2009) 97.
- [23] M. Kok, *Int. J. Adv. Technol.* 52. (2010) 207.
- [24] M. Yousefieh, M. Shamanian, A. Saatchi, *J. Alloy Compd.* 509. (2011) 782.