

Full Length Research Paper

Application of response surface methodology for electrochemical destruction of cyanide

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This study investigated the influence of experimental factors on the electrochemical cyanide destruction efficiency in a flow-through reactor using response surface methodology. Central composite experimental design was used to obtain the four main operating factors, such as current density, initial cyanide concentration, chloride concentration, and electrolysis time, on the response surface of cyanide destruction efficiency. Analysis of variance (ANOVA) showed a high coefficient of determination value (R^2) and insignificant lack of fit for the quadratic response surface model. The Pareto analysis gave the percentage effect of each factor on the response.

Key words: Response surface methodology, cyanide destruction, electrolysis.

INTRODUCTION

Cyanide is an important chemical extensively used in industries, especially in electroplating industry and mining industry. Due to its deadly toxicity, cyanide-containing wastewaters and cyanide wastes are not allowed to be discharged without adequate treatment and detoxication. There are numerous techniques proposed for the treatment of cyanide including chlorination, electrochemical and photochemical oxidation, biological treatment and oxidation with hydrogen peroxide (Monteagudo et al., 2004), ozone (Novak and Sukes, 1981). The mostly used process is chlorination, that is, oxidation of cyanide with chlorine and/or sodium hypochlorite, in industries. However, this chemical treatment is relatively expensive and produces a large quantity of sludge. Moreover, if the reaction is not complete, poisonous cyanogen chloride gas is formed and evolved.

Electrochemical treatment of cyanide is an alternative to destroy cyanide in solution (Midler et al., 1992; Bakir et al., 1999; Cañizares et al., 2005). Many investigations on

the direct or indirect electrochemical destruction of free cyanide or complex cyanide have been reported by researchers. Most of the previous studies focused on the investigation of the reaction mechanisms and anode material, such as graphite (Arikado et al., 1976), tin dioxide (Fujivara et al., 1996), lead dioxide (Hine et al., 1986), stainless steel (Szpyrkowicz et al., 1998), cobalt oxide (Stavart and Lierde, 2001), reticulated vitreous carbon (Felix-Navarro et al., 2011) on the destruction efficiency. For solution containing high concentration cyanide, direct electrochemical oxidation can be suitably employed and its efficiency is high. On the other hand, as cyanide concentration in solution is reduced to less than 500 ppm, the direct electrochemical oxidation becomes ineffective and uneconomic because of its low current efficiency. In such cases, this disadvantage can be effectively mitigated using indirect electrochemical oxidation that is, adding chloride ion, used as redox mediators, into solution. Chloride ions in an alkaline solution will be oxidized at anode to produce hypochlorite which can oxidize cyanide more effectively.

In previous investigations, the traditional one-factor-at-a-time approach was usually used for electrochemical destruction of cyanide. The one-factor-at-a-time (OFAT)

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approach varies only one factor or variable at a time while keeping others fixed. However, interactions of factors are not estimable from OFAT experiments. A designed experiment is a more effective way to determine the impact of two or more factors on a response than an OFAT experiment. Designed experiment requires fewer resources (experiments, time, material, etc.) for the amount of information obtained. Moreover, the estimates of the effects of each factor are more precise using designed experiment technique. The response surface methodology (RSM) is an important subject in the statistical design of experiments. It had been successfully used in several processes for water treatment, including adsorption (Tripathi et al., 2009; Sudamalla et al., 2012), electrocoagulation (Ölmez, 2009; Prabhakaran et al., 2010), chlorine disinfection (Umar et al., 2011), Fenton-related process (Khataee et al., 2010) and electrochemical oxidation (Körbahti, 2007). The response surface methodology uses mathematical and statistical techniques for the modeling and analysis of problems in which a response of interest is influenced by several variables. The objective of RSM is to evaluate the relative significance of several affecting factors and finally obtain the best operating conditions by optimizing this response.

In this study we used response surface methodology to investigate the influence of experimental parameters on the electrochemical cyanide destruction efficiency in a flow-through reactor. The cyanide destruction efficiency was selected as the response for obtaining the functional relationship between the response and the most significant independent factors by means of experimental design. Four main factors were chosen as independent factors: current density (A dm^{-2}), initial cyanide concentration (ppm), chloride concentration (ppm), and electrolysis time (min).

MATERIALS AND METHODS

Experimental setup

The flow-through reactor was made of 0.3 cm thick acrylic material, 15 cm high, 5 cm long, 5 cm wide, and separated into an anodic chamber and a cathodic chamber with a separator made of a perforated plastic plate of thickness 0.1 cm. Seven Pt/Ti screens with a total surface area 78 cm^2 were packed to compose the anode. The thickness of the anode was about 3.1 cm and the void fraction was estimated to be 0.59. Fifty graphite Rasching rings were packed randomly for use as the cathode. Two current feeders, made of titanium plates, were placed in the anodic and the cathodic chambers, respectively. The Pt/Ti screens and graphite rings were pickled in alkaline and acidic solutions alternatively for ten-minute cleaning before the electrolysis. The solution volume of 3 dm^3 was introduced by a pump into the bottom of the reactor; flowed out of the top, and returned to the reservoir in each experimental run. The constant flow rate of $0.5 \text{ dm}^3 \text{ min}^{-1}$ was employed in this study. The electrolyses were conducted using a constant-current operation. The direct current was supplied by a DC power supply (GW, GPR-25H30D).

For the determination of cyanide concentration, the sample was

treated with phosphate buffer solution (pH=7) in a distillation device. The gaseous HCN liberated from the top of distillation device was absorbed in a NaOH solution. The amount of cyanide was determined using a standard 0.01N AgNO_3 solution with rodanine (0.02% in acetone) as an indicator.

Response surface methodology

The optimization experimental design was performed using RSM. The Face Centered Central Composite Design (CCD) was used to create a set of designed experiments by Design-Expert software (version 7, trial). To find the optimum experimental conditions for the cyanide destruction in the flow-through electrochemical reactor, the selected main 4 factors such as current density, NaCl concentration, cyanide concentration and electrolysis time were designed. The ranges of these factors (independent variables) selected for this study were current density (x_1), 2 to 6 A dm^{-2} , cyanide concentration (x_2) 100 to 300 ppm, chloride concentration (x_3) 300 to 900 ppm, and electrolysis time (x_4), 120 to 200 min. It is appropriate to use coded variables for describing these factors in the (-1, 1) interval according to the following definitions:

$$A = \frac{x_1 - x_0}{\Delta x_1}, B = \frac{x_2 - x_0}{\Delta x_2}, C = \frac{x_3 - x_0}{\Delta x_3}, D = \frac{x_4 - x_0}{\Delta x_4} \quad (1)$$

where A, B, C, D is the dimensionless coded value of the *i*th independent variable (*i*=1 for A, *i*=2 for B, *i*=3 for C, *i*=4 for D), respectively, x_0 is the uncoded value of the *i*th independent variable at the center point, and Δx_i is the step change value between low level (-1) and high level (+1). When there is a curvature in the response surface, a second-order model is useful to approximate a portion of the true response surface. Therefore, the mathematical relationship of the response Y on these independent variables A, B, C and D was approximated by second-order polynomial equation as shown:

$$Y = b_0 + b_1A + b_2B + b_3C + b_4D + b_{12}AB + b_{13}AC + b_{14}AD + b_{23}BC + b_{24}BD + b_{34}CD + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 + b_{44}D^2 \quad (2)$$

where Y is the predicted response; b_0 the constant; b_1, b_2, b_3 and b_4 the linear coefficients; $b_{12}, b_{13}, b_{14}, b_{23}, b_{24},$ and b_{34} the cross-product coefficients; and $b_{11}, b_{22}, b_{33},$ and b_{44} are the quadratic coefficients. The analysis of variance (ANOVA) was used to obtain the interaction between the process variables and the responses. Examination of the fitted model is important if the model provides an adequate approximation of the true response surface. This study used normality, analysis of variance, regression analysis, and lack of fit test to examine the response model.

The cyanide destruction efficiency was defined as follows:

$$\text{Cyanide destruction efficiency (\%)} = \frac{M_0 - M}{M^0} \times 100\% \quad (3)$$

where M_0 is the initial cyanide concentration and M is the measured cyanide concentration.

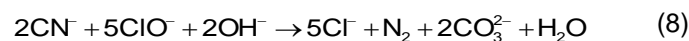
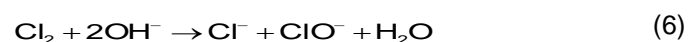
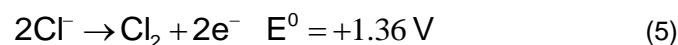
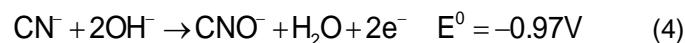
RESULTS AND DISCUSSION

The main electrochemical and chemical reactions for direct and indirect oxidation of cyanide in

Table 1. The design of experiment and experimental response.

A (A dm ⁻³)	B (ppm)	C (ppm)	D (min)	Y (%)
4	100	900	120	49.7
8	300	300	120	30.9
6	100	600	160	70.6
6	200	600	160	54.3
6	200	600	160	52.9
6	200	600	160	55.6
6	200	600	160	52.8
4	300	300	120	16.8
4	100	300	200	44.2
4	100	300	120	28.1
8	200	600	160	64.7
6	200	600	120	42.7
8	300	900	200	78.6
4	300	900	200	45.2
8	300	300	200	47.9
6	200	300	160	38.3
4	300	900	120	30.8
6	300	600	160	45.9
6	200	600	160	55.4
8	100	300	200	72.5
8	300	900	120	55.9
8	100	900	120	80.6
4	300	300	200	27.1
6	200	600	200	64.5
4	100	900	200	70.5
8	100	900	200	95.9
6	200	600	160	50.9
6	200	900	160	65.4
4	200	600	160	38.5
8	100	300	120	50.1

chloride-containing solution can be described as:



Apparently, cyanide can be oxidized to cyanate through direct electrochemical oxidation (Equation 4) or indirect chemical oxidation (Equations 7). Factors including applied current density, chloride concentration, cyanide concentration, solution pH, treatment time, and anode

material may influence the destruction of cyanide. Because hydrogen cyanide theoretically predominates when the solution pH is below 9.3, the initial pH in this study was chosen to be 11 to avoid the release of hydrogen cyanide gas. Based on the previous studies (Yen et al., 1991), we chose the four significant factors, such as applied current density, chloride concentration, cyanide concentration and treatment time, as the operating variables to investigate the cyanide destruction using RSM technology.

A face-centered central composite experimental design with a total number of 30 experiments, as shown in Table 1, was used for RSM modeling. Table 1 also shows the experimental data of cyanide destruction efficiency. This study used a quadratic model to fit the experimental data to obtain the most suitable regression equation because a quadratic model is useful in approximating a portion of the true response surface with parabolic curvature (Sudamalla et al., 2012).

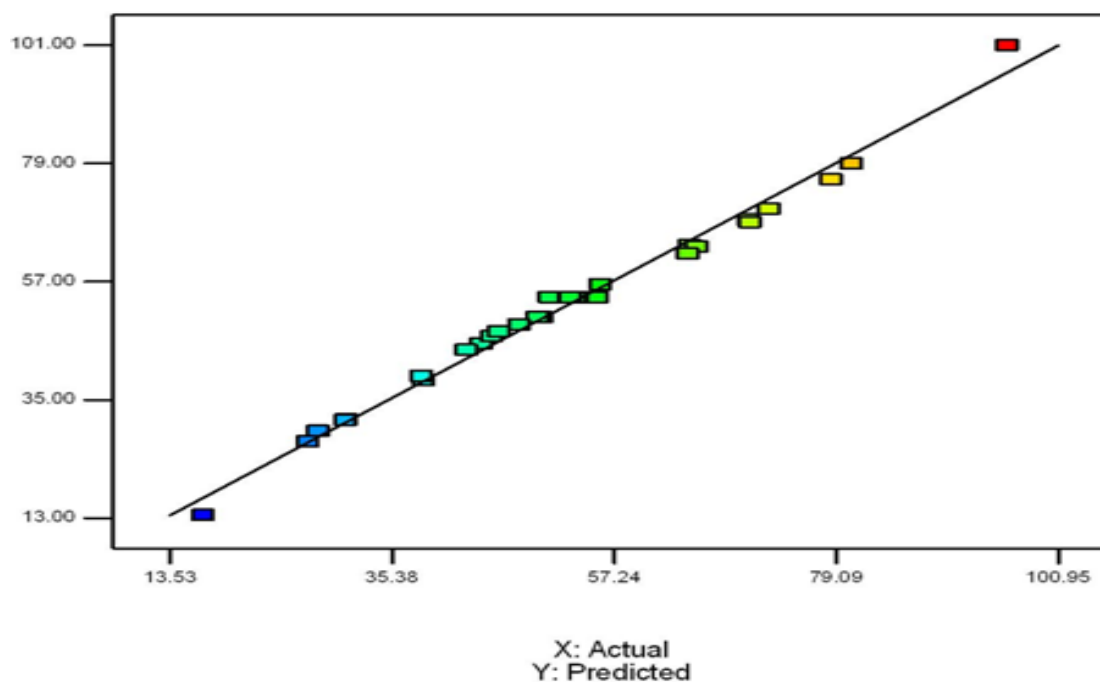
The ANOVA of this study confirms the adequacy of the quadratic model (the Model Prob>F is less than 0.05). Table 2 shows the probability values for each individual term in the quadratic model. The Model F-value of 93.52 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.05 indicate model terms are significant. In this case A, B, C, D, AC, B² are significant model terms. In addition, we used the "Lack of Fit Tests", also shown in Table 2, to compare residual error with "Pure Error" from replicated design points. Theoretically, if there is significant lack of fit, as shown by a low probability value ("Prob>F"), then be careful about using the model as a response predictor. The "Lack of Fit F-value" of 2.68 and Prob > F 0.1445 implies the Lack of Fit is not significant relative to the pure error. There is a 14.45% chance that a "Lack of Fit F-value" this large could occur due to noise. Consequently, the quadratic model, identified earlier as the likely model, does not show significant lack of fit.

How well the estimated model fits the experimental data is measured by the value of R². As R² is closer to 1, the estimation of regression model better fits the experimental data. In this work the quadratic model comes out best because it exhibits low standard deviation (2.61) and a high R² value (0.9887). The "Pred R²" of 0.9292 is in reasonable agreement with the "Adj R²" of 0.9781 in this work. Figure 1 shows the comparison of experimental and predicted value for cyanide destruction efficiency. It can be seen that the present model well fits the experimental data and consequently we can use the model to predict the cyanide destruction in the experimental range of variables.

A good estimated regression model shall explain the variation of the dependent variable in the sample. Tests of hypotheses about the model parameters can help the measurement of the effectiveness of the model. These tests require for the error term to be normally and

Table 2. ANOVA analysis.

Source	Sum of squares	df	F Value	p-value	Prob > F
Model	8944.86	14	93.52	< 0.0001	significant
A-current density	2842.58	1	416.08	< 0.0001	
B-cyanide	1862.53	1	272.63	< 0.0001	
C-chloride	2608.83	1	381.86	< 0.0001	
D-time	1436.48	1	210.26	< 0.0001	
AB	10.89	1	1.59	0.2260	
AC	54.76	1	8.02	0.0126	
AD	15.60	1	2.28	0.1515	
BC	12.25	1	1.79	0.2005	
BD	6.50	1	0.95	0.3447	
CD	3.42	1	0.50	0.4899	
A ²	20.84	1	3.05	0.1012	
B ²	37.69	1	5.52	0.0330	
C ²	17.33	1	2.54	0.1321	
D ²	1.81	1	0.27	0.6142	
Residual	102.48	15	6.83		
Lack of Fit	86.34	10	2.68	0.1445	Not significant
Pure error	16.13	5	3.23		

**Figure 1.** Predicted versus actual values for cyanide destruction efficiency.

independently distributed with mean zero and variance. We used normal plot of the internally studentized residuals to check the normality of the experimental data, shown in Figure 2. The studentized residuals are normally distributed if the data points are approximately

linear. When a non-linear pattern exists, it indicates non-normality in the error term and thus response should be corrected. Figure 2 shows the normality assumption in the present model was satisfied.

Consequently, the ultimate RSM model, in terms of the

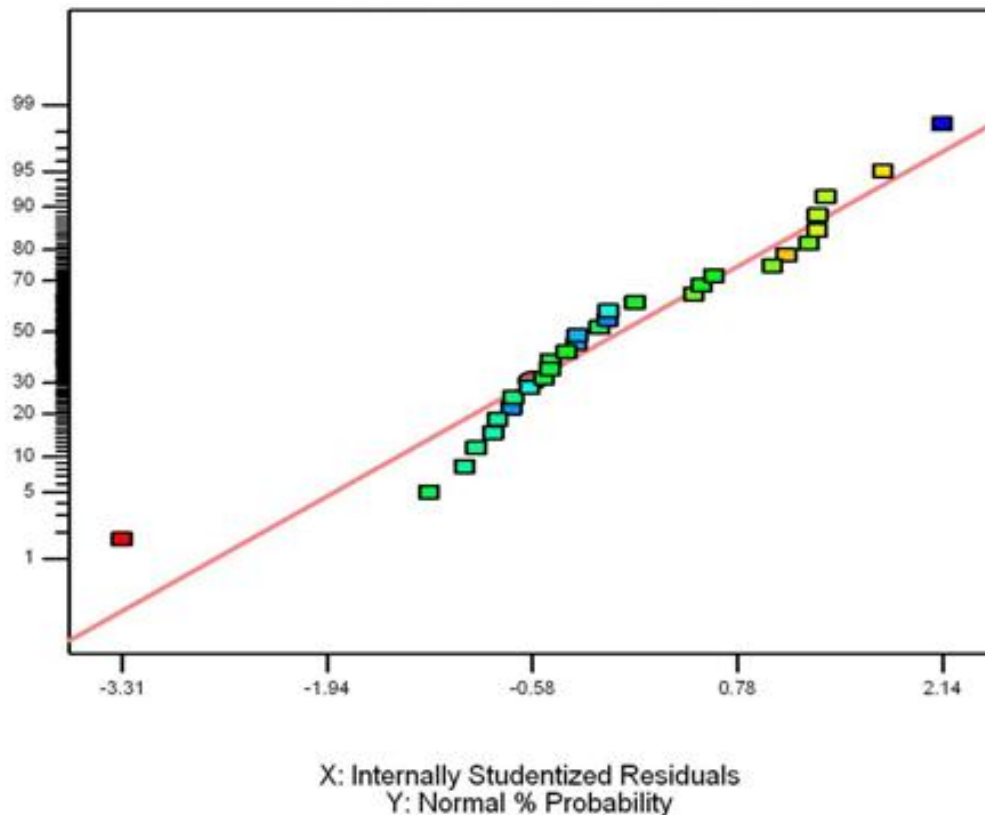


Figure 2. Normal probability plot of the internally studentized residuals.

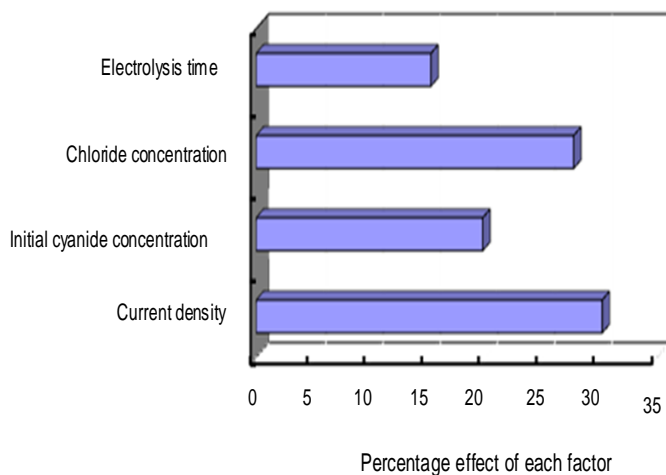


Figure 3. Pareto graphic analysis.

coded factors, for cyanide destruction efficiency can be described as:

$$Y = 54.05 + 12.57A - 10.17B + 12.04C + 8.93D - 0.83AB + 1.85AC + 0.99AD - 0.88BC - 0.64BD + 0.46CD - 2.84A^2 + 3.81B^2 - 2.59C^2 - 0.84D^2 \quad (9)$$

A positive coefficient of a factor results in an increase in the cyanide destruction efficiency when the factor level increases. On the contrary, a negative coefficient of a factor means the cyanide destruction efficiency decreases with increasing factor level. Consequently, the main positive effects were the individual factors of current density, chloride concentration and electrolysis time. On the other hand, the main negative effect was initial cyanide concentration.

The Pareto analysis describes the percentage effect of each factor on the response according to the coefficient of coded equation:

$$P_i = \left(\frac{b_i^2}{\sum b_i^2} \right) \times 100 \quad (i \neq 0) \quad (10)$$

Figure 3 shows the result of the Pareto analysis for the highest four values of P. The percentage of each factor was 30.23, 19.79, 27.74, 15.26% for the current density, initial cyanide concentration, chloride concentration, and electrolysis time, respectively. Therefore, the current density was the most important factor for cyanide destruction in this work.

Figure 4 shows the three-dimensional surface plot and the contour plot at 600 ppm chloride concentration and

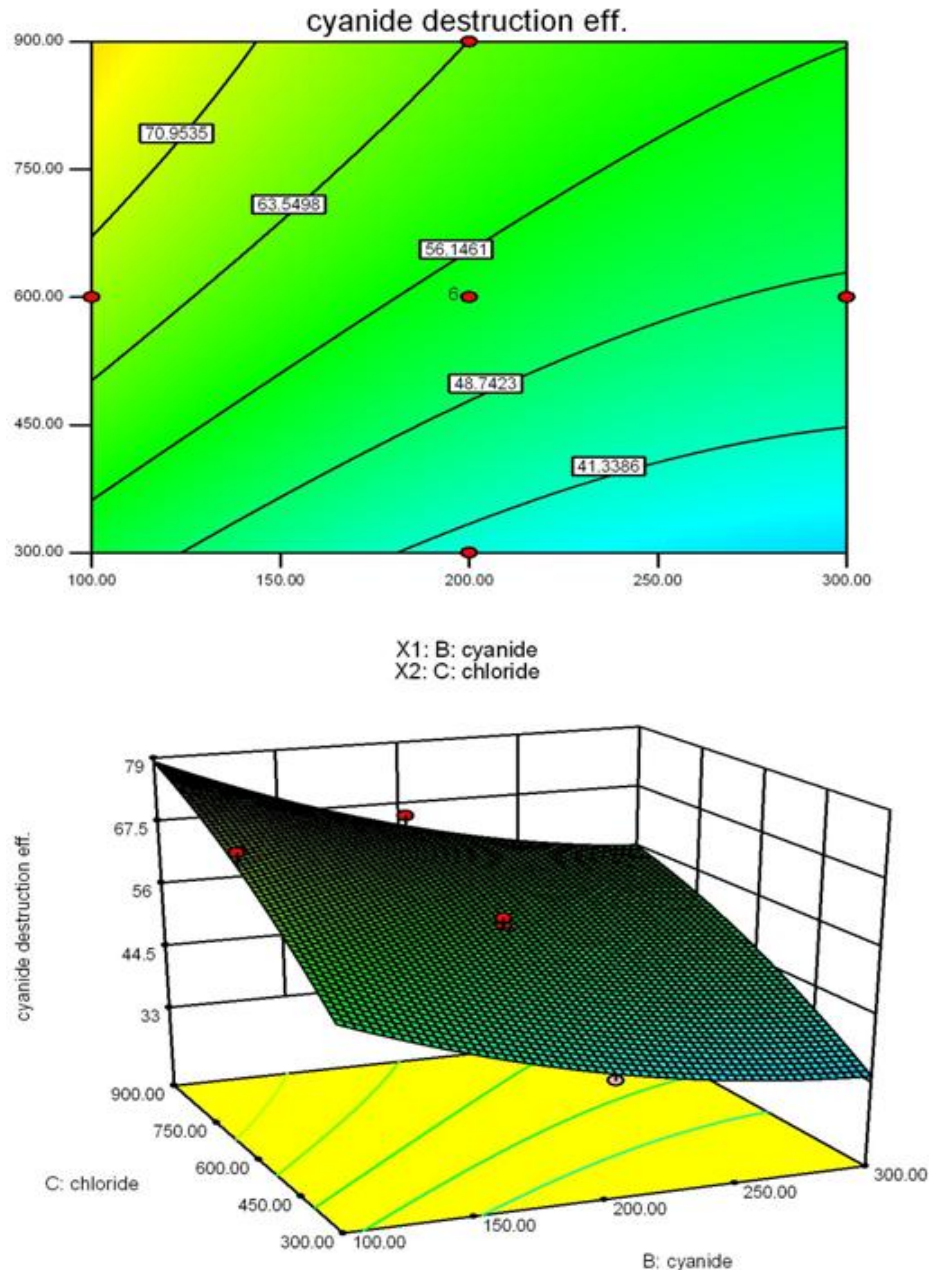


Figure 5. Contour plot and three-dimensional plot showing cyanide destruction efficiency as a function of chloride concentration and initial cyanide concentration (other variables were held constant at center levels).

160 min electrolysis time using the current density and the initial cyanide concentration as the variables. The contour plot can show contour lines of variable pairs that have the same response value. The cyanide destruction efficiency significantly increased with increasing the current density. Increase in current density means the direct oxidation of cyanide at the anode probably increases if mass transfer limitation of cyanide does not exist. Also, the rate of hypochlorite production is higher,

causing more indirect cyanide destruction according to Equations (7) and (8), because larger current is applied. At the central point of this experimental design, the cyanide destruction efficiency was 54.05% using Equation (9). Additionally, higher initial cyanide concentration reduced the cyanide destruction efficiency if keeping the current density constant.

Figure 5 shows the three-dimensional surface plot and the contour plot at 6.00 A/dm^2 current density and 160

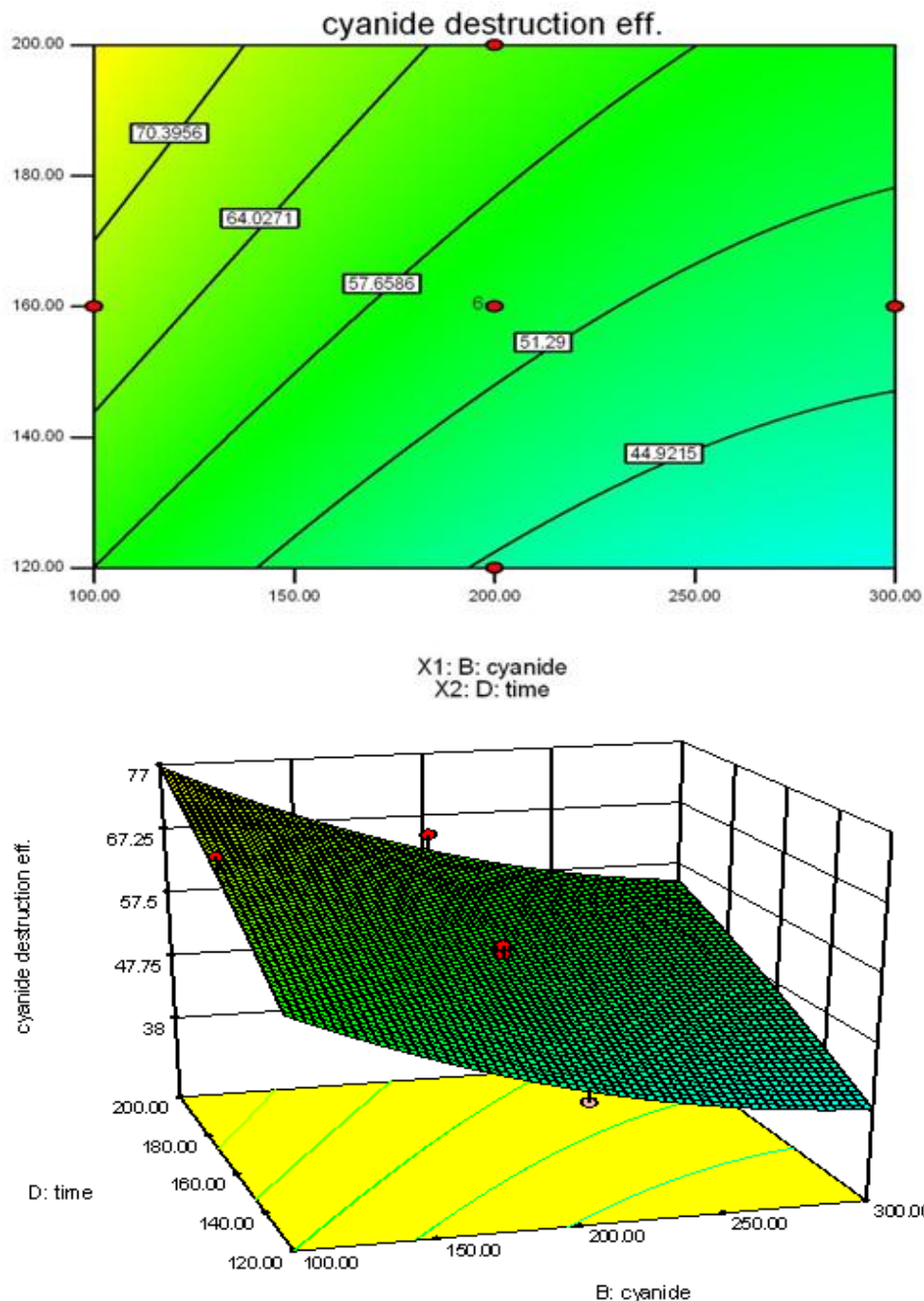


Figure 6. Contour plot and three-dimensional plot showing cyanide destruction efficiency as a function of electrolysis time and initial cyanide concentration (other variables were held constant at center levels).

electrolysis time using the chloride concentration and the initial cyanide concentration as the variables. The positive effect of chloride concentration on the cyanide destruction efficiency was observed due to the fact that chloride ions can easily be oxidized at Pt/Ti anode to produce Cl_2 and subsequently in alkaline media it converts to hypochlorite which is an effective oxidizing

agent for cyanide destruction. The destruction rate of cyanide was probably controlled by the hypochlorite production rate because the reaction between cyanide and hypochlorite was fairly fast.

Figure 6 shows the three-dimensional surface plot and the contour plot at 6.00 A/dm^2 current density and 600 ppm chloride concentration using the initial cyanide

concentration and electrolysis time as the variables. More time was needed to achieve the desired cyanide destruction efficiency when the initial cyanide concentration was higher. This result was consistent with the previous studies (Felix-Navarro et al., 2011).

Conclusions

The electrochemical treatment of cyanide destruction was studied in a flow-through reactor in the presence of chloride ions. Central composite design was adopted to obtain the response surface of cyanide destruction efficiency as a function of current density, initial cyanide concentration, chloride concentration and electrolysis time. Agreement of the quadratic model with the experimental data was satisfactory from the ANOVA analysis. The effect of the coded operating factors on the cyanide destruction efficiency followed the order: current density > chloride concentration > initial cyanide concentration > electrolysis time.

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REFERENCES

- Arikado K, Iwakura C, Yomeyama H, Tamura H (1976). Anodic oxidation of potassium cyanide on graphite electrode. *Electrochim. Acta* 21:1021-1027.
- Bakir Ü, Törü E, Koparal S (1999). Removal of cyanide by anodic oxidation for wastewater treatment. *Water Res.* 33:1851-1856.
- Cañizares P, Díaz M, Domínguez JA, Lobato J, Rodrigo MA (2005). Electrochemical treatment of diluted cyanide aqueous wastes. *J. Chem. Technol. Biotechnol.* 80:565-573.
- Felix-Navarro RM, Lin SW, Violante-Delgadillo V, Zizumbo-Lopez A, Perez-Sicairos S (2011). Cyanide degradation by direct and indirect electrochemical oxidation in electro-active support electrolyte aqueous solutions. *J. Mex. Chem. Soc.* 55(1):51-56.
- Fujivara CS, Sumodjo PTA, Cardoso AA, Benedetti AV (1996). Electrochemical decomposition of cyanides on tin dioxide electrodes in alkaline media. *Analyst* 121:541-545.
- Hine F, Yasuda M, Ijida T, Ogata Y (1986). On the oxidation of cyanide solutions with lead dioxide coated anode. *Electrochim. Acta* 31:1389-1395.
- Khataee AR, Zarei M, Moradkhannejhad L (2010). Application of response surface methodology for optimization of azo dye removal by oxalate catalyzed photoelectro-Fenton process using carbon nanotube-PTFE cathode. *Desalination* 258:112-119.
- Körbahti BK (2007). Response surface optimization of electrochemical treatment of textile dye wastewater. *J. Hazard. Mater.* 145:277-286.
- Midler M, Bagner CM, Wildman AS, Venkataranami ES (1992). Destruction of cyanides by alkaline hydrolysis in a pipeline reactor. *Env. Prog.* 11:251-255.
- Monteagudo JM, Rodríguez L, Villaseñor J (2004). Advanced oxidation processes for destruction of cyanide from thermoelectric power station waste waters. *J. Chem. Technol. Biotechnol.* 79:117-125.
- Novak F, Sukes G (1981). Destruction of cyanide waste-water by ozonation. *Ozone Sci. Eng.* 3:61-66.
- Ölmez T (2009). The optimization of Cr (VI) reduction and removal by electrocoagulation using response surface methodology. *J. Hazard. Mater.* 162:1371-1378.
- Prabhakaran D, Basha CA, Kannadasan T, Aravinthan P (2010). Removal of hydroquinone from water by electrocoagulation using flow cell and optimization by response surface methodology. *J. Environ. Sci. Health Part A* 5:400-412.
- Szpyrkowicz L, Zilio-Grandi F, Kaul SN, Rigoni-Stern S (1998). Electrochemical treatment of copper cyanide wastewaters using stainless steel electrodes. *Water Sci. Tech.* 38:261-268.
- Stavart A, Lierde AV (2001). Electrooxidation of cyanide on cobalt oxide anodes. *J. Appl. Electrochem.* 31:469-474.
- Sudamalla P, Saravanan P, Matheswaran M (2012). Optimization of operating parameters using response surface methodology for adsorption of crystal violet by activated carbon prepared from mango kernel. *Sustain. Environ. Res.* 22:1-7.
- Tripathi P, Srivastava VC, Kumar A (2009). Optimization of an azo dye batch adsorption parameters using Box-Behnken design. *Desalination* 249:1273-1279.
- Umar M, Aziz HA, Yusoff MS (2011). Assessing the chlorine disinfection of landfill leachate and optimization by response surface methodology (RSM). *Desalination* 274:278-283.
- Yen SC, Wang CT, Wang JS (1991). The indirect electrochemical destruction of dilute cyanide solutions by packed-bed electrodes. *Chem. Eng. Commun.* 109:167-180.