*Journal of Mining and Environment (JME) Vol. 13, No. 3, 2022, 839-849*

Shahrood University of Technology

Journal of Mining and Environment (JME)

Journal homepage: www.jme.shahroodut.ac.ir

Iranian Society of Mining Engineering (IRSME)

# Modeling, Optimizing, and Characterizing Elimination Process of Cyanide Ion from an Industrial Wastewater of Gold Mine by Caro's Acid Method

Hassan Vafaei and Seyyed Mohammad Seyyed Alizadeh Ganji*

*Department of Mining Engineering, Lorestan University, Lorestan, Iran*

## Article Info

*Received 23 June 2022*
*Received in Revised form 11 August 2022*
*Accepted 25 August 2022*
*Published online 25 August 2022*

DOI:10.22044/jme.2022.12027.2198

## Keywords

*Wastewater*
*Cyanide ion*
*Removal*
*Caro's acid*
*Response surface modeling*

## Abstract

The present work is aimed to examine the elimination of cyanide ions from the wastewater derived from the Agh-Darreh gold mine using the Caro's acid method. The response surface modeling is utilized to evaluate and optimize the influential parameters such as the sulfuric acid/hydrogen peroxide ratio, pH, Caro's acid concentration, and contact time on the elimination process. The results obtained indicate that the increase in the Caro's acid concentration and contact time has a positive impact on the elimination of the free cyanide ions, while the increment in the weight ratio of sulfuric acid/hydrogen peroxide and pH higher than 9.5 demonstrate a negative impact. Also it is found that the quadratic effect of pH has the highest influence on the removal of cyanide ion, and the linear effect of the ratio of sulfuric acid/hydrogen peroxide has the lowest degree of importance. Additionally, the optimization process is carried out, and about 96.4% of the cyanide ions is eliminated from the wastewater under the optimal conditions including 2 g/L Caro's acid concentration, 9.3 pH, 8 min contact time, and sulfuric acid to hydrogen peroxide (weight) ratio of 2.

## 1. Introduction

About one million tons of cyanide is produced annually throughout the world, which is useable in different industries such as mining to extract gold and silver, and also in the paint and textile industry, and automotive and metal plating industries [1]. It is estimated that about 13% of this amount is used in the mining and metallurgy industries [2-6]. Therefore, the wastewater of these industries contains various amounts of free cyanide ions that their concentrations should be brought to an allowable level to meet the environmental considerations. It is accepted that permissible limit for cyanide in effluent is less than 0.2 mg/L [7]. Also the allowable level of cyanide ions in drinking water and the aquatics ecology was announced by US EPA to be 200 and 50 ppb, respectively [8, 9].

Different methods such as base chlorination, hydrogen peroxide, biological oxidation, activated carbon, Caro's acid, natural decomposition, electrowinning, plasma discharge technology, ion exchange, ozonation, electrolysis, ultraviolet ray, and pressure oxidation for eliminating cyanide ion were utilized and developed [7, 9, 11-23], each one having operational strengths and weaknesses. For instance, Mondal *et al*. [7] have obtained an adsorption capacity of 12.3 mg/g using coke breeze at pH 7 and temperature of 25 °C for removal of cyanide from steel plant effluent (Sinbuathong (*et al*. [11])). Removal of cyanide ($CN^-$) from laboratory wastewater using sodium hypochlorite ($NaOCl$) and calcium hypochlorite ($Ca(OCl)_2$) were performed at the reaction time of 30 minutes. The product of chlorination at an alkaline pH of 12.3 was CNO-which could be oxidized further to $N_2$. Yeddou *et al*. [16] have worked on the removal of cyanide in aqueous solution by oxidation with hydrogen peroxide in the presence of activated carbon prepared from olive stones. The removal of free cyanide in the absence of activated carbon showed very slow kinetics. The presence of

Corresponding author: Ganji.m@lu.ac.ir (S.M. Seyyed Alizadeh Ganji).

activated carbon has increased the reaction rate, showing thus a catalytic activity.

Moussavi *et al*. [17] have investigated the influence of the operational parameters on elimination of cyanide from wastewater using the electrocoagulation process under different conditions. The result showed that the increase of the current densities of 2 to 15 mA/cm2 resulted in an increase of cyanide removal from 43% to 91.8% after 20 min of reaction in the absence of aeration. Under similar conditions, aeration of the reactor enhanced the removal efficiencies from 45% to 98%. Bahrami *et al*. [21] have worked on solation and removal of cyanide from tailing dams in a gold processing plant using natural bitumen. The result showed that the maximum adsorption of 61.64% was obtained in the size range of −1+0.5 and −2+1 mm of gilsonite. With increasing adsorbent weight and mixing time, the cyanide adsorption rate was increased.

Montalvo Andia *et al*. [24] have worked on combined treatment based on synergism between hydrodynamic cavitation and $H_2O_2$ for degradation of cyanide in effluents, and the results obtained showed that in optimal conditions, cyanide degradation using only HC reached 70%, and using solely $H_2O_2$ as the oxidizing agent, it reached 63%. Efficiency of the combined treatment process was evaluated on the basis of their synergetic effect as it turned out to be more effective showing a 99.9% cyanide degradation in less than 120 min. Liu *et al*. [25] have studied zinc cyanide removal by precipitation with quaternary ammonium salts, finding that 92.17% of 60 mg/L of cyanide and 88.86% of 50 mg/L of zinc (molar ratio Zn/CN = 1:3) can be removed using 0.4 g/L of octadecyl trimethyl ammonium bromide at a pH of 10. The concentration of the residual CN cyanide was less than the critical concentration.

Caro's acid or peroxysulfuric acid ($H_2SO_5$) is a strong oxidizer, and is prepared by mixing hydrogen peroxide (with higher than 50% concentration) and concentrated sulfuric acid (98%). This reaction is instantaneous and exothermic, and the reaction temperature may rise to 120 °C [26]. Additionally, Caro's acid is a very reactive and powerful acid, which is quickly dissociated in water at neutral pH levels [27]. Since the yielded Caro's acid is unstable in such temperature, it cannot be stored as a normal chemical. For this reason, the prepared Caro's acid is immediately cooled and used for the neutralization of the cyanide ions in the wastewater. Eq. (1) shows the reaction of Caro's acid formation [28].

$$H_2O_2 + H_2SO_4 \leftrightarrow H_2SO_5 + H_2O \quad (1)$$

The oxidation reaction of Caro's acid with free cyanide ion is shown in reaction (2).

$$H_2SO_5 + 2OH^- + CN^- \rightarrow CNO^- + 2H_2O + SO_4^{2-} \quad (2)$$

The oxidation of weak metallic cyanide complexes is also similar to that of the free cyanide ions, as shown in reaction (3).

$$M(CN)_4^{2-} + 2H_2S_5 + 10OH^- \rightarrow M(OH)_2(s) + 4CNO^- + 8H_2O + 4SO_4^{2-} \quad (3)$$

The resultant cyanate ions are slowly hydrolyzed in some hours according to reaction (4).

$$CNO^- + 2H_2O \rightarrow NH_3 + HCO_3^- \quad (4)$$

The ferrocyanide complexes in the wastewater are not oxidized, and are precipitated in the form of a cyanide salt according to reaction (5).

$$2M^{2+} + Fe(CN)_6^{4-} \rightarrow M_2Fe(CN)_6(s) \quad (5)$$

Also the thiocyanate can be oxidized via Caro's acid according to the following reaction [29]:

$$SCN^- + 4H_2SO_5 + 10OH^- \rightarrow 5SO_4^{2-} + CNO^- + 9H_2O \quad (6)$$

In fact, strong oxidizers such as hydrogen peroxide, hypochlorite, Caro's acid, and oxygen gas convert the free cyanide ion in the wastewater to a cyanate ion that is 1000 times less toxic [30].

In the recent years, although a great number of research works have been carried out on the treatment of industrial wastewater containing cyanide as considered in the literature, generally, the above studies indicate that the principle of the removal methods for cyanide is the oxidation of cyanide ion, and its conversion to cyanate ion. Meanwhile, it is found that the Caro's acid method is appropriate for the elimination of the free cyanide ions. Based on the investigations, this method was chosen as the method of cyanide ion removal due to its simplicity, safety, time, and practicality [20]. Moreover, the optimum operating conditions for eliminating cyanide ion from different wastewaters are different, and also there is little information on the synergistic impacts between parameters, so in this work, special attention is paid to modeling, optimizing, and characterizing the elimination process of cyanide ion from an industrial wastewater of gold mine. Modeling, examining parameters and their interaction using the method of designing experiments and performing this method on a real sample is some of the innovations of this article.

## 2. Materials and methods

### 2.1. Sampling and preparing representative sample

The Agh-Darreh gold processing plant, as the second gold mine of Iran, is managed by the Pouya Zarkan Agh-Darreh Company, and is located in the Takht-e-Soleyman region, at a distance of 30 km from the Takab city in the West Azerbaijan Province, Iran. The samples were collected from the output pulps, transferred to a tailing dam to perform the related tests. In fact, the sampled pulp with 70% solids was filtrated at first, and its solid materials were separated from the solution using a filter press. The solution obtained from the filtration process contained 80 ppm free cyanide ions, and it was used as the experiment sample.

### 2.2. Chemicals

The required chemicals for the examinations include sulfuric acid (98% purity) and hydrogen peroxide (10% purity), which were purchased from the Merck Company in Germany. A limewater solution (10% purity) was used to control the pH level. A wireless pH-meter, model HANNA, made in the USA was used to measure the pH level. Digital scale and magnetic stirrers that were available in the processing laboratory of the Agh-Darreh gold mine were also used for performing the experiments.

### 2.3. Elimination experiments

All experiments were carried out on 1-liter samples under the ambient temperature and specific string speed. Since the temperature and mixing rotation speed had little effects in examining the parameters by the scenario method, both were considered constant in all experiments. In order to conduct the experiments of free cyanide ion elimination, the prepared Caro's acid with a pre-determined weight ratio and concentration was added into solution, and pH was controlled at the targeted values by a 10% limewater. A magnetic stirrer with a fixed rotation speed was used for mixing, within a contact time desired. After each experiment, the concentration of the remaining free cyanide ions in the solution was measured through titration, and the percentage of free cyanide ion elimination was also calculated according to Eq. (7). Titration was used to determine the concentration of the remaining free cyanide ions in the test solution samples. In this method, a pure rhodanine (paradimethylamino) solution was used along with the addition of silver nitrate (0.0102 M), which caused the change in the color of the solution.

$$C_{cy} = \frac{W \times V_{sn} \times M}{V_i} \tag{7}$$

in which $C_{cy}$ is the concentration of cyanide (ppm), $V_{sn}$ denotes the used volume of silver nitrate (mL), $M$ depicts the molarity of silver nitrate, and $V_i$ represents the used volume of the initial water sample (mL).

### 2.4. Design of experiments

To eliminate cyanide ion from the gold wastewater and to characterize the four effective parameters including the pH, Caro's acid concentration, sulfuric acid to hydrogen peroxide ratio, and contact, a series of 27 experiments were designed based on the response surface methodology (RSM) and central composite design (CCD) and applying Design-Expert (DX) software. Table 1 shows the different operating parameters and their levels. Table 2 also indicates the experimental conditions performed and the values of removal percentage of cyanide ion obtained for each experiment.

**Table 1. Selected parameters and their actual and coded values through Design-Expert (DX) software.**

| Factors | Levels (actual and coded) | | | | |
|---|---|---|---|---|---|
| | Axial low level (-2) | Factorial low level (-1) | Central level (0) | Factorial high level (+1) | Axial high level (+2) |
| A: Time (min) | 2.5 | 5 | 7.5 | 10 | 12.5 |
| B: The weight ratio of sulfuric acid/hydrogen peroxide (g/g) | 1.5 | 2 | 2.5 | 3 | 3.5 |
| C: Caro's acid concentration (g/L) | 1.25 | 1.5 | 1.75 | 2 | 2.25 |
| D: pH | 8.5 | 9 | 9.5 | 10 | 10.5 |

**Table 2. Conditions and results of the experiments recommended by software for cyanide elimination by Caro's acid method.**

| Test No. | Effective parameters | | | | Cyanide removal percentage |
|---|---|---|---|---|---|
| | A | B | C | D | |
| 1 | 10 | 2 | 2 | 10 | 75 |
| 2 | 7.5 | 2.5 | 2.25 | 9.5 | 87.5 |
| 3 | 2.5 | 2.5 | 1.75 | 9.5 | 75 |
| 4 | 10 | 3 | 1.5 | 10 | 75 |
| 5 | 7.5 | 2.5 | 1.75 | 8.5 | 75 |
| 6 | 10 | 2 | 1.5 | 10 | 62.5 |
| 7 | 10 | 3 | 1.5 | 9 | 87.5 |
| 8 | 5 | 2 | 2 | 9 | 75 |
| 9 | 10 | 2 | 2 | 10 | 75 |
| 10 | 5 | 2.5 | 2 | 10 | 75 |
| 11 | 7.5 | 2 | 1.75 | 9.5 | 87.5 |
| 12 | 10 | 3 | 1.25 | 9 | 87.5 |
| 13 | 5 | 3 | 1.75 | 10 | 62.5 |
| 14 | 7.5 | 2.5 | 2 | 9.5 | 75 |
| 15 | 7.5 | 1.5 | 1.5 | 9.5 | 62.5 |
| 16 | 7.5 | 3 | 1.5 | 9.5 | 87.5 |
| 17 | 10 | 2 | 2 | 9 | 87.5 |
| 18 | 5 | 3 | 1.5 | 10 | 87.5 |
| 19 | 5 | 2 | 1.5 | 9 | 75 |
| 20 | 5 | 2.5 | 2 | 9 | 75 |
| 21 | 7.5 | 3 | 1.75 | 9.5 | 87.5 |
| 22 | 5 | 2.5 | 1.5 | 10 | 75 |
| 23 | 7.5 | 2 | 1.75 | 10 | 62.5 |
| 24 | 10 | 2 | 1.5 | 9 | 75 |
| 25 | 7.5 | 2.5 | 1.75 | 9.5 | 87.5 |
| 26 | 12.5 | 2.5 | 1.75 | 9 | 87.5 |
| 27 | 5 | 2 | 1.5 | 9.5 | 62.5 |

## 3. Results and discussion

### 3.1. Statistical analysis and modeling

Firstly, analysis of variance (ANOVA) was used to realize the suitable model and behavior of parameters influencing the process. ANOVA is a technique used for screening the significant parameters (significance) on the response. In fact, the purpose of ANOVA is to identify the effective parameters and their order of significance in the responses of the experiments through mathematical operations. The selected model based on the results of ANOVA should have significance with the highest capability of data fitting, which statistically means that its p-value should be less than 0.05, and its $R^2$ should be higher than 0.8 [21, 30]. The results of ANOVA for cyanide ion elimination by Caro's acid method are displayed in Table 3. As it can be seen from the ANOVA results in Table 3, all parameters are effective at the 95% confidence level. Also it is found from the F values that the degree of influence of the parameters is in the order of the quadratic impact of pH > linear effect of time > linear impact of Caro's acid concentration > linear effect of the ratio of sulfuric acid/hydrogen peroxide. Meanwhile, the p value of model fitted is less than 0.0001, showing that the suggested model is suitable and adequate for predicting the removal amount of cyanide. Table 4 indicates the statistical characteristics and the fitted model. Additionally, the proposed mathematical model by the software to predict the percentage of free cyanide ions eliminated by Caro's acid method is presented in Eq. (8). This model developed was obtained after removing the insignificant terms based on the p-values higher than 0.05.

$$
\begin{aligned}
R_{CN} &= +87.5 + 3.56\times A - 3.12\times B + 6.25\times C - 3.65\times D - 2.34\times A\times D - 3.91\times B\times C \\
&\quad -1.95\times A^2 - 1.95\times B^2 - 3.52\times C^2 - 5.08\times D^2 + 5.47 A^2\times B - 3.915.47 A^2\times C
\end{aligned}
\tag{8}
$$

where $R_{CN}$, A, B, C, and D represent the value of removal (%), contact time (min), weight ratio of sulfuric acid/hydrogen peroxide (g/g), acid concentration (g/L), and pH. The obtained model is based on the coded values of factors ranging from -2 to 2. The factors were codified via the following equation:

$$X_i = \frac{x_i - x_0}{\Delta x}, i = 1,2,3,..., n \tag{9}$$

in which $X_i$ denotes the coded magnitude of the $i$th factor, $x_i$ displays the actual magnitude of the factor, $x_0$ depicts the value of $x_i$ at the center point, and $\Delta x$ represents the step change magnitude.

According to Table 4, the high values of $R^2$ (0.9460) and adjusted $R^2$ (0.8998), imply the accuracy of the model. Adequate precision is another criterion to assess the efficiency of the model, and it is the signal-to-noise ratio, and its desired value should be greater than 4. As seen, the adequate precision value was obtained to be 13.888, which indicates that sufficient signal and can be utilized to navigate the design space.

**Table 3. Second-order model proposed for elimination of cyanide through Caro's acid method based on RSM.**

| Source | Sum of squares | Degree of freedom | Mean squares | F-value | P-value |
|---|---|---|---|---|---|
| Model | 2167.97 | 12 | 180.66 | 20.45 | < 0.0001 |
| A: Time | 319.01 | 1 | 319.01 | 36.11 | < 0.0001 |
| B: Ratio of sulfuric acid/hydrogen peroxide | 78.13 | 1 | 78.13 | 8.84 | 0.0101 |
| C: Caro's acid concentration | 312.50 | 1 | 312.50 | 35.37 | < 0.0001 |
| D: pH | 319.01 | 1 | 319.01 | 36.11 | < 0.0001 |
| AD | 87.89 | 1 | 87.89 | 9.95 | 0.0070 |
| BC | 244.14 | 1 | 244.14 | 27.63 | 0.0001 |
| $A^2$ | 81.38 | 1 | 81.38 | 9.21 | 0.0089 |
| $B^2$ | 81.38 | 1 | 81.38 | 9.21 | 0.0089 |
| $C^2$ | 263.67 | 1 | 263.67 | 29.84 | < 0.0001 |
| $D^2$ | 550.13 | 1 | 550.13 | 62.26 | < 0.0001 |
| $A^2B$ | 159.51 | 1 | 159.51 | 18.05 | 0.0008 |
| $A^2C$ | 81.38 | 1 | 81.38 | 9.21 | 0.0089 |
| Net error | 0.000 | 2 | 0.000 | | |
| Cor Total | 2291.67 | 26 | | | |

**Table 4. Statistical characteristics of model fitted.**

| Source | Std. Dev. | $R^2$ | Mean | C.V.% | Adjusted $R^2$ | Adequate precision | Press |
|---|---|---|---|---|---|---|---|
| Value | 2.97 | 0.9460 | 76.39 | 3.89 | 0.8998 | 13.888 | 1743.06 |

### 3.2. Main effects of parameters

The ANOVA table (Table 3) was also used to determine the effective parameters on the elimination of cyanide ions by the Caro's acid method. It is distinguished that among the major parameters, the pH (D) and the sulfuric acid/hydrogen peroxide weight ratio (B) have the highest effects, respectively, in removing the cyanide ion, due to the higher value of F and lower value of P. Also the linear and second effects of all parameters, interactive effects of AD and BC as well as A2D and A2C were the significant terms due to p values less than 0.05. Meanwhile, it is noteworthy that the parameters with $p$ values higher than 0.05 were omitted from the model. Figures 1 and 2 reveal the perturbation graphs and the plots of main effects of the parameters on the free cyanide ions elimination by the Caro's acid method, respectively. The perturbation plot shows the relative significance of important parameters, and it assists to appraise the influence of all the parameters at a special point in the design space and a steep slope or curvature proves that the value of removal is sensitive to that parameter. As it can be observed, the findings derived from this graph support the results of the ANOVA table. Moreover, the following results can be achieved from the observations presented in Figures 1 and 2.

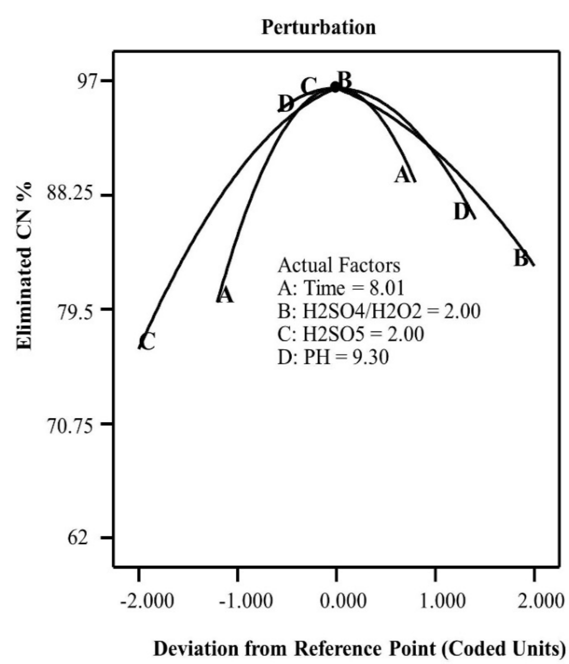


**Figure 1. Perturbation graph indicating relative importance of parameters on free cyanide ion elimination by Caro's acid method.**

The yield of free cyanide ion elimination increase from 80% to 90% by increasing the reaction time from 5 to 10 minutes (Figure 2a); this shows that cyanide elimination reaction by the Caro's acid method has a fast kinetic and it just takes about 10 minutes that about 90% of cyanide ions convert into cyanate ion.

The effect of sulfuric acid to hydrogen peroxide ratio on the percentage of free cyanide ion elimination is presented in Figure 2b. As seen in this graph, when other parameters are in their middle level, an increment in the weight ratio of sulfuric acid/oxidant from 2 to 3 will decrease the percentage of free cyanide ion elimination. This behavior may be owing to the fact that the amount of hydrogen peroxide, which has the main role of the oxidant in the preparation of Caro's acid, decreases under this condition, and accordingly, it causes the reduction in the value of cyanide elimination.

Also the elimination percentage of cyanide ion sharply promoted from about 77.5% to 92% with an increment in the Caro's acid concentration from 1.5 to 2 g/L (Figure 2c).

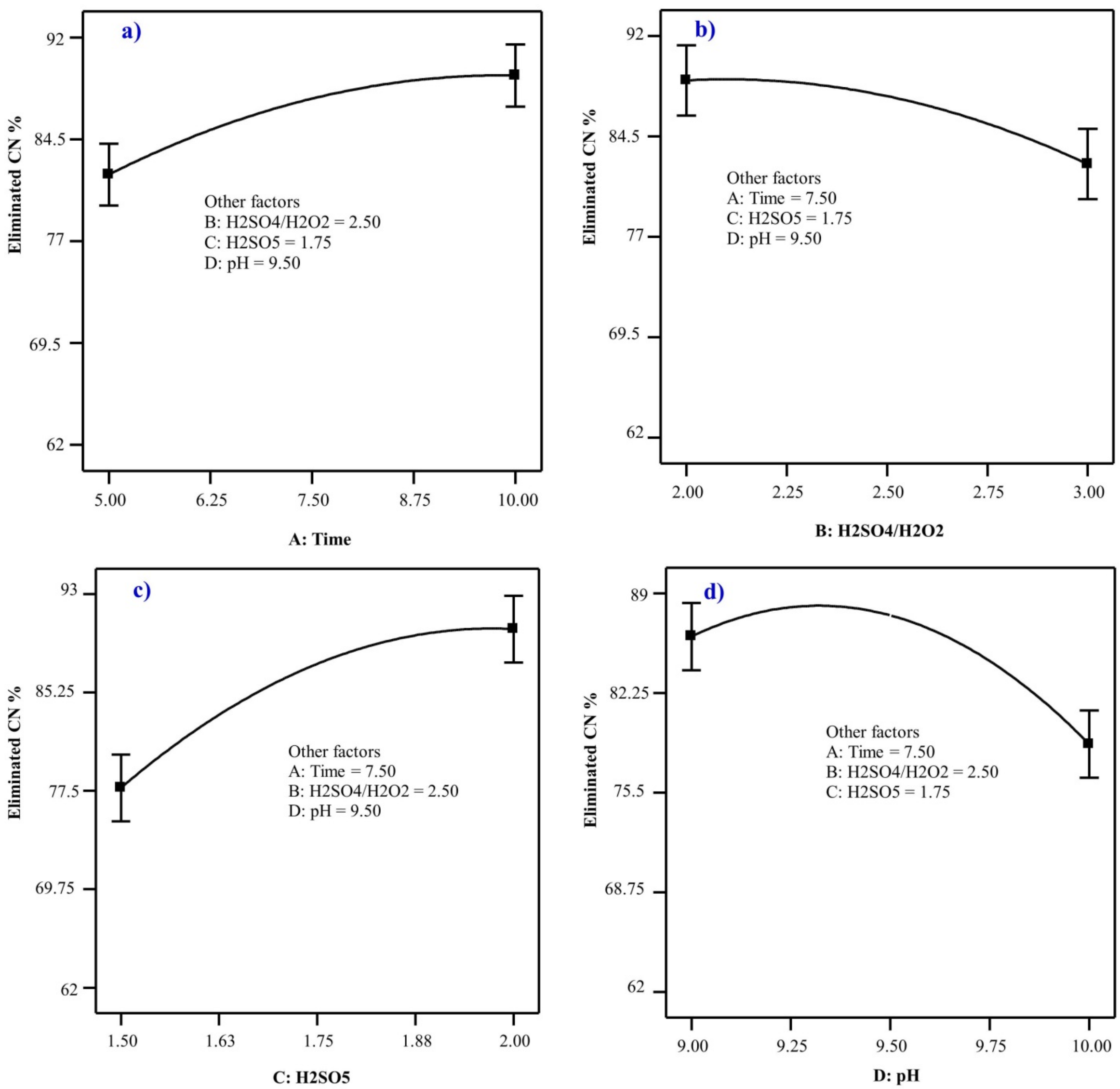


**Figure 2. Main effects of effective parameters on elimination percentage of cyanide ion.**

In other words, a change of 0.5 g/L in the concentration of Caro's acid leads to nearly 14.5% rise in the elimination value of cyanide ion. This behavior shows that Caro's acid plays a main role in the cyanide ion oxidation to cyanate, and the enhancement of concentration intensifies the oxidation amount of cyanide ion; therefore, the percentage of free cyanide ion elimination from the solution increases as well.

Figure 2d shows the effect of pH on the elimination percentage of cyanide ion, which has a parabolic shape with a maximum point at pH of about 9.3. The maximum removal of cyanide ion in this pH is about 87% and further enhancement in the value of pH has a negative effect on the conversion of cyanide ion to cyanate ion.

### 3.3. Process optimization

After selection of the model, the optimization was performed applying the DX7 software and the desirability function for achieving the maximum elimination of free cyanide ion from the wastewater of Agh-Darreh mine. Figure 3 shows a ramp graph for determining the optimal conditions. As it can be seen, the highest elimination value is obtained to be about 96.42% a desirable value of 0.9 at the reaction time of 8 min, sulfuric acid to hydrogen peroxide weight ratio of 2 (g/g), Caro's acid concentration of 2 g/L, and pH of 9.3. It also needs to be pointed out that three verification experiments were carried out at the suggested optimal conditions, and the mean value of the three experiments was determined to be 96.01%, and this indicated that the real results of these experiments were very close to the predicted values by the model and DX7 software.

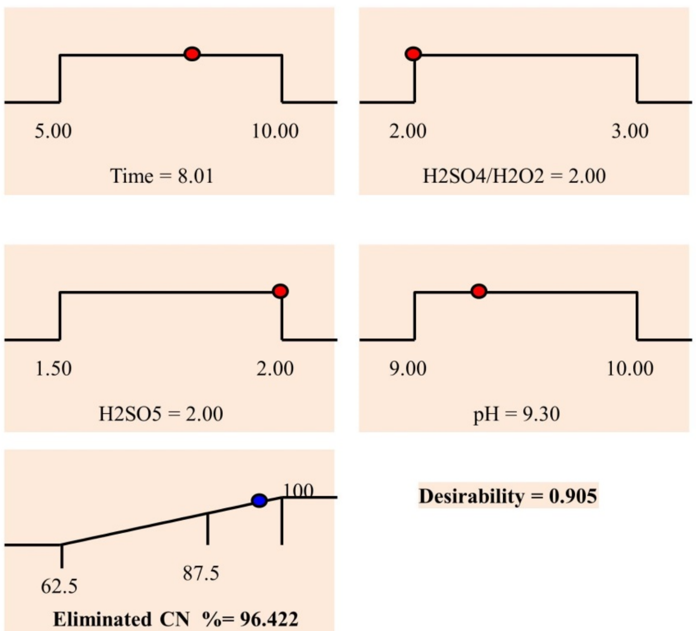


**Figure 3. Optimum conditions proposed to gain highest removal value of cyanide ion.**

### 3.4. Interactive effects of parameters

In addition to the main effects and optimization of parameters, the interactive effects between factors were evaluated on the removal percentage of cyanide ion from the wastewater, as shown in Figures 4 and 5.

Figure 4 shows the contour plots and the synergistic effects of two factors pH and time and Caro's acid concentrations and the weight ratio of sulfuric acid/hydrogen peroxide on the elimination value of cyanide ion under optimal conditions. It is obvious from Figure 4 that the elimination rate increases with increasing the time and pH but only up to a certain maximum level (8 min and 9.3) and after that reduces. The impact of pH may be due to by numerous mechanisms such as ion exchange, physical snare, complexation, and electrostatic contact. Also the pH of a solution can be led to the changes in the specification of pollutant and degree of ionization [31].

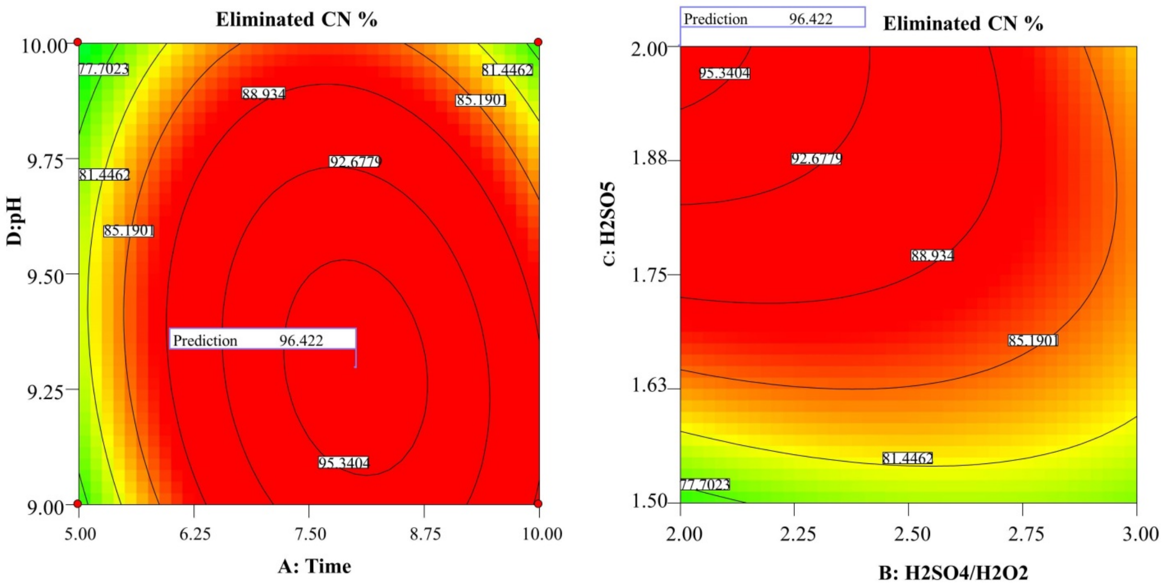


**Figure 4. Contour-plot showing effect of pH and time and Caro's acid concentrations and the weight ratio of sulfuric acid/hydrogen peroxide on removal percentage of cyanide when all other parameters were kept at their optimum level.**

It was also observed from the figure that at high Caro's acid concentrations, the enhancement in the weight ratio of sulfuric acid to hydrogen peroxide resulted in to a linear reduction in the elimination percentage of free cyanide ion from about 95% to 83%. However, at low Caro's acid concentrations, the elimination percentage of cyanide ion slightly increased from 74% to 78% by increasing the weight ratio. Additionally, it is found from Figure 4 and the ANOVA table that the interaction between sulfuric acid/hydrogen peroxide weight ratio and Caro's acid concentration has a remarkable influence on the value of removal. The 3D response surface plot and the interaction graph were employed to show a better understanding of this term as shown in Figure 5. It is clear that if sulfuric acid to hydrogen peroxide weight ratio is set on the minimum value, the enhancement of Caro's acid concentration will increase the percentage of free cyanide ion elimination up to 96.4%.

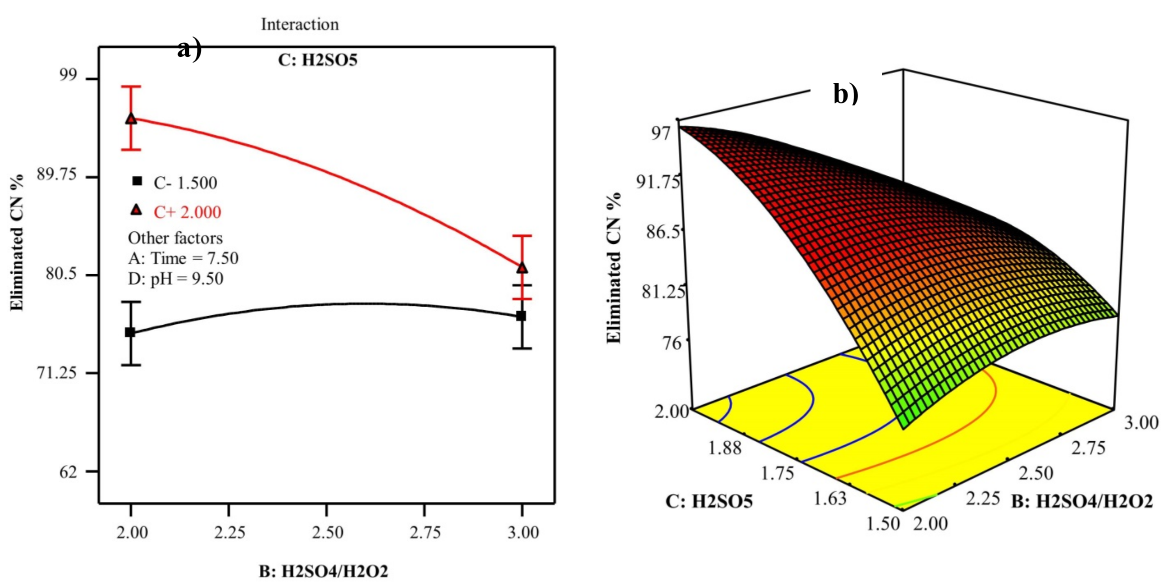


**Figure 5. Interaction (a) and 3D response surface (b) plots showing effect of the weight ratio of sulfuric acid/hydrogen peroxide and Caro's acid concentration.**

## 4. Conclusions

Since the cyanidation process is applied to extract gold in the Agh-Darreh mine, the wastewater produced from this mine contains about 80 ppm of free cyanide ion, which needs to be removed before these wastewaters can be discharged to the receiving environments. In this research work, the chemical method of Caro's acid was used for the elimination of cyanide ion from the wastewater of this mine. In this approach, the cyanide ion is oxidized and converts into the less toxic cyanate ion. In this regard, the statistical design of experiments and response surface methodology was employed for investigating and optimizing the effective parameters on the elimination of free cyanide ion. The findings showed that increasing the Caro's acid concentration and time could increase the elimination value of free cyanide ion. On the other hand, the elimination rate of cyanide ion decreased with an enhancement in the sulfuric acid/hydrogen peroxide ratio and the pH (higher than 9.5). It was also distinguished that the importance degree of the important parameters was in the order of the quadratic effect of pH > linear effect of contact time > linear impact of Caro's acid concentration > linear effect of the sulfuric acid/hydrogen peroxide ratio. Moreover, the maximum removal of free cyanide ion (96.42) was obtained after 8 min contact time at the sulfuric acid to hydrogen peroxide weight ratio of 2, pH of 9.3, and Caro's acid concentration of 2 g/L.

## Acknowledgment

The authors would like to appreciate Lorestan University for financial support during this research work.

## Compliance with Ethical Standards

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

## References

[1]. Mudliar, R., Umare, S.S., Ramteke, D.S., and Wate, SR. (2009). Energy efficient-Advanced oxidation process for treatment of cyanide containing automobile industry wastewater. Journal Hazard Mater 164,1474–1479.

[2]. Mudder, TI. and Botz, MM. (2001). The Cyanide Monograph (Eds.). Mining Journal Books Limited, London, UK.

[3]. Akcil, A. (2002). First application of cyanidation process in Turkish gold mining and its environmental impacts. Mineral Engineering. 15 (9): 695–699.

[4]. Mudder, T. and Botz, M. (2004). Cyanide and society: a critical review. The European Journal of Mineral Processing and Environmental Protection 4, 62–74.

[5]. Akcil, A. (2006). Managing cyanide: health, safety and risk management practices at Turkey's Ovacik gold–silver mine. Journal of Cleaner Production. 14(8): 727–735.

[6]. Akcil, A. (2010). A New global approach of cyanide management: international cyanide management code for the manufacture, transport, and use of cyanide in the production of gold. Mineral Processing Extractive Metallurgy Review. 31 (3): 135–149.

[7]. Mondal, M., Mukherjee, R., Sinha, A., Sarkar, S., and De, S. (2019). Removal of cyanide from steel plant effluent using coke breeze, a waste product of steel industry. Journal Water Process Engineering. 28: 135–143.

[8]. Environmental Protection Agency, U.S. (1985). Drinking water criteria document for cyanide, Environment Criteria and Assessment office, Cincinnati, EPA/600/X-84-192-1.

[9]. Dash, RR., Majumder, CB., and Kumar, A. (2008). Treatment of metal cyanide bearing wastewater by simultaneous adsorption biodegradation (SAB). Journal Hazard Mater. 152,387–396.

[10]. Dash, RR. and Balomajumdar, C. (2014.) Treatment of cyanide bearing effluents by adsorption, biodegradation and combined processes: effect of process parameters. Desalination and Water Treatment. 52, 3355–3366.

[11]. Sinbuathong, N., Kongseri, B., Plungklang, P. and Khun-anake, R. (2000). Cyanide removal from laboratory wastewater using sodium hypochlorite and calcium hypochlorite. Witthayasan Kasetsat. 34 (1): 74-78.

[12]. Barter, J., Lane, G., Mitchell, D., Kelson, R., Dunne, R., Trang,C. and Dreisinger, DB. (2001). In Cyanide: Social, Industrial and Economic Aspects, Ed. Young C, Tidwell L, Anderson C, The Minerals, Metals and Materials Society Annual Meeting, 549-562.

[13]. Parga, J., Shukla, S. and Carrillo-Pedroza, F. (2003). Destruction of cyanide waste solutions using chlorine dioxide, ozone and titania sol. Waste Management journal. 23,183–191.

[14]. Dash, RR., Gaur, A., and Balomajumder, C. (2009). Cyanide in industrial wastewaters and its removal: A review on biotreatment. Journal of Hazardous Material. 163 (1): 1–11.

[15]. Yazıcı, EY., Deveci, H. and Alp, İ. (2009). Treatment of cyanide effluents by oxidation and

adsorption in batch and column studies. Journal of Hazardous Material. 166: 1362–1366.

[16]. Yeddou, AR., Nadjemi, B., Halet, F., Ould-Dris, A., and Capart, R. (2010). Removal of cyanide in aqueous solution by oxidation with hydrogen peroxide in presence of activated carbon prepared from olive stones. Mineral Engineering. 23,32–39.

[17]. Moussavi, G., Majidi, F. and Farzadkia, M. (2011). The influence of operational parameters on elimination of cyanide from wastewater using the electrocoagulation process. Desalination journal. 280,127–133.

[18]. Hijosa-Valsero, M., Molina, R., Schikora, H., Müller, M. and Bayona, JM. (2013). Removal of cyanide from water by means of plasma discharge technology. Water Resistant journal. 47 (4): 1701-1707.

[19]. Dwivedi, N., Balomajumder, C. and Mondal, P. (2016), Comparative investigation on the removal of cyanide from aqueous solution using two different bio-adsorbents. Water Resources India. 15: 28–40.

[20]. Alizadeh Ganji, S.M.S. and Hayati, M. (2018). Selecting an appropriate method to remove cyanide from the wastewater of Moteh gold mine using a mathematical approach. Environmental Science and Pollution Research. 25 (23): 23357–23369.

[21]. Bahrami, A., Kazemi, F., Alighardashi, A., Ghorbani, Y., Abdollahi, M. and Parvizian, A. (2020). Isolation and removal of cyanide from tailing dams in gold processing plant using natural bitumen. Journal of Environmental Management. 262:110286.

[22]. Mamelkina, MA., Herraiz-Carboné, M., Cotillas, S., Lacasa, E., Sáez, C., Tuunila, R., Sillanpää, M., Häkkinen, A. and Rodrigo, MA. (2020). Treatment of mining wastewater polluted with cyanide by coagulation processes: A mechanistic study. Separation and Purification Technology. 237,116345.

[23]. Eskandari, P., Farhadian, M., Solaimany, AR.and Goshadrou, A. (2020). Cyanide adsorption on activated carbon impregnated with ZnO, $Fe_2O_3$, $TiO_2$ nanometal oxides: a comparative study. nternational Journal of Environmental Science and Technology . https://doi.org/10.1007/s13762-020-02791-0.

[24]. Montalvo Andiaa, JP. and Ticona Cayteb, A E. (2021). Combined treatment based on synergism between hydrodynamic cavitation and $H_2O_2$ for degradation of cyanide in effluents. Minerals Engineering. 171: 107119.

[25].Liu, Q., Zhang, M., Peng, B. and Barvor, J B. (2021). Zinc cyanide removal by precipitation with quaternary ammonium salts. Separation and Purification Technology. 274, 119057.

[26]. Teixeira, LAC., Andia, JPM., Yokoyama, L., Araújo, FVF. and Sarmiento, CM. (2013). Oxidation of cyanide in effluents by Caro's Acid. Mineral Engineering. 45: 81–87.

[27]. Ghanbari, F. and Moradi, M. (2017). Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants: Review. Chemical Engineering Journal. 310: 41-62.

[28]. Loveitt, E. (1981). The preparation of Caro's Acid from hydrogen peroxide and sulphuric acid or oleum. Solvay Interox Research Report, UK.

[29]. Smith, RH. and Wilson, IR. (1966). The mechanism of the oxidation of thiocyanate ion by peroxomonosulphate in aqueous solution. I. Stoichiometry of the reaction. Australian Journal of Chemistry. 19 (8): 1357–1363.

[30]. Kuyucak, N. and Akcil, A. (2013). Cyanide and removal options from effluents in gold mining and metallurgical processes. Mineral Engineering. 50–51,13–29.

[31]. Jauto, AH., Memon, SA., Channa, A. and Khoja, AH. (2019). Efficient removal of cyanide from industrial effluent using acid treated modified surface activated carbon. Energy Sources . 41 (22): 2715-2724.

# مدل‌سازی، بهینه‌سازی و شناسایی پارامترهای فرآیند حذف یون سیانید از پساب صنعتی معدن طلا به روش اسید کارو

**حسن وفایی و سید محمد سید علیزاده گنجی***

**گروه فرآوری مواد معدنی، گروه مهندسی معدن، دانشگاه لرستان، لرستان، ایران**

ارسال ۲۰۲۲/۰۵/۲۳، پذیرش ۲۰۲۲/۰۸/۲۵

* نویسنده مسئول مکاتبات: Ganji.m@lu.ac.ir

**چکیده:**

بررسی حذف یون های سیانید از پساب معدن طلای آق دره با استفاده از روش اسید کارو از اهداف اصلی این مقاله می باشد. برای ارزیابی و بهینه‌سازی پارامترهای تأثیرگذار مانند نسبت اسید سولفوریک/پراکسید هیدروژن، pH، غلظت اسید کارو و زمان تماس از مدل‌سازی سطح- پاسخ در فرآیند حذف یون سیانید استفاده گردید. نتایج به‌دست‌آمده نشان می‌دهد که افزایش غلظت اسید کارو و زمان تماس تأثیر مثبتی بر حذف یون‌های سیانید آزاد دارد، در حالی که افزایش نسبت وزنی اسید سولفوریک به پراکسید هیدروژن و pH بالاتر از ۹/۵ اثرات منفی در حذف یون سیانید داشته است. همچنین نتایج نشان داده است که pH به صورت یک معادله درجه دوم بیشترین تأثیر را در حذف یون سیانید دارد و نسبت اسید سولفوریک به پراکسید هیدروژن به صورت یک معادله خط کمترین درجه اهمیت را دارد. علاوه بر این تحت شرایط بهینه شامل غلظت اسید کارو ۲ گرم در لیتر، pH برابر ۹/۳، زمان تماس ۸ دقیقه و نسبت وزنی اسید سولفوریک به پراکسید هیدروژن ۲ حدود ۹۶/۴ درصد از یون سیانید آزاد موجود در محلول پساب به صورت یون سیانات تبدیل شده است.

**کلمات کلیدی:** پساب، حذف یون سیانید، اسید کارو، مدل سازی سطح- پاسخ.