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# Simulation of cyanide oxidation using calcium and sodium hypochlorite in the Moteh Gold Mine Tailing Dam, Iran

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## ABSTRACT

Cyanide, as one of the most toxic pollutants existing in the gold mine tailing dams, threatens human health and other species life. The main objective of this study was to simulate the oxidation of cyanide from mineral effluent of the Moteh Tailing Dam (Iran), as a method for removing cyanide. We employed PHREEQC software to model the oxidation of cyanide using calcium hypochlorite ($Ca(OCl)_2$) and sodium hypochlorite (NaOCl). The results indicated that $Ca(OCl)_2$ and NaOCl concentrations, as well as pH, influenced the oxidation of cyanide. The model was run in the constant temperature of 12°C and pH between 12 to 13. By rising $Ca(OCl)_2$ concentration from 0.71 to 1.43 g/l and NaOCl concentration from 1.72 to 5.18 g/l, the removal rates of cyanide increased from 97.01% to 99.20% and 95.46% to 95.90%, respectively. The coefficient of determination ($R^2$), index of agreement (IA), and Nash- Sutcliffe efficiency (E) were used to assess the predicted removal rate of cyanide in comparison with experimental observations, which demonstrated a suitable agreement: $Ca(OCl)_2$ = 0.71 mg/l, $R^2$ = 0.97, IA = 0.91 and E = 0.73; $Ca(OCl)_2$ = 0.85 mg/l, $R^2$ = 0.99, IA = 0.99, E = 0.96; $Ca(OCl)_2$ = 1.43 mg/l, $R^2$ = 0.97, IA = 0.92, E = 0.79; NaOCl = 1.72 mg/l, $R^2$ = 0.97, IA = 0.92, E = 0.74; NaOCl = 3.45 mg/l, $R^2$ = 0.91, IA = 0.91, E = 0.71; NaOCl = 5.18 mg/l, $R^2$ = 0.96, IA = 0.91, E = 0.77.

*Keywords:* Cyanide; Oxidation; Calcium hypochlorite; Sodium hypochlorite; PHREEQC

## 1. Introduction

Cyanide ($CN^-$) is a chemical compound of carbon and nitrogen, which hydrogen cyanide (HCN), sodium cyanide (NaCN) and potassium cyanide (KCN) are examples of simple cyanide combinations. The lethal doses of HCN, NaCN and KCN are 50–100 mg/l, 150 mg/l and 200 mg/l, respectively. Cyanide, as a dangerous substance, is discharged to the environment by waste dams of mineral processing industries and sewage of chemical industries [1]. However, cyanide is a prevalent compound in a great variety of industries such as mining, electroplating, pharmaceutical, plants for fiber production, photography and etc. [2,3].

Cyanide ion is stable at pH more than 9 and converts to HCN in pH less than 7. Four groups of cyanide compounds which are important for the biological and toxicity standpoint are free cyanide ($CN_f$), cyanide can be divided by weak acid ($CN_{wad}$), iron cyanide, and cyanide-iron complexes [4].

Many techniques are available to reduce or remove cyanide from wastewater such as biological methods, ion exchange, adsorption, and chemical oxidation using hydrogen peroxide, sodium and calcium hypochlorite, ozone gas and polysulfide [5].

$Ca(OCl)_2$ and NaOCl are frequently used to oxidize cyanide, as an efficient and accepted technique for cyanide removal under controlled pH [6,7]. Through the oxidation, $CN^-$ converts to cyanate ($CNO^-$), which its environmental

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impact is 1000 times less than $CN^-$ [Eqs. (1)–(3)]. Afterwards, $CNO^-$ can be converted into carbon dioxide ($CO_2$) and nitrogen dioxide ($N_2O$) or ammonia oxide ($NH_4OH$) [Eq. (4)] [8,9].

$$Ca^{+2} + 2OCl^- \leftrightarrow Ca(OCl)_2 \tag{1}$$

$$Na^+ + OCl^- \leftrightarrow NaOCl \tag{2}$$

$$CN^- + OCl^- \leftrightarrow OCN^- + Cl^- \tag{3}$$

$$CNO^- + 2H_2O \leftrightarrow CO_2 + NH_3 + OH^- \tag{4}$$

The redox equations of cyanide and calcium hypochlorite are shown in the following:

$$CN^- + 2OH^- \leftrightarrow OCN^- + H_2O + 2e^- \tag{5}$$

$$H_2O + OCl^- + 2e^- \leftrightarrow Cl^- + 2OH^- \tag{6}$$

$$CN^- + OCl \leftrightarrow OCN^- + Cl^- \tag{7}$$

Several experiments have been carried out to remove cyanide from the wastewater of tailing dams. However, a limited number of studies have simulated the behaviour of cyanide precipitation from solution using $Ca(OCl)_2$ and NaOCl. Teixeira et al. studied the influence of hydrogen peroxide and hypochlorite on the oxidation of cyanide. This process was effective for a pH between 9 to 11 and cyanide concentration up to 1000 mg/l. The final concentration of residual cyanide was obtained less than 0.2 mg/l, which $\frac{([H_2O_2]+[NaOCl])}{[CN]} = 2:1$ concentration of 100 mg/l [7].

Khodadadi et al. succeeded to remove cyanide using sodium and calcium in different pH and temperature. The optimum pH was 12.3. The higher temperature triggered the evaporation of cyanide as HCN and reduced cyanide concentration [8]. Zheng et al. investigated removing cyanide of gold mine using electrodialysis. The removal efficiency was 87.14% at the voltage of 30 V [10].

Halim et al. simulated the leaching of heavy metals including lead (Pb), cadmium (Cd), arsenic (As), and chromium (Cr) from cementitious waste using PHREEQC. Martens et al. compared the simulation and experimental data for leaching of heavy metals from cementitious waste at pH between 1 and 12 using PHREEQC software. The modelling and experimental results indicated a good consensus for leaching of Ca, Mg, and Al [11]. Kim et al. applied PHREEQC software to analyse the solubility of actinides (such as amorphous uranium [U], americium [Am], thorium [Th], neptunium [Np] and plutonium [Pu]) at bentonite pore water. The results were evaluated using Multi-Geochemical Reaction Equilibrium (MUGREM) and EQ3/6 models [12]. Motalebi Damuchali et al. simulated the effective parameters in the transfer of heavy metals from wastes of lead and zinc mines via soil into water resources using PHREEQC software. The grade size distribution, pH variation and heavy metal concentrations affected the heavy metal movement through soil [13]. Cravotta and Brady simulated the priority pollutants of untreated and treated samples in coal mining using PHREEQC software. The most priority pollutants including aluminium (Al), iron (Fe), manganese (Mn), Cd, Cr, cobalt (Co), copper (Cu), Pb, nickel (Ni), zinc (Zn), thallium (Tl), uranium (U), and selenium (Se), were unfavourably influenced by pH [14]. Walinder employed PHREEQC software to simulate ion exchange method for perfluoroalkyl substances (PFASs) adsorption at water treatment. The PFASs substance removal was increased by growing the PFASs' chain length [15]. Bisone et al. simulated As the behavior of a contaminated gold mining soil in France using PHREEQC software. The pH, climate, fluctuating groundwater levels, and activity of microorganisms were effective in As removal [16].

The main objective of our study was to simulate removal of cyanide, by adding calcium and sodium hypochlorite at different pH using PHREEQC software to determine the capability of the model to predict cyanide removal of the gold mine tailing dam. The model's result was evaluated by the experimental observations.

## 2. Methods

### 2.1. The study area

The Moteh gold mine in central Iran is located in a dry and hot climate region, the southwest of Tehran. The annual precipitation is averagely varied between 180–200 mm. The average temperature fluctuates between 0 in the winter and 39 in the summer. The Moteh tailing dam structure mainly consists of clay and quartzitic materials; and consequently, the dam may be subjected to the water and wind erosions. The heavy metals, including As, barium (Ba), Co ,Cr, rubidium (Rb), thorium (Th), tungsten (W), Zn, cerium (Ce) and neodymium (Nd) are another environmental pollution from the Moteh tailing dam (Table 1) [17].

PHREEQC is a geochemical computation tool at aqueous environments. The software calculates the reaction path and inverse modelling for the transfer of water and gas moles in the aqueous environment. The model is based on the chemical equilibrium of the aqueous solution in reaction with minerals, solid solution, exchange and absorbent surfaces. The model can evaluate the element concentrations, activity of aquatic species, molality, pH, electron

Table 1
The avrage concentration of heavy metals (ppm) in the Moteh tailing dam [17]

| As | 20.2 |
|---|---|
| Ba | 1288 |
| Co | 38.30 |
| Cr | 34.00 |
| Rb | 115.6 |
| Th | 13.90 |
| W | 170.4 |
| Zn | 99.60 |
| Ce | 71.40 |
| Nd | 56.40 |

activity (pE), saturation index and molar transfer in different phases [18].

### 2.2. Mathematical equations for simulation

The PHREEQC software simulates the oxidation process of chemical reactions. The rate of kinetic reaction of minerals and solid compounds can be computed as follows [19]:

$$R_k = r_k A_0 / V \left( \frac{m_k}{m_{0k}} \right)^n \tag{8}$$

where $r_k$ is the specific rate (mol/m$^2$/s), $A_o$ is the initial solid surface area (m$^2$), $V$ is the solution amount (kgw), $m_{ok}$ is the initial moles of solid and $m_k$ is the moles of solid at a given time. $\left( \frac{m_k}{m_{0k}} \right)^n$ is a factor to account for changes in $\frac{A_0}{V}$ during dissolution and also for selective dissolution as well as aging of the solid. For uniformly dissolving spheres and cubes $n = 2/3$.

Based on the availability of data, the specific rate can be illustrated in various forms. The specific rate for super-saturation and under-saturation can be estimated by Eq. (9). The specific rate in the equilibrium state is assumed to be zero [20].

$$r_k = k_k \left( 1 - \left( \frac{IAP}{K_k} \right)^\sigma \right) \tag{9}$$

where $k_k$ is an empirical constant, $IAP/K_k$ is the saturation ratio (SR). The coefficient is associated with the stoichiometry of the reaction once an activated complex is formed (usually $\sigma = 1$).

Eq. (10) shows the rate expression based on the saturation index.

$$r_k = k_k \sigma \log \left( \frac{IAP}{K_k} \right) \tag{10}$$

Rate expressions often comprise concentration-dependent terms such as Monod equation [21]:

$$r_k = r_{\max} \left( \frac{C}{K_m + C} \right) \tag{11}$$

where $r_{max}$ is the maximal rate, and $K_m$ is the concentration that the rate is half of the maximal rate. The Monod rate expression is commonly applied to the simulation of the sequential steps in the organic matter oxidation [18].

The limitations of PHREEQC were as follows: creating chemical equilibrium, failure in considering the time (there are no synthetic reactions), and applying an electric potential.

### 2.3. Model efficiency

For model efficiency, we used the coefficient of determination (R$^2$), index of agreement (IA) and Nash- Sutcliffe efficiency (E) [Eqs. (12)–(14)].

$$R^2 = \left( \frac{\sum_{i=1}^{i} \left(A_t - \bar{A}\right)\left(F_t - \bar{F}\right)}{\sum_{i=1}^{n} \left( \left(A_t - \bar{A}\right)^2 \right) \sum_{i=1}^{i} \left( \left(F_t - \bar{F}\right)^2 \right)^{0.5}} \right)^2 \tag{12}$$

$$IA = 1.0 - \frac{\sum_{t=1}^{n} \left(A_t - F_t\right)^2}{\sum_{t=1}^{n} \left( | F_t - \bar{A}) + | A_t - \bar{A} | \right)^2} \tag{13}$$

$$E = 1.0 - \frac{\sum_{t=1}^{n} \left(A_t - F_t\right)^2}{\sum_{t=1}^{n} \left( | F_t - \bar{A}) + | A_t - \bar{A} | \right)^2} \tag{14}$$

where, $A_t$, $F_t$, $\bar{A}$ and $\bar{F}$ are the observed data (experimental), predicted data (simulated), the average experimental data and the average simulated data, respectively [22,23]

### 2.4. Applied experimental data for simulation

The experimental data were based on Khodadadi et al. [8], who used $Ca(OCl)_2$ and NaOCl for cyanide removal in the Moteh gold plant tailing dam. To determine the concentration of cyanide, the wastewater was separated by filtration at the Tarbiat Modares University's laboratory. The samples were titrated using a solution of pure para-dimethyl-amino-benzylidine-redanine. The cyanide concentration was obtained 270 mg/l.

Tables 2 and 3 indicate the levels of residual cyanide concentrations at a constant temperature of 12°C and pH = 12 in the different concentrations of $Ca(OCl)_2$ and NaOCl. Table 4 presents the residual cyanide concentration during the experimental campaign with three selective concentrations of $Ca(OCl)_2$ and NaOCl at different pH and temperature of 12°C [8].

Table 2
The residual cyanide concentrations (mg/l) at different $Ca(OCl)_2$ concentrations, T = 12°C, pH = 12 [8]

| Calcium hypochlorite (g/l) | Residual cyanide (mg/l) |
|---|---|
| 0.710 | 9.90 ± 0.183 |
| 0.850 | 4.99 ± 0.198 |
| 1.43 | 3.10 ± 0.130 |
| 7.15 | 0 |
| 14.3 | 0 |
| 28.6 | 0 |
| 42.9 | 0 |
| 57.2 | 0 |
| 71.5 | 0 |
| 143 | 0 |

Table 3
The residual cyanide concentrations (mg/l) at different NaOCl concentrations, T = 12°C, pH = 12 [8]

| Sodium hypochlorite (g/l) | Residual cyanide (mg/l) |
|---|---|
| 1.72 | 15.9 ± 0.142 |
| 3.45 | 14.7 ± 0.100 |
| 5.18 | 11.0 ± 0.146 |
| 6.91 | 6.31 ± 0.095 |
| 8.64 | 0 |

Table 4
The residual cyanide concentrations (mg/l) at three selected concentrations of $Ca(OCl)_2$ and NaOCl at varied pH values between 12 to13 [8]

| pH | Calcium hypochlorite (g/l) | | | Sodium hypochlorite (g/l) | | |
|---|---|---|---|---|---|---|
| | 1.43 | 0.85 | 0.71 | 5.18 | 3.45 | 1.72 |
| 12.0 | 3.10 ± 0.161 | 4.99 ± 0.198 | 9.98 ± 0.327 | 10.0 ± 0.142 | 14.7 ± 0.206 | 15.9 ± 1.02 |
| 12.1 | 2.00 ± 0.089 | 4.54 ± 0.171 | 9.00 ± 0.220 | 10.8 ± 0.161 | 12.3 ± 0.171 | 14.3 ± 0.793 |
| 12.2 | 0 | 4.21 ± 0.162 | 8.50 ± 0.216 | 9.30 ± 0.164 | 11.1 ± 0.330 | 12.9 ± 1.87 |
| 12.3 | 0 | 3.59 ± 0.140 | 6.90 ± 0.234 | 8.15 ± 0.122 | 9.70 ± 0.370 | 11.6 ± 1.41 |
| 12.4 | 0 | 5.12 ± 120 | 9.10 ± 0.219 | 13.2 ± 0.137 | 16.0 ± 1.58 | 19.2 ± 2.64 |
| 12.5 | 1.32 ± 0.066 | 8.61 ± 0.133 | 15.2 ± 0.216 | 17.0 ± 0.184 | 22.1 ± 0.740 | 25.3 ± 4.13 |
| 12.6 | 2.49 ± 0.068 | 13.6 ± 0.146 | 18.4 ± 0.167 | 22.9 ± 0.452 | 27.8 ± 0.930 | 29.2 ± 1.74 |
| 12.7 | 6.99 ± 0.158 | 17.3 ± 0.062 | 28.5 ± 0.238 | 28.7 ± 0.137 | 30.8 ± 2.77 | 34.8 ± 5.04 |
| 12.8 | 9.30 ± 0.136 | 21.7 ± 0.097 | 24.0 ± 0.303 | 31.1 ± 0.202 | 32.9 ± 1.45 | 39.2 ± 5.04 |
| 12.9 | 18.7 ± 0.136 | 25.3 ± 0.136 | 31.2 ± 0.229 | 34.2 ± 0.358 | 36.8 ± 2.33 | 24.4 ± 1.81 |
| 13.0 | 24.1 ± .158 | 30.0 ± 0.102 | 36.2 ± 0.294 | 39.4 ± 1.04 | 42.0 ± 2.93 | 45.7 ± 3.03 |

## 3. Results and discussion

### 3.1. Simulation of Cyanide removal by Calcium Hypochlorite

According to Eqs. (11)–(13), the simulation was conducted by adding 1 mole $Ca(OCl)_2$ to 1 mole oxidised cyanide in the proportion of 1 to 1 [24–26].

Fig. 1 illustrates the estimated residual cyanide concentrations in the wastewater for the temperature of 12 and pH of 12 at 0.75, 0.85 and 1.43 g/l of $Ca(OCl)_2$. In the acidic condition, the cyanide can be converted to hydrogen cyanide [4]. In the high concentrations of $Ca(OCl)_2$, the residual cyanide was insignificant. The results had an appropriate agreement with the experimental data ($R^2 = 0.97$, IA = 0.95 and E = 0.87).

Fig. 2 presents the estimated cyanide removal at the temperature of 12 and pH of 12–13 using 0.71 g/l $Ca(OCl)_2$. The results had a good agreement with the experimental data ($R^2 = 0.97$, IA = 0.91 and E = 0.73). In pH between 12–12.4, a slight reduction in the residual cyanide concentration was observed. In pH higher than 12.4, the residual cyanide concentrations were increased. The optimal condition for cyanide removal was predicted to be in pH of 12.3, as verified by the experimental data.

Fig. 3 depicts the comparison between the experimental and the modeling results for the removal of cyanide in pH between 12 to 13 using 0. 85 g/l $Ca(OCl)_2$, which is similar to Fig. 2. By increasing the pH from 12 to 12.3, the residual cyanide concentration in the wastewater was decreased. In pH higher than 12.3, the cyanide concentration was increased. The convergence between the experimental data and simulation results was satisfactory ($R^2 = 0.99$, IA = 0.99 and E = 0.96).

Fig. 4 describes the comparison between the experimental and simulation results for removal cyanide at a temperature of 12°C and pH = 12–13 using 1.43 g/l $Ca(OCl)_2$. The model's predictions were satisfactory in comparison with the experimental observations ($R^2 = 0.97$, IA = 0.92 and E = 0.79).

### 3.2. Simulation of cyanide removal by using sodium hypochlorite

The simulation was conducted by adding 1 mole NaOCl to 1 mole oxidise cyanide in the proportion of 1 to 1 [27].

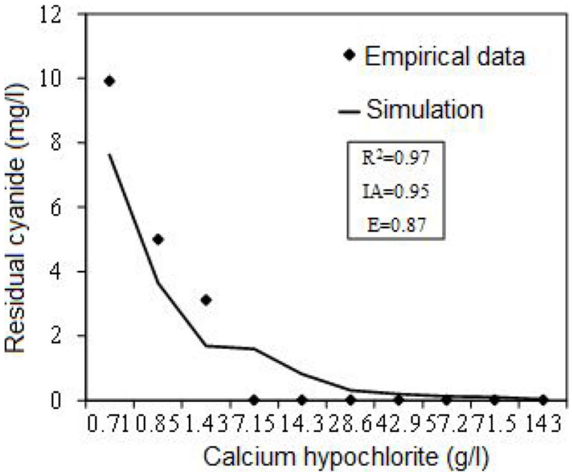

Fig. 1. Comparison between the experimental and the simulation results of cyanide removal from wastewater of the gold tailing dam using different concentrations of $Ca(OCl)_2$.

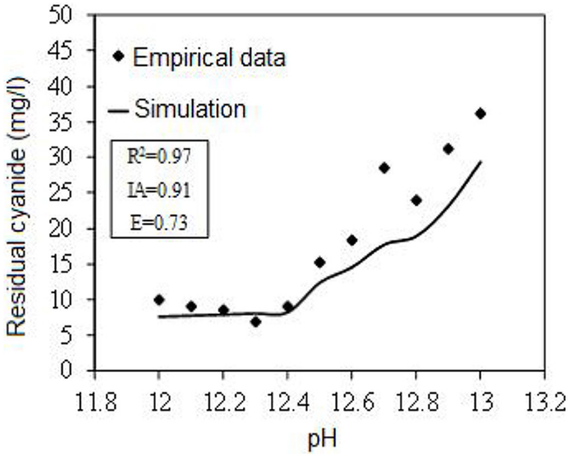

Fig. 2. Comparison between the experimental and the simulation results of cyanide removal from wastewater of gold tailing dam at pH = 12–13 and $Ca(OCl)_2 = 0.71$ g/l.

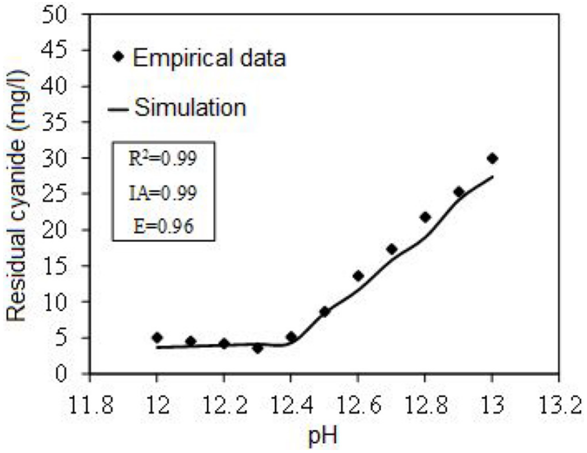

Fig. 3. Comparison between the experimental and the simulation results of cyanide removal from wastewater of gold tailing dam at pH = 12–13 and $Ca(OCl)_2$ = 0.85 g/l.

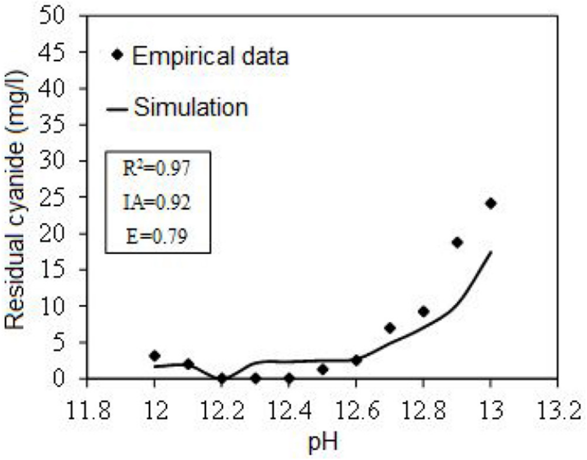

Fig. 4. Comparison between the experimental and the simulation results of cyanide removal from wastewater of gold tailing dam at pH = 12–13 and $Ca(OCl)_2$ = 1.43 g/l.

Fig. 5 indicates the comparison between the simulation and experimental results of cyanide removal at the temperature of 12°C and pH of 12, which existed a good agreement between them ($R^2$ = 0.9, IA = 0.95 and E = 0.85).

In temperature of 12, pH of 12 to 12.3 and 1.72 g/l NaOCl, the cyanide residual concentration had a smooth decreasing trend. At pH higher than 12.3, the residual concentration had a remarkable increasing trend. The pH of 12.3 could be assumed as the optimal point for cyanide removal. As shown in Fig. 6, the empirical data had a good agreement with simulation results ($R^2$ = 0.97, IA = 0.92, E = 0.74).

In 3.45 g/l NaOCl, the optimum pH was 12.2, which the minimum residual cyanide concentration was observed. As indicated in Fig. 7, the empirical and simulation results had a good consensus ($R^2$ = 0.91, IA = 0.91, E = 0.71).

In 5.18 g/l NaOCl, the optimal pH was 12.3, which the minimum residual cyanide was observed. As demonstrated in Fig. 8, the accuracy of the model was assessed

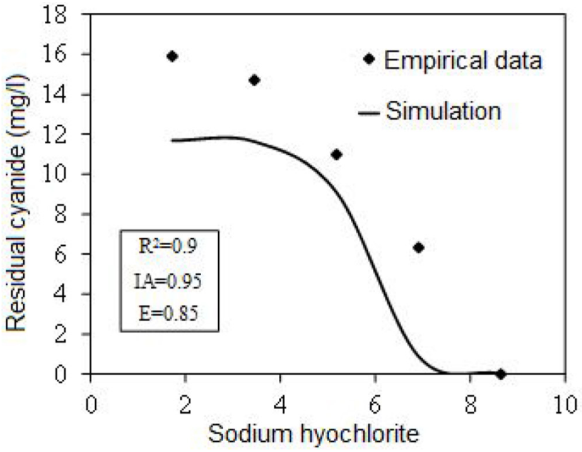

Fig. 5. Comparison between the experimental and the simulation results of cyanide removal from wastewater of the gold tailing dam using different concentrations of NaOCl.

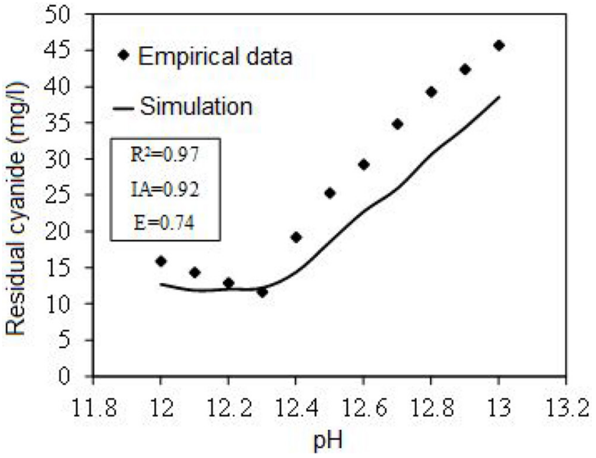

Fig. 6. Comparison between the experimental and the simulation results of cyanide removal from wastewater of gold tailing dam at pH = 12–13 and NaOCl = 1.72 g/l.

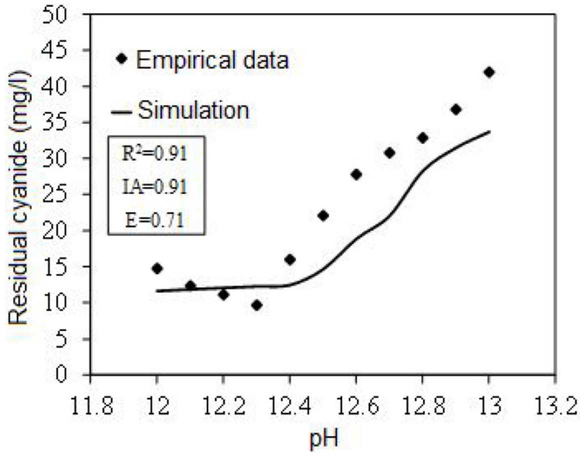

Fig. 7. Comparison between the experimental and the simulation results of cyanide removal from wastewater of gold tailing dam at pH = 12–13 and NaOCl = 3.45 g/l.

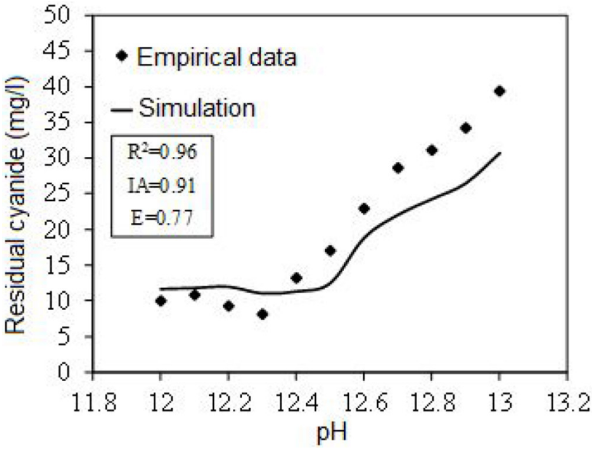

Fig. 8. Comparison between the experimental and the simulation results of cyanide removal from wastewater of gold tailing dam at pH = 12–13 and NaOCl = 5.18 g/l.

and had a good convergence with empirical data ($R^2$ = 0.96, IA = 0.91, E = 0.77).

## 4. Conclusion

Taking into consideration the results and discussions of the simulation of removal and detoxification of cyanide using NaOCl and $Ca(OCl)_2$ in the wastewater, the following conclusions can be made:

1. The simulation depicted that NaOCl and $Ca(OCl)_2$ effectively contributed to cyanide removal. However, the cyanide removal with $Ca(OCl)_2$ were more efficient in comparison with NaOCl.
2. The simulation and experimental results indicated that $Ca(OCl)_2$ concentration of 1.43 g/l and NaOCl concentration of 5.18 g/l were the optimum values in cyanide removal.
3. The highest cyanide removal in the simulation and experiments was 99.2% using 1.43 g/l $Ca(OCl)_2$ and 95.9% using 5.18 g/l NaOCl.
3. The simulation results of using $Ca(OCl)_2$ had a good agreement with experimental data. The coefficients of determination ($R^2$) using 0.71, 0.85, and 1.43 g/l $Ca(OCl)_2$ concentrations were 0.95, 0.99, and 0.94, respectively. The indices of agreement (IA) were 0.91, 0.99, and 0.92, respectively. The Nash- Sutcliffe efficiencies were 073, 0.96, and 0.79, respectively.
4. The simulation results of using NaOCl concentrations on cyanide removal indicated that $R^2$ between the experimental data and the simulation data using 1.72, 3.45, and 5.18 g/l NaOCl were 0.97, 0.91, and 0.96, respectively. The index of agreement (IA) were 0.92, 0.91, and 0.91, respectively. In addition, the Nash- Sutcliffe efficiencies were obtained 0.74, 0.71, and 0.77, respectively.
5. The simulation results of cyanide removal using $Ca(OCl)_2$ indicated that PHREEQC software was capable to simulate cyanide removal from wastewater of tailing dam. The removal ranges of cyanide using $Ca(OCl)_2$ were between 89.1% to 99.2%.
6. The simulation results of cyanide removal with NaOCl indicated the efficiency of PHREEQC software. The result was in a good agreement with experimental observations. The cyanide removal ranges using NaOCl were between 85.7% to 95.9%.
7. The study depicted that the PHREEQC software was applicable and efficient in the simulation of cyanide removals.

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