Degradation of cyanide from gold processing effluent by H_2O_2, NaClO and Ca(ClO)$_2$ combined with sequential catalytic process

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This work investigates the removal of cyanide as a noxious pollutant in the gold processing effluent (Aq-Dara mine, Takab, Iran) using H_2O_2, H_2O_2+Fe(II) (Fenton), H_2O_2+Cu(II), NaClO and Ca(ClO)$_2$ oxidants. Implementation of purification operation was carried out by varying the parameters including pH, oxidant dosage, temperature and time of the reaction. The results show that the oxidants have the highest efficacy at pH 10-12, while the Fenton process has the highest efficiency at pH 8. The results confirm that Ca(ClO)$_2$ is the best oxidant due to the shorter time, low reaction rate, high degradation of cyanide and low cost. The obtained results of response surface methodology optimization show that cyanide degradation has a direct relation to temperature, amount of oxidant, time and catalyst dosage parameters and has an inverse relation to pH. Also, the cyanide elimination efficiency is more than 99.5% and residual cyanide less than Environmental Protection Agency standards and 40% of the consumed water can be compensated by the effluent treatment and its return to the factory's processing circuit.

Keywords: Oxidation Process; Gold Processing Effluents Treatment; Cyanide Degradation; Non-linear Kinetic Modeling, Response Surface Method.

INTRODUCTION

Water pollution by organic and inorganic substances became a critical environmental problem [1-5]. Cyanide is a highly toxic, dangerous and hazardous chemical compound in gaseous, liquid and solid phases [6-8]. Cyanide is an important industrial chemical which is produced on a large scale for use in gold ore extraction, electroplating and many other industries [9, 10]. Such industries discharge large amounts of cyanide-containing liquid waste which often contains significant amounts of heavy metals and is a highly toxic and hazardous effluent [11-13]. Accordingly, environmental contamination by harmful compounds is considered as a big challenge [14, 15]. It is estimated that more than 100,000 tons of anthropogenic cyanide enter the environment annually [16-18]. Because of the potential hazards associated with cyanide, the discharge of these effluents into the environment without treatment is forbidden [19]. Literally, several methods are reported for removal of cyanide from wastewater such as alkaline chlorination [20], destruction on trickling filters [21], oxidation with ozone [22], Fenton oxidation [23], sulfur dioxide [24], ultrasonic [25], ion exchange [26], Caro's acid [27, 28], photocatalytic degradation [29], adsorption process [30, 31], polymerization with formaldehyde [32], biodegradation [33] and Fenton catalytic degradation [34]. Hydrogen peroxide (H_2O_2) is widely used in the industry for the treatment of cyanide-containing effluents, as it is a strong oxidant [35]. H_2O_2 reacts with cyanide to produce cyanate which hydrolyzes ammonium and carbonate ions [36]. The reaction is conducted at a pH value of around 10 [37]. H_2O_2 can oxidize cyanide to cyanate in the presence of a transition metal (Cu, Ag, V, Ru, Mg) as a catalyst [38]. The final products are carbonate and ammonia compounds [25]. Fenton's oxidation is one of the best-known metal-catalyzed oxidation reactions of water-miscible organic compounds [39]. The mixture of FeSO$_4$ or any other ferrous complex and H_2O_2 (Fenton's reagent) at enough low pH, results in Fe(II) catalyzed decomposition of H_2O_2 and proceeds *via* a free radical chain process that produces hydroxyl radicals which have extremely high oxidizing ability [40]. Transition metal salts can activate H_2O_2 to form hydroxyl radicals which are strong oxidants [41]. The main advantage is the complete destruction of contaminants to harmless

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compounds, water and inorganic salts [42]. Two major advantages of Fenton over other advanced oxidation processes include the lack of sophisticated equipment and facilities requirement and lack of limitation effects on mass transfer. In addition, it is a cost-effective and environmentally friendly method [23].

Likewise, alkaline chlorination has been well known for a long time as an effective means of treatment for industrial wastewaters [43], does not require a catalyst and is reported to be easy to operate [23]. Cyanide oxidation by calcium or sodium hypochlorite (Ca(ClO)$_2$ or NaClO) is an acceptable technique for cyanide wastewater treatment [44], where the reaction occurs in two stages. The first stage is the free cyanide rapid reaction with the hypochlorite ion ClO$^-$ in aqueous solution forming as the intermediate compound the cyanogen chloride (CNCl) [45]. The second stage of the process involves cyanate (OCN$^-$) hydrolysis and bicarbonate/nitrogen decomposition. This process needs strict pH control in order to prevent the release of cyanogen chloride which is highly toxic [46].

So this work focused on comparing the efficiency and conducting an experimental study on the kinetics of the oxidation of aqueous cyanide ion by alkaline chlorination and hydrogen peroxide by different catalyst processes in the removal of cyanide from gold processing wastewater (Aq-Dareh gold mine, Iran). In addition, nonlinear kinetic modeling and wastewater treatment economical assessment were done for each reaction. So, this paper presents the fundamentals and the approaches utilized in the development of the most efficient, economical and environmentally acceptable water management system possible for a particular mineral processing operation utilizing the cyanidation process.

MATERIALS AND METHODS

Samples and chemicals

Samples were collected from the wastewater that is contaminated with cyanide from the Aq-Dareh mine and gold processing plant located 32 km from Takab city in Western Azerbaijan province, Iran. The wastewater consists of a colorless solution that is clear but contains 40 mg/L of cyanide plus sewage. Calcium hypochlorite (Ca(ClO)$_2$), sodium hypochlorite (NaClO), iron sulfate heptahydrate (FeSO$_4$.7H$_2$O), hydrogen peroxide (H$_2$O$_2$, 30%) and copper sulfate pentahydrate (CuSO$_4$.5H$_2$O) of analytical grade were purchased from Merck. Solution pH values

were adjusted using reagent-grade NaOH and HCl solutions with different molar concentrations. All chemicals were used without further purification and all solutions were prepared using freshly prepared distilled water.

Experimental apparatus and procedures

All experiments were performed at room temperature and ambient light in order to reproduce full-scale operational conditions. Homogeneous samples were taken at different times from the part of the gold processing flow sheet that is named Paste Production and Storage Mechanism (PPSM). The samples were collected in sterile plastic containers and kept in the dark at the environmental temperature for less than one hour before being analyzed in the laboratory. Cyanide concentrations were determined by a colorimetric method on a UV–Visible spectrophotometer (Unico-2300) at a wavelength of 578 nm [16]. A pH meter Metrohm 827 model (Swiss mode) was used for pH measurements or adjustment. All samples were agitated with a magnetic stirrer (200 rpm) to provide an aerated environment and perfect mix. Chemical oxidation processes have higher operating costs but they are faster, more efficient and reliable for the breakdown of cyanide by comparison with natural degradation. This experimental study was designed to compare cyanide removal using H$_2$O$_2$ (no catalyst), Fenton (H$_2$O$_2$+Fe(II)), H$_2$O$_2$+Cu(II), and alkaline chlorination processes on a laboratory scale. During the processes, the effect of the main parameters, namely, pH, oxidant dosage, temperature and reaction time on the removal of cyanide from gold processing wastewater was studied (Table 1).

According to Table 1, the pH values were changed from 8 to 13, where at pH values less than 8 the soluble cyanide is volatile [16, 47] and same when temperatures values are more than 35 °C [48]. Obtained data from temperature changing on cyanide removal were used for thermodynamical studies [49]. Different oxidant with various dosages was used. The result of oxidants dosages changes was utilized for nonlinear kinetic modeling. At pre-selected times, 100 mL of contaminated wastewater was collected from the PPSM and added oxidant reagents solution to quench the residual radical reaction. At least three replicate runs were carried out for each experiment in order to ensure reproducible data and the results presented herein represent the average of these replicates, with a standard deviation of 0.16.

Table 1. The ranges of main parameters applied to the wastewater treatment process

Oxidant	pH	Reaction time (min)	Temperature (°C)	Dosage (g/L)
H_2O_2		0-300		0.04-4.78
Fenton		0-130		0.05-1.00
H_2O_2/Cu(II)	8-13	0-220	20-35	0.04-1.09
Ca(ClO)$_2$		0-25		0.08-0.90
NaClO		0-35		0.07-1.32

RESULTS AND DISCUSSION

Effect of pH

The pH effect on cyanide degradation efficiency was investigated and is shown in Fig. 1. Based on Eh-pH diagram of the aqueous cyanide system and pH-dependent fractionation of HCN and CN^-, cyanide essentially exists in the form of HCN at pH below 9.3 under non-oxidizing conditions [50]. The level of free cyanide (CN^-) in equilibrium with HCN decreases by increasing acidity. In order to avoid the cyanide volatilization, the pH was selected in the range of 8-13.

Figure 1 depicts the influence of pH on various oxidation processes for cyanide (40 mg/L) degradation. The optimum pH value for effective treatments in H_2O_2, Fenton, H_2O_2+Cu(II), Ca(ClO)$_2$ and NaClO process are equal to 10, 8, 10, 11.5 and 12, respectively. The amount and rate of cyanide degradation increased at higher pH by all oxidants except Fenton. Based on Fig. 1, with pH value increasing, the cyanide degradation by Fenton decreased from 60 to 2.5%. Whereas for other oxidants by increasing pH, the cyanide removal increased. The findings support that the Fenton process has better efficiency at low pH. On the other hand, cyanide at pH lower than 8 produces HCN - a dangerous gas. As mobility and solubility of toxic elements increased and hydrogen radicals competed with metal ions for cation exchange, thereupon the efficiency decreased. Fenton process with higher degradation efficiencies has been also reported at acidic conditions (pH ≈ 3) for some other contaminants such as citrate, Reactive Black 5 dye, and arsenic compounds [51]. As the amount of generated OH radicals increases at alkaline pH value and by rising pH up to 11, cyanide removal was increased. At pH 11, cyanide is entirely in ionic form, but at pH > 11, because of the competitive absorption between CN^- and HO^-, the cyanide removal rate decreases, hence the maximum cyanide degradation occurs at pH 11. When cyanide is completely oxidized to CO_2 and N_2 (as illustrated in reaction 1), two moles of H^+ are possibly produced when one mole of cyanide was degraded by H_2O_2. Thus, as pH decreases the reaction cannot be favored to produce CO_2 and N_2 as final products.

$$2CN^- + 2H_2O_2 \rightarrow 2CO_2 + N_2 + 4H^+ + 6e^- \qquad (1)$$
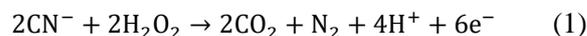
Significant enhancement of H_2O_2 decomposition was observed at pH 11 in the presence of Cu(II) ions. This was possible because Cu(II) ions would consume OH^- to hydroxyl complexes or hydroxide precipitate and accelerate the reactions [25]. The generated H_2O_2 could be decomposed to HO_2^- *via* reaction 2 when the solution pH is higher than 10. HO_2^- anions have good stability, but their oxidation potential is lower than that of H_2O_2 (oxidation potential E = 1.763 V at pH = 0 and E = 0.878 V at pH = 14). Therefore, it is found that the oxidation of cyanide proceeds rather slowly in this system [52].

$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O \qquad (2)$$
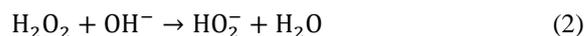
For NaClO and Ca(ClO)$_2$ oxidants, by increasing pH the cyanide removal increased and high degradation occurred at pH 12 and 11.5, respectively. For higher pH values the efficiency severely decreased and this phenomenon refers to the evaporation process. Therefore, the degradation reaction was done at highly alkaline pH. On the other hand, for pH above 12, Cl^- ion consumption increased and consequently, cyanide treatment decreased. At lower pH, as illustrated by reactions 3 and 4, the dominant form of active chlorine is hypochlorous acid ($E_{(HClO/Cl2)}$ = 1.63 V or $E_{(HClO/Cl)}$ = 1.48 V), which exhibits considerably higher oxidation potential than hypochlorite ($E_{(ClO/Cl)}$ = 0.89 V) in alkaline media. In this study, removal of cyanide was performed at the optimal alkaline condition in order to avoid the generation of evaporated HCN. Therefore, the cyanide oxidation process by ClO^- is limited [45]:

$$NaClO + H_2O \rightarrow HClO + Na^+ + OH^- \qquad (3)$$

$$Ca(ClO)_2 + 2H_2O \rightarrow 2HClO + Ca^{2+} + 2OH^- \qquad (4).$$

Effect of oxidant dosage

Different tests were performed to study cyanide oxidation. In these tests, an industrial solution of pH 10 containing 40 mg/L of cyanide was used.
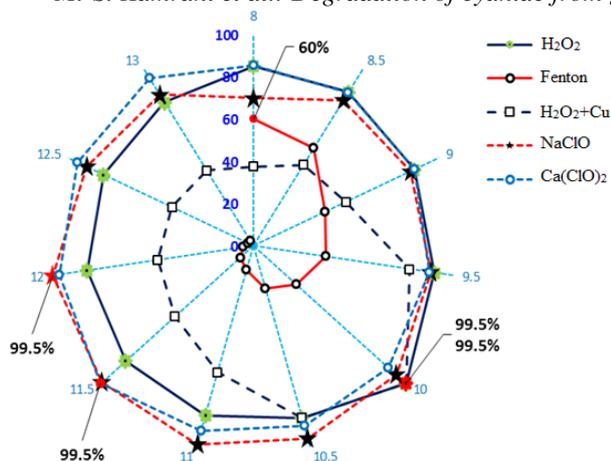
Fig. 1. Effect of different pH on the cyanide removal for five processes

The effect of oxidant dosage on cyanide removal was studied in the presence of different oxidants. The obtained results for oxidants dosage are shown in Fig. 2. The suitable dosages for effective treatments by H_2O_2 (no catalyst), Fenton, H_2O_2+Cu(II), Ca(ClO)$_2$ and NaClO process are 4.78, 1.00, 1.09, 0.90 and 1.19 g/L, respectively. As shown in Fig. 3, the hypochlorites are effective for chemical oxidation, which leads to reduced concentration of cyanide below the permitted level (less than 0.2 mg/L). However, to reach complete cyanide degradation, the amount of calcium hypochlorite used is lower than that of sodium hypochlorite, which is due to the stronger reactivity of calcium than sodium. The increase in other oxidants amounts also has similar results and with the increase in oxidant dosage, the cyanide degradation increases, but it is different for each one. When H_2O_2 was used, the oxidation was less evident due to the lack of a catalyst and almost three times the amount of catalyst that was used to increase the H_2O_2 consumption to cyanide degradation, completely oxidation of cyanide when copper is used as a catalyst is rapidly increased and the amount of hydrogen peroxide is lower. Hydroxyl radicals are devoid of any charge and have a high affinity for electrons, they can quickly strip any chemical of electrons including cyanide thus causing their oxidation. Depending on the amount of used H_2O_2, hydroxyl radicals react with cyanide thus causing its oxidation to form cyanate which further oxidizes to bicarbonate and nitrogen. Reaction stoichiometry is 1:1 when cyanate is formed and it increases further to 1:3 when nitrogen is formed [53]. Besides this decomposition reaction, it has been suggested for the removal of pollutants using different advanced oxidation processes combined with H_2O_2 that the hydroxyl

radicals formed can be scavenged by an excess of H_2O_2 to form much less oxidative H_2O_2 radicals [54]. Due to the fact that the reaction of Fenton was carried out at alkaline pH, the increase in the amount of H_2O_2 has increased the oxidation of cyanide up to 36% and did not show any increase in the amount of H_2O_2 oxidation by adding cyanide. Fe(OH)$_3$ sediment formed and prevented the reaction of free radicals [55]. Oxidant consumption during the process in aqueous solution is higher than the values predicted by stoichiometric number in the concentration. This behavior is probably due to the presence of other species that may also react with oxidation, thus the oxidant consumption was increased [56].

Effect of temperature on cyanide degradation

Temperature is an important parameter for the determination of cyanide oxidation rate. The effect of temperature on cyanide degradation was evaluated by changing the temperature between 20 and 35 °C. As mentioned, free cyanide would volatilize at temperatures slightly above ambient temperatures because its boiling point is 25.6 °C. However, the availability of metals would stabilize cyanide in the metallic complex form and thereby cause its retention in the environment at temperatures far above ambient temperature. As a consequence of reaction 5, the relative abundances of CN and HCN depend on pH.

$$HCN \rightleftharpoons H^+ + CN^- \tag{5}$$

So, the temperature has the most significant effect on the volatilization rate of free cyanide and most metal cyanide complexes were studied. The highest level of toxicity was observed at low pH and high temperature. As shown in Fig. 3, the rate of cyanide degradation increases by increasing temperature for all of the oxidants, which may be explained by the following presumption: for 25 °C in the solutions prepared with pure water CN and HCN are equally abundant at pH 9.2. The pH changes with temperature, increasing to 9.6 as the temperature is lowered to 10 °C and decreasing to 8.9 as the temperature is raised to 40 °C. Ionic strength also affects the abundances of CN$^-$ and HCN, but the effect is relatively small. For ionic strengths like those encountered in actual leach solutions, pH for 25 °C decreases from 9.2 to 9. As explained, a part of cyanide degradation at high temperature is the concern to the cyanide evaporation process.
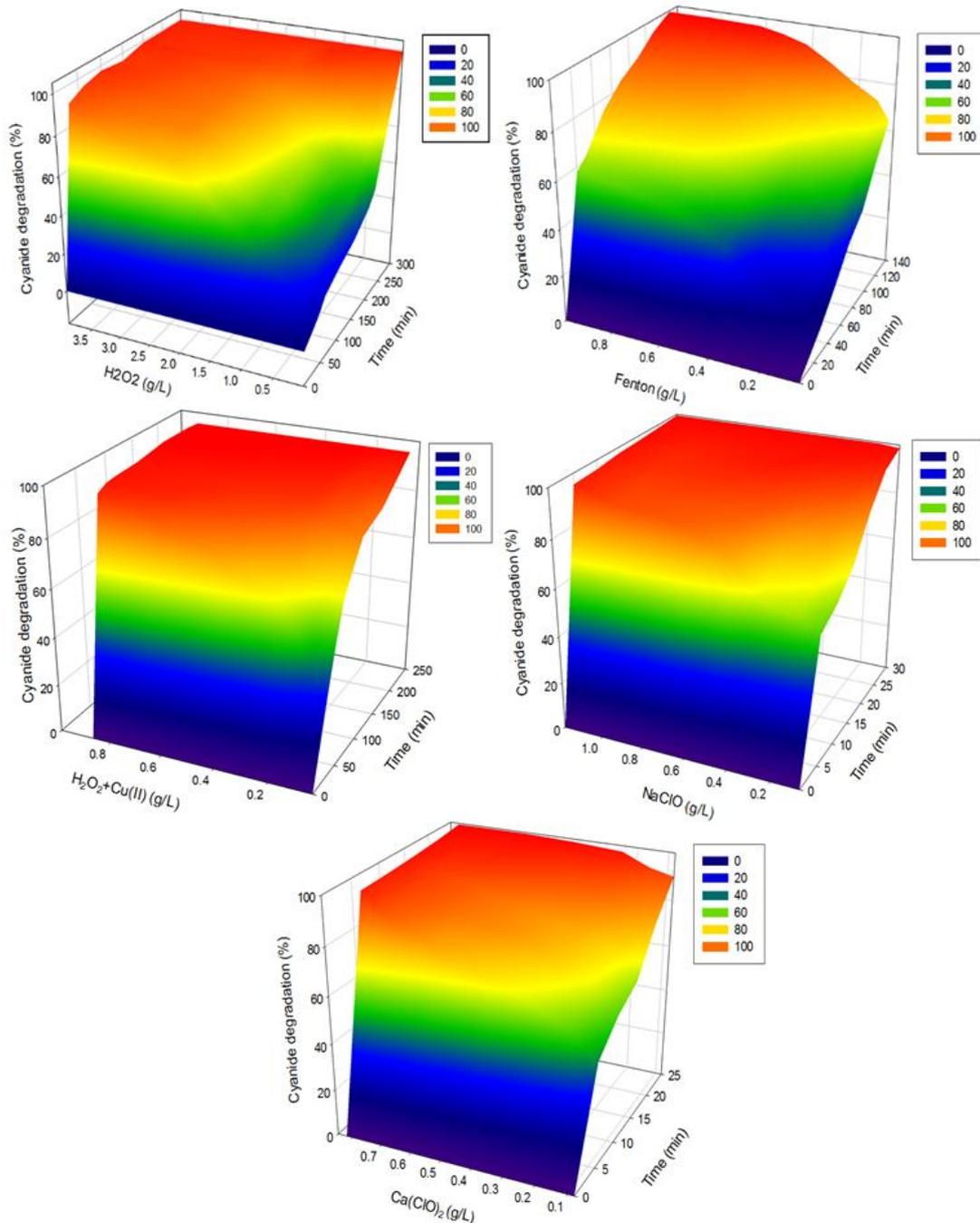
Fig. 2. Effect of oxidant dosage on the cyanide removal using different oxidants

According to Fig. 3, with increasing temperature the cyanide degradation decreases which is the least degradation regarding H_2O_2 (no catalyst). This phenomenon is a concern to cyanide degradation and reaction rate. Also for Fenton the low degradation is observed for wastewater with alkaline pH. Increase in the temperature for alkaline chloride has the strongest impact that has specified complexity. According to reactions 6 and 7, cyanide degradation leads to cyanogen chloride gas that as a mediator or catalyzer can generate Cl⁻ ion which leads to further degradation. On the other hand, the reaction was done in temperature range between 40-50 °C because in this temperature range

O_3Cl^- ion was practically not produced and in this situation chloride anion is dominant.

$$CN^- + Cl_2 \rightarrow CNCl + Cl^- \tag{6}$$

$$CNCl + 2HO^- \rightarrow OCN^- + H_2O + Cl^- \tag{7}$$
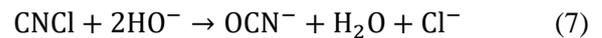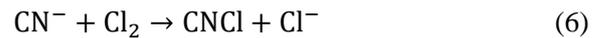
Both the initial rate and ultimate extent of cyanide degradation were generally higher at higher temperatures compared with those found at lower values. The presence of excess catalyst dosage overcomes the negative impacts of lower temperatures.
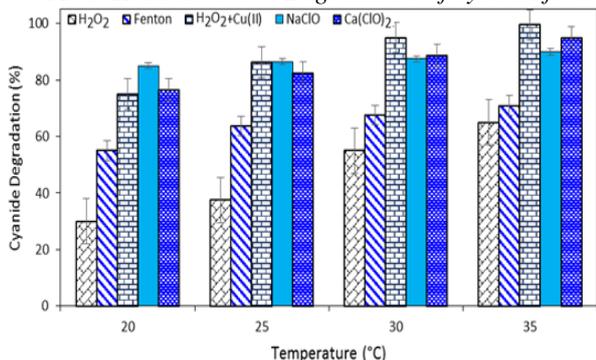
Fig. 3. Effect of temperature on cyanide degradation using different oxidants.

Non-linear kinetic modeling

Chemical kinetics help in identification of the reaction parameters and deal with experimental measurements of the velocities in batch, semi-batch or continuous reactors [57]. The matching of experimental data and the predicted value models were expressed by the correlation coefficients (R^2). For all of the oxidants, based on reaction stoichiometry and using the initial rates from the previous performance to calculate the real, exact and quantitative order of reaction (a) with respect to [CN], according to an empirical equation ([CN]/dt=k[CN]$^\beta$), taking the log(d[CN]/dt) /log[CN] linear representation, gave a slope value of β and values of k and α according to the least squares method that is obtained using the code

logging of the MATLAB program. The reaction rate or velocity (*v*) is defined mathematically as follows [27, 58].

$$v = \frac{d[CN^-]}{dt} = k[CN^-]^\alpha[oxidant]^\beta \qquad (8)$$
$$\beta = \log(d[CN^-]/\log[oxidant] \qquad (9)$$

where [CN$^-$] and [oxidant] are the molar concentrations of the reactants; α and β exponents represent the order of the reaction between cyanide and oxidant, respectively, and k is the reaction rate constant. Sometimes the values for the exponents in the rate expression are equal to the coefficients in the equilibrium equation. The coefficients in the equilibrium equation are a consequence of the reaction stoichiometry. According to Fig. 2, cyanide degradation was studied as a function of time for each oxidant with variables dosage. In Fig. 4, the kinetic plot of cyanide degradation is shown for all oxidants.

Oxidants reaction rate can be determined by plotting log(-d[CN$^-$]/dt) *versus* log[oxidant] as shown in Fig. 4. The obtained results show that R^2 for all oxidants is less than 1. After calculating the velocity and reaction orders, the non-linear kinetic model (Eq. 10) and its parameters (a, b, c and R^2) are listed in Table 2:

$$-\frac{d[CN^-]}{dt} = k[CN^-]^a x[H_2O_2]^b \qquad (10)$$

Table 2. Non-linear kinetic models and its parameters

Oxidant	Parameters			R^2
	k	a	b	
H_2O_2	0.0000918	1.1774	1.1887	0.9724
Fenton	0.1692950	1.1289	0.1599	0.9852
H_2O_2+Cu(II)	0.0036600	1.1165	0.3000	0.9989
Ca(ClO)$_2$	0.0008020	1.1472	0.5017	0.9886
NaClO	0.0274700	1.1329	0.2260	0.9771

A series of experiments were performed to determine the relationship between the rate of reaction and the concentration of reactants. Perfect cyanide degradation by oxidants does not happen in one step but to convert to the fewer toxicity products multi-steps were required.

As explained, cyanide concentration reduction was not equal for oxidants and did not follow a regular trend. This phenomenon was confirmed by different reaction rates. Cyanide degradation reaction orders for all oxidants are non-integer numbers between 1 and 2 (1 < (α+β) < 2). Moreover, the reaction rate constant (k) for H_2O_2 (no catalyst), Fenton, H_2O_2+Cu(II) , Ca(ClO)$_2$ and NaClO oxidants are 0.0000918, 0.01692950, 0.0036600, 0.000802 and 0.0244700 min^{-1},

respectively. So, kinetic rate constants show that the reaction velocity of cyanide degradation is higher for NaClO and Fenton than for others and it is predictable for H_2O_2 less than all oxidants. Fenton and H_2O_2+Cu(II) oxidants in the presence of more free radicals due to the existence of catalysts have a higher velocity than H_2O_2.

In addition, Visual MINTEQ 3.1 software output (NaClO system: HCN$_{(aq)}$ = 0.419 mg/L, ionic strength = 0.0441, CN$^{-1}_{(g)}$ = 99.581%; Ca(ClO)$_2$ system: HCN$_{(aq)}$ = 0.128 mg/L, ionic strength = 0.0662, CN$^{-1}_{(g)}$ = 99.872%) in optimized conditions for cyanide reaction with Ca(ClO)$_2$ and NaClO obtained results show that the Ca(ClO)$_2$ reaction rate should be above NaClO reaction rate.
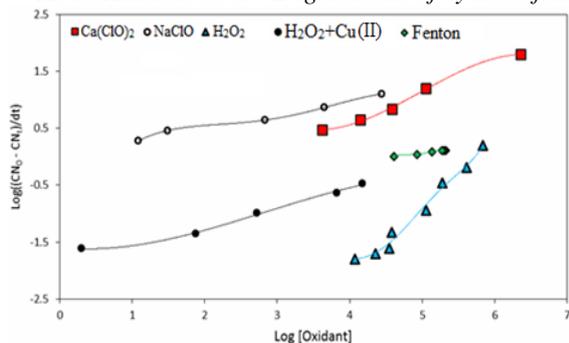
Fig. 4. Kinetic plots of cyanide degradation by various oxidations.

The results of non-linear kinetic modeling show the reverse status. For Ca(ClO)$_2$ and NaClO oxidants comparison is necessary to explain that in the gold processing plant flow sheet a portion of NaClO that was used in the elution stage to separate gold and silver and the reaction velocity is affected by the residual oxidizing agent.

The removal efficiency of the cyanide, calculated by the concentration differences between the initial and final values, was the criterion for process efficiency evaluation. Meanwhile, the absolute rate constant method was employed to evaluate the effect of various parameters on cyanide removal under the condition of constant H_2O_2 concentration, which refers to a pseudo-first-order kinetic equation. For each experiment, the apparent kinetic rate constant (K_{app}) for cyanide removal was derived from the linear representation of $\ln([C_o]/[C_t])$ *versus* time, where, $[C_0]$ and $[C_t]$ are the cyanide initial concentration and at t time, respectively. Figure 5 shows the relationship between Fe(II) and Cu(II) feeding time and the apparent kinetic rate constants for the second step. In the initial step, Fe(II) and Cu(II) dosage was fixed at 150 mg L^{-1}. The feeding time of Fe(II) and Cu(II) had a direct influence on the apparent kinetic rate constant. Firstly, up to 10 min, the corresponding k_{app} slightly increased, but was still somewhat lower than that of the first step, which might be attributed to the free radical scavenging. The further feeding time of Fe(II) and Cu(II) greatly increased the apparent kinetic rate constant and consequently achieved the highest value of 0.40 and 1.14 min^{-1} at 40 and 60 min, respectively. Whereas for Fe(II) the value declined to 0.25 min^{-1} when the feeding time was postponed to 50 min. Thus, the optimum feeding time is 30-40 min for

Fe(II) and 50 min for Cu(II).

Temperature increase leads to an increase in the reaction rate constant and the fraction of molecules that have energy equal to or higher than the activation energy.
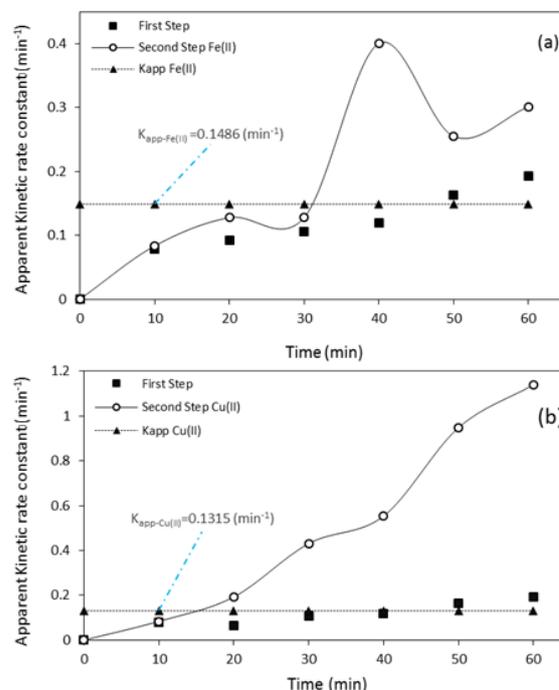
Fig. 5. The relationship between Fe(II) (a) and Cu(II) (b) feeding time and kinetic rate constants.

Figure 6 shows the relationship between ln(k) and 1/T, where k is the rate constant and T is the reaction temperature. A reaction that has large activation energy is slow because only a small fraction of the molecules collide with sufficient energy to reach the transition state. The rate of the reaction increases when the temperature increases as more molecular collisions occur with energy equal to or greater than the activation energy. Also, the more molecules present, the greater is the probability of collision and the faster is the rate. Thus reaction rate increases with the increase in the concentration of reactant molecules. So, the results in Table 3 show that the activation energy of the reaction H_2O_2 was about 13.09 kJ/mol, the activation energy of the reactions where Cu(II) was added was about 8.56 kJ/mol, and the activation energy of the Fenton process was about 10.62 kJ/mol.
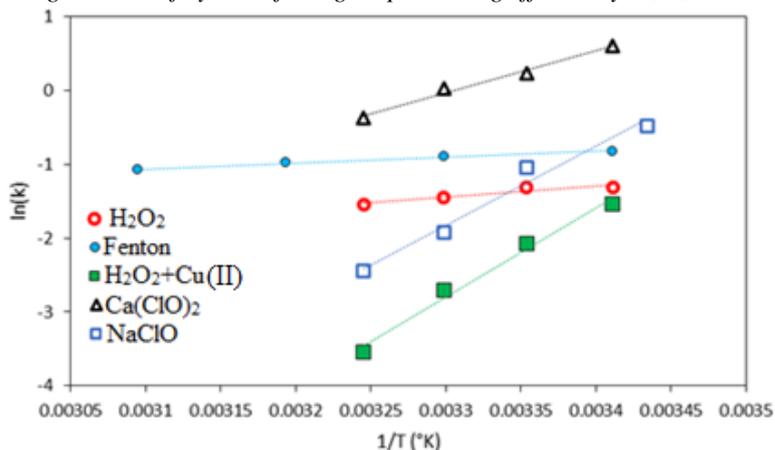
Fig. 6. Kinetic rate *versus* temperature for calculation of oxidation process activation energy.

Table 3. The values of activation energy, kinetic constant rate and correlation coefficient.

Oxidant	Activation energy (kJ/mol)	K $(min^{-1}) \times 10^{-3}$	R^2
H_2O_2	13.09	0.0918	0.9848
Fenton	10.62	16.9295	0.9542
$H_2O_2+Cu(II)$	8.56	3.6600	0.9865
$Ca(ClO)_2$	47.32	0.8202	0.9865
NaClO	94.96	24.4700	0.9824
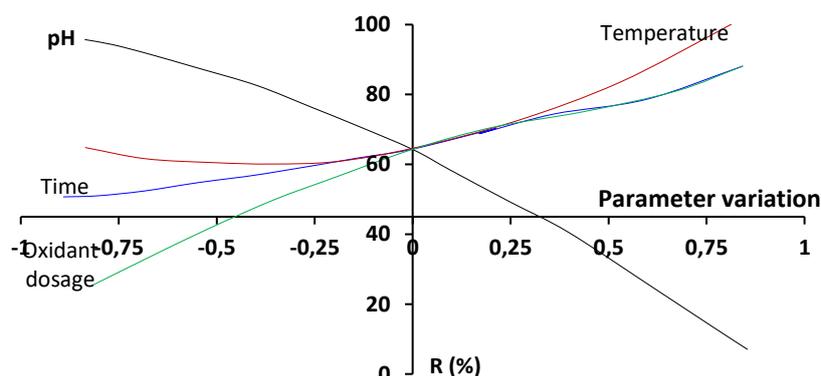
Fig. 7. The effect of influential parameters (pH, temperature, amount of oxidant, time and catalyst dosage) on the removal of cyanide at optimum conditions.

Modeling by response surface method

Response surface method (RSM) is one of the useful designs to fit the empirical models to the investigational data obtained from experimental design [60-63]. RSM contains many types of design two of which are extensively utilized in chemical methods such as advanced oxidation process [62, 64-66]. Design Expert 11 software was employed to obtain the experimental design for determining the interaction between operational independent parameters consisting of pH, time, temperature, catalyst dosage and amount of oxidant. The variation of operational parameters values was based on Table 1. According to the experimental studies, among the five processes, $Ca(ClO)_2$ process was selected as the optimal process and modeled. The effect of the five operational parameters

obtained by RSM is illustrated in Fig. 7. The obtained results show that cyanide degradation has a direct relation with temperature, amount of oxidant and time parameters and has an inverse relation with pH parameter. For calcium hypochlorite oxidant, the optimum conditions are: pH 11.5, time 20-25 min, temperature 35 °C and amount of oxidant 0.4 g/L which resulted in maximum cyanide degradation of 99.5% experimentally which was near to the RSM predicted cyanide degradation of 99.15%.

CONCLUSIONS

In this work, cyanide degradation was done by three oxidants in five processes. Sodium hypochlorite, calcium hypochlorite and hydrogen peroxide without and with Fe(II) and Cu(II) catalyst

were utilized for cyanide removal from gold processing wastewater. Major parameters that may affect the cyanide degradation such as pH, temperature, oxidants dosage and the reaction time were investigated. The maximum cyanide degradation happened at alkaline pH. All of the processes were considered at 20-30 °C. The dosage of different oxidants for the five processes was varied between 0.9-4.87 g/L. Also, non-linear kinetic modeling was done and each process was modeled as a mathematical equation that is flexible to calculate the required oxidant for any cyanide concentration. So, the comparison of kinetic rate constants (k) is as follows: NaClO > Fenton > H_2O_2+Cu(II) > Ca(ClO)$_2$ > H_2O_2. In addition, reaction activation energies for all five oxidants were calculated and the order is: NaCLO > Ca(ClO)$_2$ > H_2O_2 > Fenton > H_2O_2+Cu(II). The cyanide release is an inevitable phenomenon in gold mines and given the environmental regulations and the obligation to reduce the amount of cyanide toxicity before entering the tailing dam, such studies can help in the selection of an oxidizing agent with higher efficiency and lower cost.

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

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