KINETICS OF THE OXIDATION OF FREE AND COPPER CYANIDES IN AQUEOUS SOLUTIONS WITH HYDROGEN PEROXIDE

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Abstract

This paper reports the results of a kinetic study on the oxidation of free cyanide and Cu-cyanide complex ions with H_2O_2. The variables and respective ranges studied were the following:

[CN] total = 10 - 500 mg/l;
pH = 10 - 11;
(H_2O_2/CN) mole ratio = 1 - 3;
(Cu/CN) mole ratio = 0.10 - 0.25.

The results were interpreted by a semi-empirical model that incorporates the useful oxidation reactions and the parallel alkaline decomposition of H_2O_2.

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INTRODUCTION (1,9)

Hydrogen peroxide is becoming the preferred oxidant for the destruction of cyanides in effluent streams. The main reasons for its success are: It is cost efficient, environmentally compatible, stable on storage, and it is simple to dose in the detoxification processes.

Oxidation of aqueous cyanides with hydrogen peroxide yields cyanate ions, which in their turn hydrolyse producing carbonate and ammonium ions, according to the following equation:

$$CN^- + H_2O_2 + H_2O = CNO^- + 2\,H_2O = CO_3^{2-} + NH_4^+$$

If the cyanide is acting as a complexant of metal cations, the oxidation of the ligand will gradually release the metal, leaving it available for hydrolysis, and - given the adequate pH range - it will eventually lead to precipitation of the metal hydroxide, according to the following equations:

$$M(CN)_n^{2-} + n\,H_2O_2 = n\,CNO^- + M^{2+} + n\,H_2O$$

$$n\,CNO^- + M^{2+} + (2n+2)\,H_2O = n\,CO_3^{2-} + n\,NH_4^+ + M(OH)_2\,(s) + 2\,H^+$$

Iron is an exception to this reaction. Its cyano-complexes are very stable, and difficult to break by oxidation. Nevertheless, these complexes may be removed from the effluent by precipitating the complex $Fe(CN)_6^{4-}$ with transition metal cations (M^{2+}) such as Cu^{2+}, Zn^{2+} and Fe^{2+}, forming $M_2(Fe(CN)_6)$ (s).

Copper is a common contaminant in cyanide containing effluents - either derived from gold extraction operations (in low concentrations) or plating shops. Cyanide complexes copper in the cuprous oxidation state, which adds to an extra demand of peroxide in the detoxification process for copper oxidation.

Due to the frequency of cases of treatments of these types of copper-cyanide-containing effluents, it was decided to study the kinetics of that detoxification reaction with a view to learning more about this process, and to developing a model that could be used as a helping tool for the design and optimisation of treatment plants.

EXPERIMENTAL

The experiments were conducted following a sequence of two factorial designs. The variables listed bellow were studied within their respective corresponding ranges of variation, and their effects on the kinetics measured by the half-life time of free [CN], as CN^- ions disappear with time.

pH = 10 - 11
(H_2O_2/CN) initial mole ratio = 1 - 3
initial [CN-] = 10 - 100 - 500 mg/l
(Cu/CN) initial mole ratio = 0.10 - 0.25

Temperature was maintained fixed at 25 °C.

The experiments were conducted in a 5 litre open glass reactor equipped with a stirrer and a pH electrode. The effluent solutions were made up from KCN, CuCN and distilled water - and were prepared immediately before each experiment. Hydrogen peroxide was added as a 5 % wt solution.

The reaction started with the instant addition of the required amount of H_2O_2 into the cyanide solution. A series of samples were then withdrawn at intervals, and immediately conditioned for analyses of CN, and Cu.

The time length of each experiment was 4 hours. Cu was analysed by atomic absorption, and CN was determined as free CN by titration with silver nitrate. Free [CN] was chosen as a control variable rather than total [CN] as it is determined by a much simpler analytical routine frequently adopted in the industrial practice.

RESULTS

Table 1 reports the results of the factorial experiments. Tables 2, 3 and 4 show the results of the factorial analyses that calculated the effects and statistical significance of the considered variables and their 2-factor interactions upon the free cyanide concentration half-life time in the reaction divided by initial total [CN]. The complete results of the kinetic experiments are available elsewhere (14).

The variable codes (A, B, C, D) and their corresponding variation ranges were the following:

A - initial total [CN-] = 10 - 100 mg/l (Table 2)
= 100 - 500 mg/l (Table 3)
B - pH = 10 - 11
C - initial (H_2O_2/CN) mole ratio = 1 - 3
D - initial (Cu/CN) mole ratio = 0.10 - 0.25

The analysis of variance was done by dividing each effect by an estimate of error obtained by polling the 3 and 4 factor interactions, and comparing that ratio with the 90% probability value in the F distribution.

The analysis in Table 2 did not reveal any significant effects. The oxidations done with initial total [CN] = 10 mg/l were very slow, and were more prone to inaccuracies in the measurement of [CN] half-life than the runs done at higher initial [CN] values. This problem was particularly aggravated at pH=11, because of the more favourable condition for H2O2 decomposition. Thus it was decided to split the factorial design reported in Table 2 in two sub-sets (at pH=10, and pH=11), and conduct two other analyses of variance.

Table 1 - Free Cyanide Half-life Time ($\tau_{1/2}$) Data for Oxidation of Copper Cyanides with H_2O_2

A [CN] (mg/l)	B pH	C (H_2O_2/CN) (mole/mole)	D (Cu/CN) (mole/mole)	$\tau_{1/2}$ (min)	$\tau_{1/2}$ / [CN] (min/mg/l)
100	10	1	0.25	38	0.38
100	10	3	0.25	19.4	0.19
100	11	1	0.25	62.3	0.62
100	11	3	0.25	24	0.24
100	10	1	0.1	205.1	2.05
100	10	3	0.1	78.2	0.78
100	11	1	0.1	144.4	1.44
100	11	3	0.1	106	1.06
500	10	1	0.1	104.5	0.21
500	10	1	0.25	172	0.34
500	10	3	0.1	148.8	0.3
500	11	1	0.1	15.2	0.03
500	10	3	0.25	19.6	0.04
500	11	1	0.25	4.4	0.01
500	11	3	0.1	18.4	0.04
500	11	3	0.25	4.4	0.01
10	10	1	0.1	182	18.2
10	10	1	0.25	70.4	7
10	10	3	0.1	213.8	21.4
10	11	1	0.1	5,000	500
10	11	3	0.1	310	31
10	11	1	0.25	845	84.5
10	10	3	0.25	88.6	8.9
10	11	3	0.25	181.4	18.1

Table 2 - Analysis of variance of factorial experiments conducted with solutions containing copper cyanide with total [CN] = 10-100 mg/l.

Factorial Treatment	Effect	Mean Square	F - Snedecor Probability (%)
A ([CN])	-85.3	2.47	82.3
B (pH)	72.3	1.77	75.9
C (H_2O_2/CN)	-66.6	1.5	72.5
D (Cu/CN)	-57	1.1	65.8
AB	-72.3	1.77	75.9
AC	66	1.48	72.2
BC	-67.5	1.54	73.1
AD	56	1.06	65
BD	-50.5	0.87	60.5
CD	50.3	0.86	60.3

At pH = 11, the magnitude of error (2 and 3-factor interactions polled) was similar to that of the main effects of the variables, so no significant effects were revealed.

At pH = 10, however (Table 3), the effects of initial [CN] and (Cu/CN) were found to be significant - whilst (H_2O_2/CN) was not.

Table 3: Analysis of variance of factorial experiments conducted with solutions containing copper cyanide with total [CN] = 10-100 mg/l at pH = 10.

Factorial Treatment	Effect	Mean Square	F - Snedecor Probability (%)
A ([CN])	-13.02	21.36	99 (sig)
B (H_2O_2/CN)	0.91	0.1	23.7
C (Cu/CN)	-6.4	5.3	91.7 (sig)

The analysis of variance of the factorial experiments conducted in the higher [CN] range (100 - 500 mg/l), shown in Table 4, revealed that [CN], (H_2O_2/CN), and (Cu/CN) were significant, whilst pH was not.

Table 4 - Analysis of variance of factorial experiments conducted with solutions containing copper cyanide with total [CN] = 100-500 mg/l.

Factorial Treatment	Effect	Mean Square	F - Snedecor Probability (%)
A ([CN])	-0.72	31.32	99.7 (sig)
B (pH)	-0.11	0.66	54.7
C (H_2O_2/CN)	-0.3	5.49	93.4 (sig)
D (Cu/CN)	-0.51	15.6	98.9 (sig)
AB	-0.1	0.54	50.5
AC	0.25	3.82	89.2
BC	0.12	0.79	58.6
AD	0.47	12.98	98.5 (sig)
BD	0.09	0.46	47.2
CD	0.09	0.43	46.1

Effect of initial total [CN]

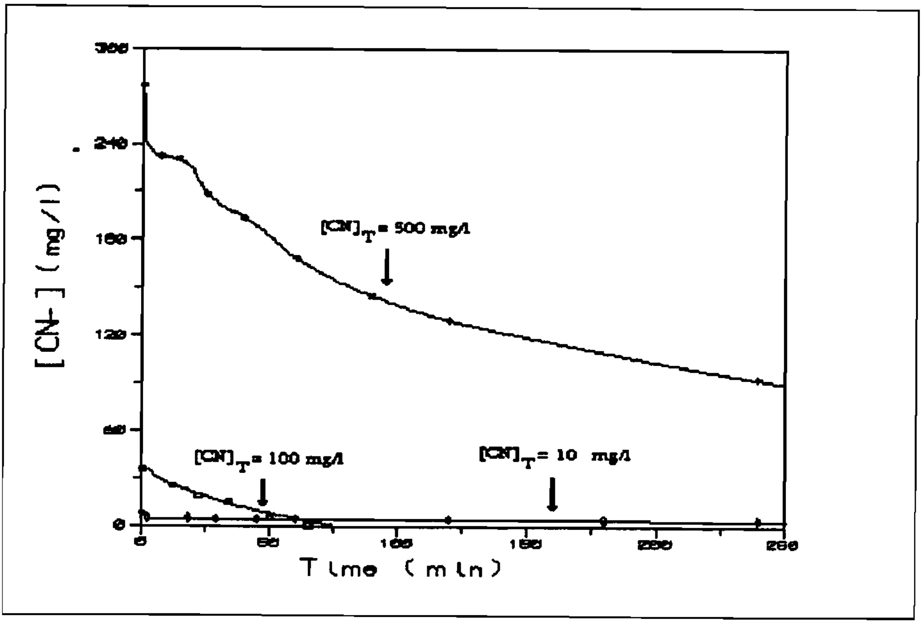

Figure 1: Illustration of the effect of initial [CN], pH=10, (H_2O_2/CN)=3, (Cu/CN)=0.25

Figure 1 illustrates the effect of initial [CN] on the reaction rate. In all set of conditions - even in the low [CN] values = 10 mg/l at pH = 11, in which the error was large - there was a definite positive trend in reaction rate with respect to [CN]. The modelling exercise presented ahead, assumed a first order dependence of the rate with respect to [CN], but that was not really possible to prove.

Effect of pH

The effect of pH was found to be non-significant (at a probability of 90%). However, this conclusion has to be taken with due care, as the variation range was relatively short (pH = 10 - 11), and the experimental error was not really small. Figure 2 illustrates this point.

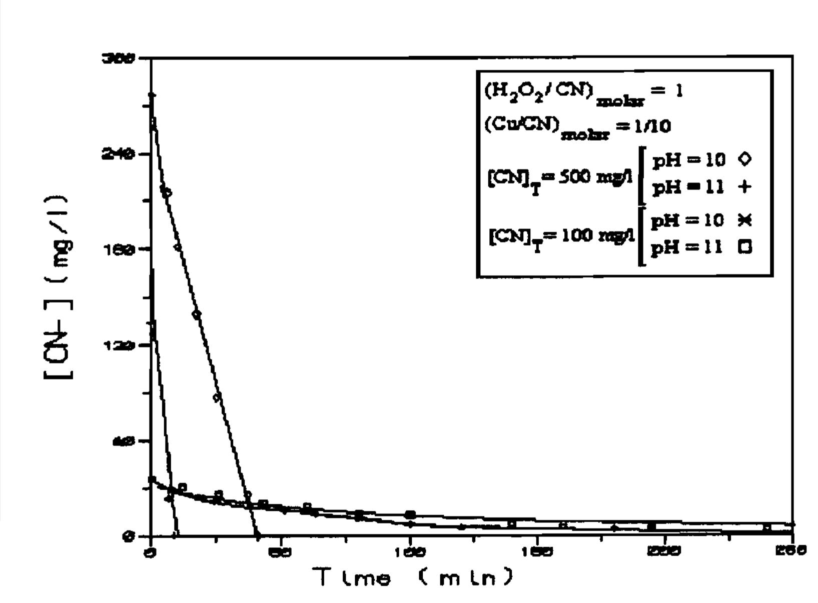

Figure 2: Illustration of the effect of pH

Effect of (H_2O_2/CN) mole ratio

The effect of the (H_2O_2/CN) mole ratio (or stoichiometric excess) encompassed the effect of $[H_2O_2]$ - the real kinetic variable. It was found significant, and again, although the model presented ahead supposed a first order dependence of the rate on $[H_2O_2]$, that could not be proved. Figure 3 illustrates this effect.

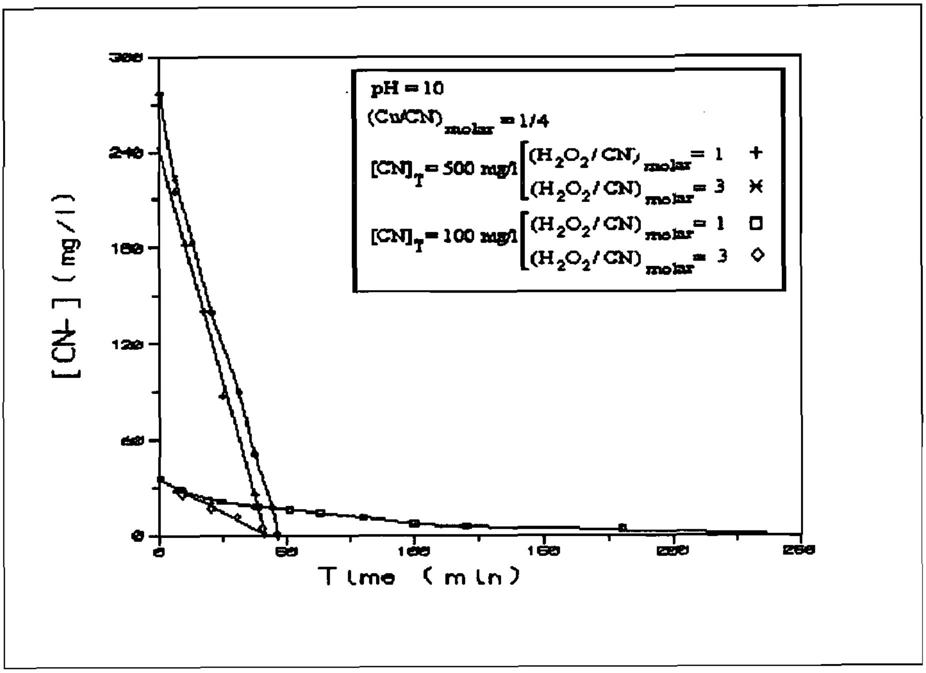

Figure 3: Illustration of the effect of (H_2O_2/CN) mole ratio

Effect of (Cu/CN) mole ratio

This effect is illustrated in Figure 4. It encompasses the effect of [Cu], the actual kinetic variable, and was found to be significant. Cu ions are known aqueous oxidation catalysts. It is possible that the complexed Cu+ ions play a catalytic role in the oxidation process. As these ions are released from the CN ligand, and oxidised, they surely act as catalysts.

KINETIC MODELLING

The kinetic results were also examined at the light of a mechanism involving the following steps:

Cu/CN complex dissociation:

$$Cu(CN)_4^{3-} = Cu(CN)_3^{2-} + CN^-$$

$$Cu(CN)_3^{2-} = Cu(CN)_2^- + CN^-$$

$$Cu(CN)_2^- = Cu^+ + CN^-$$

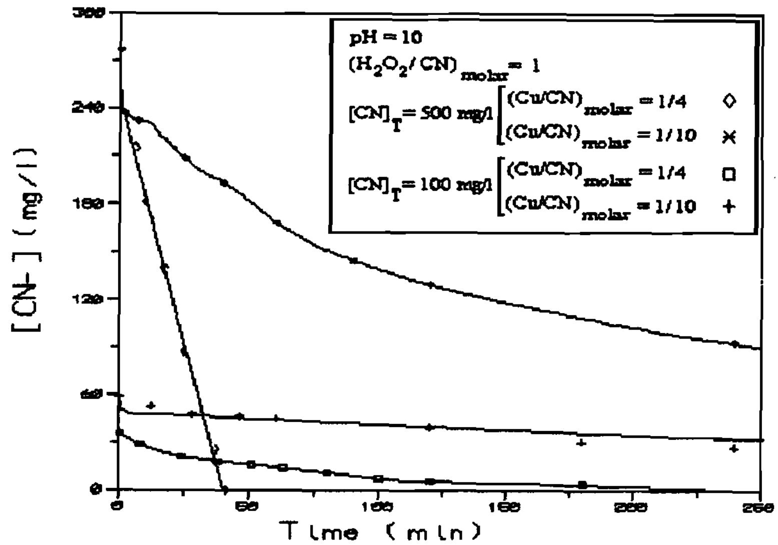

Figure 4: Illustration of the effect of the (Cu/CN) mole ratio

Cyanide oxidation:

$$CN^- + H_2O_2 = CNO^- + H_2O$$

with its corresponding rate equation: $- d[CN^-]/dt = k_1 [CN^-][H_2O_2]$

H_2O_2 alkaline decomposition (10-13):

$$2 H_2O_2 = H_2O_2 + HO_2^- + H^+ = 2 H_2O + O_2$$

with its corresponding rate equation:

$$-d[H_2O_2]/dt = k_2[H_2O_2]^2 + (k_3-k_2) [H_2O_2][HO_2^-][H^+]$$

The attempt to model the kinetics based on that simplified mechanism was based on a successful model developed in an earlier work for the oxidation of free cyanides - catalysed with copper ions.

The semi-empirical model derived from the combination of those two rate equations and the adjustment of the kinetic data is presented below - the development of this model is fully described in the same work (14).

$$[CN-] = (A\Delta t - B) + C \exp(-a\Delta t) + (D\Delta t^{b} \exp(-T^{2}) + E\Delta t) \exp(-c\Delta t)$$

where Δt is the time elapsed from the beginning of the reaction, and A, B, C, D, E, a, b, c, and T are fitted constants dependant on each set of reaction conditions. The fact that it was not possible to express these constants as functions of the process variables indicate that the proposed model may not be significantly better than a purely empirical model such as a polynomial equation.

CONCLUSIONS AND PROCESS CONSIDERATIONS

The results of this study indicated that the oxidation reaction of Cu-CN solutions with hydrogen peroxide can be operated at a flexible range of conditions, leading to a wide range of possible reaction times.

It was possible to oxidise CN in solutions containing total [CN] in the range 100 - 500 mg/l, and (Cu/CN) mole ratio = 0.10, in less than 1 hour, using a stoichiometric excess of H_2O_2 of 200 %. On the other hand, in none of the experiments done at total [CN] = 10 mg/l, it was possible to achieve total oxidation - the conversion levels obtained after 4 hours of reaction achieved only 50 - 60 %.

The effect of pH on the kinetics was not found significant in the range pH = 10 - 11. However, it is known that the higher the pH, the faster the parallel decomposition of H_2O_2 will be. Thus, if given the option, it is best to operate on the lower pH setting.

The absolute amount of copper cyanides in solution is a significant factor affecting the oxidation kinetics, disguised in the (Cu/CN) mole ratio. Thus, solutions having low [CN] levels, even at high (Cu/CN), can be difficult to oxidise, making it necessary to employ larger excesses of H_2O_2 or much longer reaction times.

When the effluent to be treated has a high (>> 10 mg/l) initial [CN], the economically recommended way to treat it will be through the combination of a first oxidation step at stoichiometric level of (H_2O_2/CN) aiming to yield a solution with about [CN] = 10 mg/l, followed by a second step that will demand a higher excess of H_2O_2, but that will be related to a low [CN], so the absolute consumption of H_2O_2 will not be so large.

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