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Kinetics and pathways of cyanide degradation at

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1   **Abstract**

2   The degradation of cyanide was performed in a 1-L semi-batch reactor at temperatures between

3   393 and 473 K and at total pressures in the range of 2.0 - 8.0 MPa. The initial pH of the solution

4   was set at 11, whereas initial concentrations ranged from 3.85 to 25 mM, which resemble the

5   typical concentrations of cyanide-containing wastewater. The change with time of cyanide

6   concentration, intermediates and final products was analyzed in order to elucidate the reaction

7   pathways. The experimental results suggest two parallel pathways of alkaline hydrolysis for the

8   degradation of the pollutant. Formate and ammonia were identified as the final reaction products

9   for one of the pathways, whereas carbon dioxide, nitrogen and hydrogen were considered to be

10   the final products for the other one. The degradation reaction results were fitted to first-order

11   kinetic equations with respect to cyanide, giving respectively activation energies of 108.2±3.3

12   and 77.6±3.0 kJ/mol. Consequently, the formation of formate and ammonia is favored at high

13   temperatures, whereas low temperatures favored the pathway leading to the formation of carbon

14   dioxide and nitrogen.

Introduction

Cyanide species (free cyanide, metal-complex cyanides and thiocyanate) are considered as hazardous water pollutants. These compounds are commonly found in effluents from various industries, such as metal cleaning, electroplating, metal processing, petroleum refining, the automobile industry, steel tempering, mining, photography, pharmaceuticals, coke, ore leaching, electronics, plastics and even some food industries[1-3].

The total cyanide content in most of these wastewaters is between 0.01 and 10 mg/L. However, cyanide concentrations up to 10 mg/L have been found in residual streams from blast furnaces, bright dip processes, the chemical industry and gold ore extraction. Likewise, cyanide concentrations higher than 1000 mg/L have been found in some aqueous wastes from coke plants and electroplating operations[2].

All forms of cyanide can be toxic at high levels, but hydrogen cyanide is the deadliest form of these toxins. At short-term exposure, cyanide causes rapid breathing, tremors and other neurological effects, and long-term exposure to cyanide causes weight loss, thyroid effects, nerve damage and even death. Skin contact with cyanide-containing liquids may produce irritation and sores[2]. Aquatic organisms, especially fish and aquatic invertebrates, are very sensitive to cyanide exposure. In fact, concentrations of cyanide between 20-76 µg/L cause the death of many species[4].

To protect the environment and water resources, cyanide-containing wastewaters must be treated before discharge into the environment. Different techniques have been proposed for the treatment of cyanide-contaminated effluents. The most commonly adopted method is the alkaline-chlorination-oxidation process, although it is relatively expensive due to the quantity of chlorine required. Besides, this process produces sludge, which requires licensed disposal[2]. Biodegradation methods, both bacterial and fungal, have also been employed in the treatment of this type of effluent[5,6]. Nevertheless, the existence of co-contaminants in these aqueous wastes

1   can cause inhibitory effects on the biodegradation process[2]. As a consequence, other treatments

2   have been studied, such as adsorption on activated carbon and novel adsorbents[7], chemical

3   oxidation[8], electrochemical oxidation[9], copper-catalyzed hydrogen peroxide oxidation[10],

4   ozonation[11], photocatalysis using Ti as catalyst[12] and gas membrane separation[13].

5   It has been proved that wet oxidation is an adequate technology for the treatment of

6   wastewaters containing various cyanide species, i.e. thiocyanate[14,15], metal-complex cyanide[16,17]

7   and acrylic acid[18] and it seems an attractive method for the treatment of effluents that contain

8   free cyanide along with these or other pollutants (for example phenolic compounds). In this

9   process organic and inorganic compounds of the liquid phase are oxidized under high

10   temperature (453-588 K) and pressure (2-15 MPa) conditions using a gaseous source of oxygen.

11   Despite the good results that have been obtained with cyanides in previous studies[14,15], to the

12   best of our knowledge, there is very little work that has focused on the study of the wet oxidation

13   of free cyanide. In these studies, the effect of several operating variables (pressure, temperature,

14   pH and initial concentration) over the rate and the degree of degradation was analyzed[19,20].

15   However, in order to understand the scope of this technique in the treatment of this kind of

16   effluent, it is also important to analyze the reaction products at different operating conditions and

17   study in depth the mechanistic pathways.

18   As a consequence, the general aim of the present work was to study thoroughly the kinetics

19   and pathways of the degradation of cyanide. The specific objectives were to determine the final

20   reaction products and the possible intermediates in order to propose a complete reaction

21   pathway. The effect of the changing the variables that comprise the operating conditions, such as

22   pressure, reaction temperature and initial concentration was analyzed in order to establish their

23   influence on the kinetics of the process and the distribution of reaction products and to provide

24   reliable kinetic data for the development of the pathway here proposed.

1   **Experimental Section**

2   *Apparatus and procedure*

3   Experiments were carried out in a 1-L capacity semi-batch reactor (Parr T316SS) equipped

4   with two six bladed magnetically driven turbine agitators. The reactor was preceded by a 2-L

5   stainless steel water reservoir. The loaded volume in each vessel was about 70% of the total in

6   order to ensure safety conditions. The equipment was charged with water, pressurized and

7   heated up to the desired working conditions. The stirrer speed was adjusted to 500 rpm for all the

8   experiments. The pH of the water was previously adjusted to a suitable value by adding NaOH,

9   so that after the addition of the cyanide solution the medium had the desired pH value, (pH=11

10   in all cases). The operating pressure was provided by bottled compressed oxygen, the oxygen

11   flow rate being adjusted to 2.33×10^{-5} m^3/s, and controlled by an electronic mass flow controller

12   (Brooks). The pressure was kept constant by means of a back pressure controller placed at the

13   end of the gas line. The oxygen was bubbled through the water reservoir in order to become

14   saturated with water and then it was sparged into the reaction vessel. Once the equipment was

15   pressurized and heated to the desired conditions, 11 ml of a concentrated cyanide solution

16   (sodium cyanide) was injected into the reactor. The concentration of this solution was calculated

17   to give the desired final concentration of cyanide inside the reactor (in most cases 3.85 mM).

18   During the preparation of this solution, it was necessary to add 2 ml of 10 M NaOH per 100 ml

19   of cyanide solution, in order to prevent the formation of hydrocyanic acid. The injection time

20   was taken as zero-time for the reaction. A valve and a coil fitted to the top of the vessel allowed

21   the withdrawal of samples during the reaction. Reaction temperature and pressure were

22   maintained constant during the experiments by a proportional integral differential (PID)

23   controller. Three bubblers filled with a concentrated sulfuric acid solution and two bubblers

24   filled with a concentrated sodium hydroxide solution were installed at the end of the gas line

25   with the purpose of absorbing ammonia and/or hydrocyanic acid, if it was formed. The gas

1   outflow was dehumidified by means of a silica gel filter and afterwards it was conducted to the

2   hydrogen gas detector. All experiments were performed in triplicate as separate, independent

3   experiments.

4   *Analytical methods*

5   The concentration of cyanide was determined potentiometrically using a cyanide ion-selective

6   electrode (ISE Crison 9653) in conjunction with a double-junction reference electrode (Crison

7   5044) and an ISE-meter capable of being calibrated directly in terms of cyanide concentration

8   (Crison pH & Ion-Meter GLP 22). The concentrations of cyanate (CNO^-), formate ($HCOO^-$),

9   nitrite (NO_2^-) and nitrate (NO_3^-) were monitored by means of an ion exchange chromatograph

10   (Dionex DX-120 Ion Chromatograph) and a suppressed conductivity detector (ASRS-ULTRA

11   Autosuppresion Recycle Mode). The eluent used was a solution of 1.8 mM Na_2CO_3 and 1.7 mM

12   $NaHCO_3$, with a flow rate of 1.07 ml/min; the precolumn was IonPac® AG4A-SC (4 x 50 mm),

13   and the column was IonPac® AS4A-SC (4 x 250 mm). Total carbon (TC), inorganic carbon (IC)

14   and total organic carbon (TOC) were estimated using a TOC analyzer (Shimadzu TOC-V$_{CSH}$).

15   The concentration of ammonia was measured using the Nessler method[21] and the pH was

16   measured by a selective electrode (pH Meter JENWAY 3510). All analytical measurements

17   were done at least in triplicate, and the standard deviation was found to be below 5 % in all

18   cases. The presence of hydrogen in the gas outflow was identified by means of a portable gas

19   detector (Gasman Crowcon detection) situated at the end of the gas line.

20   **Results and discussion**

21   *Degradation of cyanide and reaction products*

22   Figure 1a shows the change with time of the molar concentration of cyanide and the reaction

23   products obtained (ammonia and formate) during the wet oxidation of this pollutant under high

24   temperature and pressure conditions (T=453 K, P=8.0 MPa).

1   FIGURE 1

2   On viewing the results, it can be observed that the initial pH decreased slightly as the reaction

3   proceeded, although at all times the value remained within the 11.03 to 11.28 range. The same

4   behavior was observed in all runs. The concentration of cyanide decreases rapidly during the

5   first minutes of reaction, reaching a conversion greater than 99% in around 20 minutes. This

6   proved that wet oxidation is an effective method for the treatment of wastewaters contaminated

7   with cyanides. Reaction times and conversion values are in agreement with those obtained by

8   Mishra and Joshi[20] during the wet oxidation of 115.4 mM cyanide performed at 453 K and 0.3

9   MPa of oxygen partial pressure. It should be noted that the evolution of the molar concentration

10   of ammonia and formate was practically identical. The final conversion of cyanide to ammonia

11   and formate was found to be approximately 60% in both cases (see data in Figure 1a).

12   *Elemental balance and analysis of the pathways*

13   Despite being a common pollutant in some industrial wastewaters, the degradation of cyanide

14   (CN^-) in the presence of oxygen using severe conditions of temperature and pressure has been

15   little studied. Ammonia (NH_3) and formate ($HCOO^-$) have been reported as the only reaction

16   products of both the oxidative and hydrolytic routes[19,20,22].

17   In order to study the pathway in depth, the evolution of the reaction products during the

18   degradation of cyanide was analyzed by using elemental balances. In Figure 2a, the total initial

19   amount of nitrogen (dotted line) is compared with the sum of nitrogen as CN^- and nitrogen as

20   NH_3. Results showed that the amount of ammonia formed was 60% of the possible maximum,

21   considering the amount of cyanide degraded (Figure 2a).

22   Ammonia loss from the basic medium due to desorption (pK_a=9.25 at 298 K) was determined

23   by placing three bubblers, filled with a concentrated acid solution, at the end of the gas line. The

24   amount of ammonia retained in the bubblers was very small (being practically negligible in the

1   final bubbler), approximately 6% of initial nitrogen. Therefore, this phenomenon was

2   insufficient to explain the difference between the cyanide that was degraded and the ammonia

3   measured in the reaction medium.

4   In an additional experiment on the wet oxidation of ammonia (initial concentration of 5.56

5   mM; 423 K; 8.0 MP and pH=11), it was proved that the ammonia concentration remained

6   approximately constant throughout the experiment. Thus, the degradation of ammonia to other

7   products under the conditions employed was rejected. This is in accordance with other research

8   that reported that ammonia is a compound which resists oxidation and which requires the use of

9   catalysts to activate the oxidative process[23-25]. Taking into account that the desorption of

10   ammonia as the cause of product loss had been ruled out and that once ammonia is formed it

11   remains as ammonia in the medium, the formation of other nitrogen compounds is expected.

12   Therefore, tests were carried out to detect the presence of nitrites (NO_2^-) and nitrates (NO_3^-) in

13   samples withdrawn at different reaction times, but these compounds were found to be below

14   detection level in all cases (detection limits: 5.4×10^{-4} mM for nitrite and 7.3×10^{-4} mM for

15   nitrate).

16   In the same manner as with the nitrogen, the comparison between the initial amount of carbon

17   and the sum of carbon as CN^- and carbon as $HCOO^-$ was made by means of a carbon elemental

18   balance (Figure 2b). Again, the amount of cyanide that disappeared did not coincide with the

19   amount of formate that was obtained, which in this case was shown to be 62% of the expected

20   formate (if all cyanide was converted to formate). TOC was determined in samples taken at

21   different reaction times and it was observed that the amount of carbon due to cyanide and

22   formate is practically equal to the TOC value. Hence, the existence of other organic compounds

23   in the medium was excluded.

24   In an additional experiment investigating the wet oxidation of formate (initial concentration

25   of 1.33 mM; 453 K; 8.0 MPa and pH=11), it was proved that the concentration of formate

1   remained approximately constant throughout the experiment (Figure S1). This is in agreement

2   with the results reported by Shende and Levec[26], in which formate was considered a refractory

3   compound. Thus, it was confirmed that the formate formed during the process remained in the

4   medium as a final product.

5   Considering all the results described above, it is considered that the degradation of cyanide

6   under the experimental conditions employed here took place following two different pathways,

7   one of them giving ammonia and formate as final products, and the other resulting in the

8   formation of nitrogen (N_2) and carbon dioxide (CO_2). Most of the nitrogen and carbon dioxide

9   formed would be drawn off by the gas stream where they would be present in low concentration.

10 N_2 and CO_2 have also been proposed as final reaction products during the degradation of cyanide

11 by means of different treatment techniques including both oxidation and adsorption together

12 with reaction[27-30].

13 Theoretical evolution of these two species, shown in Figure 2a and 2b, was determined

14 employing the following equations:

$$N_{2,t} = [CN_0^- - (CN_t^- - NH_{4,t}^+)]/2 \qquad (1)$$

$$CO_{2,t} = [CN_0^- - (CN_t^- - HCOO_t^-)] \qquad (2)$$

17 It can be observed that the evolution of the amount of N as N_2 coincided with the evolution of

18 the amount of C as CO_2. This agrees with the consideration of both products being formed by the

19 same pathway.

20 Moreover, the evolution of molar concentrations of ammonia and formate was practically

21 identical as mentioned above (Figure 1a), indicating that both products were also obtained by the

22 same degradative pathway.

23   FIGURE 2

1   In order to know the role played by oxygen during the degradation of cyanide at high

2   temperature and pressure, the process was performed in the absence of oxygen at the same

3   conditions (453 K, 8.0 MPa and pH=11). The degradation of cyanide in absence of oxygen

4   (employing nitrogen as inert gas) is shown in Figure 1b. Considering the experimental errors,

5   this degradation was similar to that obtained in the presence of oxygen (Figure 1a). This

6   indicates that cyanide degradation took place mainly by hydrolysis and not by oxidation.

7   Taking into account all the abovementioned considerations, it has been proposed that the

8   degradation of cyanide occurs by two parallel pathways of alkaline hydrolysis.

9    $$CN^- + 3H_2O \rightarrow CO_2 + \frac{1}{2}N_2 + \frac{5}{2}H_2 + OH^- \qquad (3)$$

10   $$CN^- + 2H_2O \rightarrow NH_3 + HCOO^- \qquad (4)$$
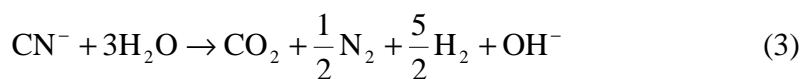
11   The first reaction (equation 3) was supported by the detection of hydrogen in the gas outflow.

12   The presence of hydrogen was qualitatively determined, using a hydrogen gas detector situated

13   at the end of the gas line (the value of hydrogen concentration remained below 7.5 mM at all

14   times as shown in Figure S2 and S3). The pathway suggested for this reaction begins with the

15   partial hydrolysis of cyanide to cyanate, this being the main reaction intermediate. Afterwards,

16   cyanate readily reacts, yielding carbon dioxide, nitrogen and hydrogen as final products[31,32]. The

17   presence of cyanate was tested at different reaction times but this compound was not found to be

18   present at any moment, as a consequence of its instability in the aqueous solution because of the

19   severe operating conditions employed. In order to prove this, additional experiments showed that

20   cyanate was totally degraded in a few minutes when it was treated by wet oxidation. The kinetic

21   constant for cyanate degradation, $(1.65\pm0.02)\times10^{-2}$ s^{-1}, was much higher than kinetic constant for

22   cyanide degradation as equation 3, $(4.37\pm0.03)\times10^{-4}$ s^{-1}; (Figure S4). Besides, when cyanate

23   concentration was calculated theoretically for different reaction times (in basis of the kinetic

1   constant obtained from the data of the Figure S4) very low values were obtained throughout the

2   experiment (Figure S7). In these runs, formate and ammonia were found as final products, but

3   elemental balances for carbon and nitrogen showed that the amount of cyanate degraded did not

4   correspond to the amount of ammonia and formate obtained (Figure S5). As NO_2^- and NO_3^- were

5   not found in any of the samples and the carbon measured as TOC coincided with the final

6   concentration of formate, the existence of other organic compounds was rejected (Figure S5b).

7   Considering these results, the formation of other products such as CO_2 and N_2 is expected (H_2

8   was also experimentally detected). The fact that cyanate wet oxidation led to the formation of

9   ammonia and formate indicates that this compound also acts as the reaction intermediate for the

10   second reaction (equation 4).

11   Another possible intermediate for the second reaction (equation 4) is formamide. In the

12   literature, it was reported that the hydrolysis of nitriles proceeds in two consecutive steps; partial

13   nitrile hydrolysis produces an amide, then amide hydrolysis produces a carboxylic acid and

14   ammonia. Sodium hydroxide in the reaction media acts as catalyst and promotes the hydrolysis

15   of cyanide[33,34]. Considering a possible analogous behavior in our case, the existence of

16   formamide was tested at different reaction times, although it was not detected at any moment.

17   This was expected due to the fact that the amide is readily hydrolyzed to formate and ammonia

18   in a basic medium[35,36]. In order to prove the fast hydrolysis of formamide in the conditions

19   employed in this work, additional experiments on the wet oxidation of formamide showed that

20   this compound was completely converted to formate and ammonia in 4.5 minutes (conversion

21   above 98.5%) for an initial concentration of 0.55 mM at 423 K, 8.0 MPa and pH=11. The kinetic

22   constant for formamide degradation, $(1.37\pm0.03)\times10^{-2}$ s^{-1}, was much higher than kinetic constant

23   for cyanide degradation as equation 4, $(5.98\pm0.01)\times10^{-4}$ s^{-1}; (Figure S6). Formamide

24   concentration was evaluated theoretically for different reaction times from the oxidation kinetic

25   constants, showing very low values throughout the experiment (Figure S7). Figure 3 sums up all

1   the abovementioned considerations. We know that formamide is transformed to ammonia and

2   formate, but we cannot confirm their presence and importance in the global reaction.

3   FIGURE 3

4   *Kinetic Analysis*

5   Considering the pathways of hydrolysis that have been proposed for the degradation of

6   cyanide, the rate equations for each compound can be expressed through a system of five

7   ordinary differential equations (ODEs), as follows:

8
$$r_{CN^-} = -\frac{dC_{CN^-}}{dt} = -(k_1 + k_2)C_{CN^-} = -k_{ov}C_{CN^-} \qquad (5)$$

9
$$r_{NH_3} = \frac{dC_{NH_3}}{dt} = k_2 C_{CN^-} \qquad (6)$$

10
$$r_{HCOO^-} = \frac{dC_{HCOO^-}}{dt} = k_2 C_{CN^-} \qquad (7)$$

11
$$r_{CO_2} = \frac{dC_{CO_2}}{dt} = k_1 C_{CN^-} \qquad (8)$$

12
$$r_{N_2} = \frac{dC_{N_2}}{dt} = \frac{1}{2} k_1 C_{CN^-} \qquad (9)$$

13   where k_1 and k_2 are the kinetic constants for the degradation of cyanide into formate and

14   ammonia, and carbon dioxide and nitrogen, respectively.

15   It should be noted that the sum of the kinetic constants (k_1+k_2), denoted as k_{ov}, is determined

16   by fitting experimental cyanide concentrations from each experiment with a pseudo-first order

17   kinetic model. Once the value of k_2 is obtained, k_1 can be calculated by difference. The

18   calculation method for determining k_2 is given in the Supporting Information (SI).

1   The fractional yield of formate, denoted as φ, can be obtained by dividing equation 7 by

2   equation 5:

$$\varphi = \frac{r_{HCOO^-}}{-r_{CN^-}} = \frac{dC_{HCOO^-}}{-dC_{CN^-}} = \frac{k_2}{k_1 + k_2} \qquad (10)$$

4   This parameter refers to the fraction of cyanide disappearing at any instant which is

5   transformed into formate, giving information about the distribution of products.

6   *Effect of the operating variables*

7   Next, the influence of the operating variables (pressure, temperature and initial concentration)

8   was studied to obtain reliable kinetic data. In addition, the effect of these variables over the

9   distribution of the reaction products was considered.

10   *Effect of the oxygen pressure*

11   Figure 4a shows the results of a set of runs performed at 453 K and pH=11, with an initial

12   cyanide concentration of 3.85 mM and oxygen pressures ranging from 2.0 to 8.0 MPa,

13   corresponding to oxygen concentrations in the reaction medium between 10^{-2} and 6.7×10^{-2} M.

14   The flow rate of oxygen, 2.33×10^{-5} m^3/s, was high enough to ensure oxygen saturation during

15   the reaction. The concentration of dissolved oxygen can be assumed as constant for a given run,

16   but varied from run to run as the oxygen pressure was changed.

17   Increments in the operating pressure from run to run revealed that reaction rates and the

18   product distribution were almost unaffected by this variable. In fact, when working at 2.0 MPa a

19   95.5% conversion was reached in 9 min and at 8.0 MPa a 96.7% conversion was achieved at the

20   same reaction time. Likewise, the value of φ ranged from 0.620±0.002 to 0.626±0.006.

21   Over the range of pressures studied, the behavior of the system was successfully fitted to a

22   pseudo-first order kinetic model with respect to the pollutant. Solid lines in Figure 4a, denote the

1   model curve according to the calculated pseudo-first order kinetic constants. These constants are

2   reported in Table 1. The equilibrium concentration of oxygen was determined by means of

3   Henry's law and an empirical correlation[37]. The oxygen reaction orders (α_i) were calculated by

4   correlating the oxygen concentration and the reaction rate constant at different working pressures

5   ($k_i = k_i^' C_{O_2}^\alpha$), yielding a value of $\alpha_1 = 0.027 \pm 0.003$ and $\alpha_2 = 0.040 \pm 0.001$ (in both cases, $r^2 = 0.99$).

6   These low values demonstrated again the limited influence of oxygen pressure both on the

7   degradation of cyanide and on product distribution. By contrast, another cyanide species, such as

8   thiocyanate and metal-complex cyanide were affected by this variable. Values of $\alpha = 0.32$, 0.61

9   and 0.81 were reported for the kinetic orders of oxygen during the wet oxidation of thiocyanate

10   in acid, slightly acid and basic media, respectively[14,15]. Mishra and Joshi[17] proposed a reaction

11   order of 0.4 for the oxidation of cyanocuprate.

12   To verify that the oxygen pressure exerted no effect on the reaction rates, a one-way analysis

13   of variance (ANOVA) was made using Statgraphics Centurion XV. Working with repeated

14   experiments involving the degradation of 3.85 mM of cyanide conducted at 453 K and pressures

15   between 2.0 and 8.0 MPa and selecting oxygen pressure as a factor and kinetic constants (k_1 or

16   k_2) as dependent variable, it was shown that the oxygen pressure did not affect the reaction rates

17   at p-value below 0.05.

18   This result is consistent with the reaction pathways of the hydrolytic route that we have

19   proposed above for the degradation of cyanide.

20   FIGURE 4a; TABLE 1

21   *Effect of initial concentration of cyanide*

22   In order to determine the effect of initial concentration of cyanide on the removal efficiency

23   and reaction products, degradation runs with initial concentrations between 3.85-25 mM were

24   performed at 453 K, pH=11 and 8.0 MPa. Similar conversions and values of product distribution

1   were achieved irrespective of the value of the initial concentration (Figure 4b). In all cases, 13

2   min was required to obtain conversions of above 99% and the values of φ ranged from

3   0.626±0.006 to 0.635±0.001. Again, the behavior of the system was successfully fitted to a

4   pseudo-first order kinetic model with respect to the pollutant (see Table 1).

5   A one-way analysis of variance (ANOVA) was carried out to verify that the reaction rates

6   were not be affected by initial cyanide concentration. Working with repeated degradation

7   experiments performed at 453 K and 8.0 MPa and initial cyanide concentrations ranging from

8   3.85-25 mM and selecting initial cyanide concentration as a factor and kinetic constants (k_1 or

9   k_2) as dependent variable, it was determined that the initial cyanide concentration did not affect

10   the rates of the reaction, at p-value below 0.05. This is in agreement with the conclusions of

11   Kojima *et al.*[19] for similar concentrations of cyanide at 423 K and 1.0 MPa. The fact that cyanide

12   degradation was not affected by the initial cyanide concentration indicates that the pathway is

13   non-radical, since in radical systems initial concentration affects the generation of radicals and

14   this has influence on the rate of degradation and/or the final products. Usually when the initial

15   concentration of pollutant is greater, more free radicals are generated and reaction times are

16   shorter[38]. A non-radical pathway is in accordance with the hydrolysis pathways that we have

17   proposed here (equation 3 and 4).

18   FIGURE 4b; TABLE 1

19   *Effect of temperature*

20   In order to determine the effect of temperature on the degradation of cyanide, a set of

21   experiments was carried out at 8.0 MPa of oxygen pressure and pH=11, with an initial cyanide

22   concentration of 3.85 mM (Figure 4c). The concentration of oxygen was varied from run to run

23   as the temperature was changed, but it can be considered constant for a given run.

1   As expected, an increase in the operating temperature implied an increase in the reaction

2   rates. Hence, when working at 393 K, a conversion of 93% was achieved in 315 min, but when

3   the temperature was 473 K, 2 min were enough to reach a similar conversion (Figure 4c). In all

4   cases, the rate of degradation was properly fitted to a pseudo-first order kinetic model (Table 1).

5   FIGURE 4c; TABLE 1

6   The formation of formate and ammonia was favored by higher temperatures and the

7   formation of carbon dioxide and nitrogen was favored by lower temperatures. The change in φ

8   values with temperature between 423 and 473 K is less significant than the change in these

9   values seen between 393 K and 423 K. The results related to the product distribution (φ) are

10   shown in Figure S8.

11   This behavior can be explained by the values of activation energies associated with each

12   reaction pathway. Assuming that the kinetic constants, k_1 and k_2, followed an Arrhenius-type

13   behavior, the values of activation energies were found to be $Ea_1=77.6\pm3.0$ and $Ea_2=108.2\pm3.3$

14   kJ/mol. Thus, the reaction with larger activation energy (equation 4) is more sensitive to

15   temperature, favoring the formation of formate and ammonia.

16   *Kinetic model*

17   Taking into account the abovementioned experimental data, the kinetic model for the

18   degradation of cyanide, and the formation of ammonia and formate can be expressed through the

19   following equations (time in seconds, temperature in Kelvin, concentrations in molarity):

20   $$-r_{CN^-} = (1.79\times10^6 e^{-9328/T} + 1.33\times10^{10} e^{-13012/T})\, C_{CN^-} \qquad (11)$$

21   $$r_{NH_3, HCOO^-} = (1.33\times10^{10} e^{-13012/T})\, C_{CN^-} \qquad (12)$$

1 The experiments on the degradation of cyanide were simulated using equations 11 and 12

2 with a good degree of concordance for cyanide, ammonia and formate concentrations ($r^2 > 0.98$);

3 (see Figure S9 and S10).

1 **Acknowledgements**

5 **Supporting Information (SI)**

6 Calculation method for the determination of the kinetic constant, k_2; degradation of formate by

7 means of wet oxidation, experimental data of hydrogen concentration, degradation runs of

8 cyanate and formamide by means of wet oxidation, effect of temperature on the product

9 distribution, comparison between the experimental data and the theoretical values obtained

10 through the kinetic model and nomenclature. This information is available free of charge via the

11 Internet at http://pubs.acs.org/

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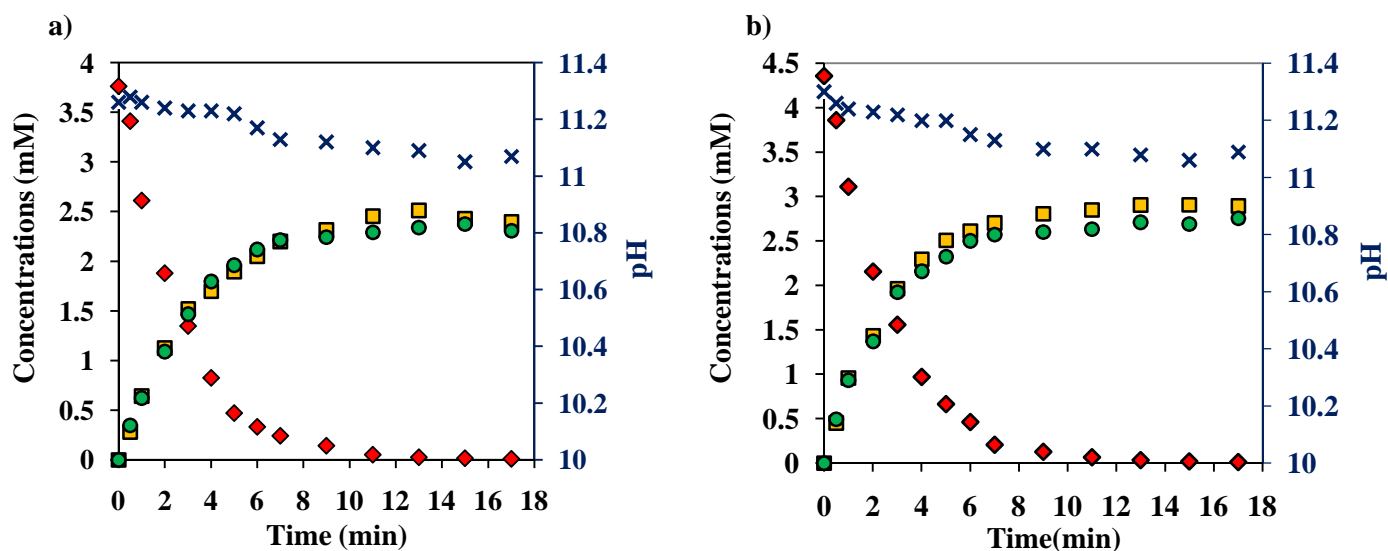
FIGURE 1

Figure 1. pH evolution and concentration of the following compounds: (×) pH, (◆) cyanide, (●) ammonia, (■) formate, during the degradation of cyanide: a) in the presence of oxygen and b) in the absence of oxygen. Operating conditions: T=453 K, P=8.0 MPa and pH=11.
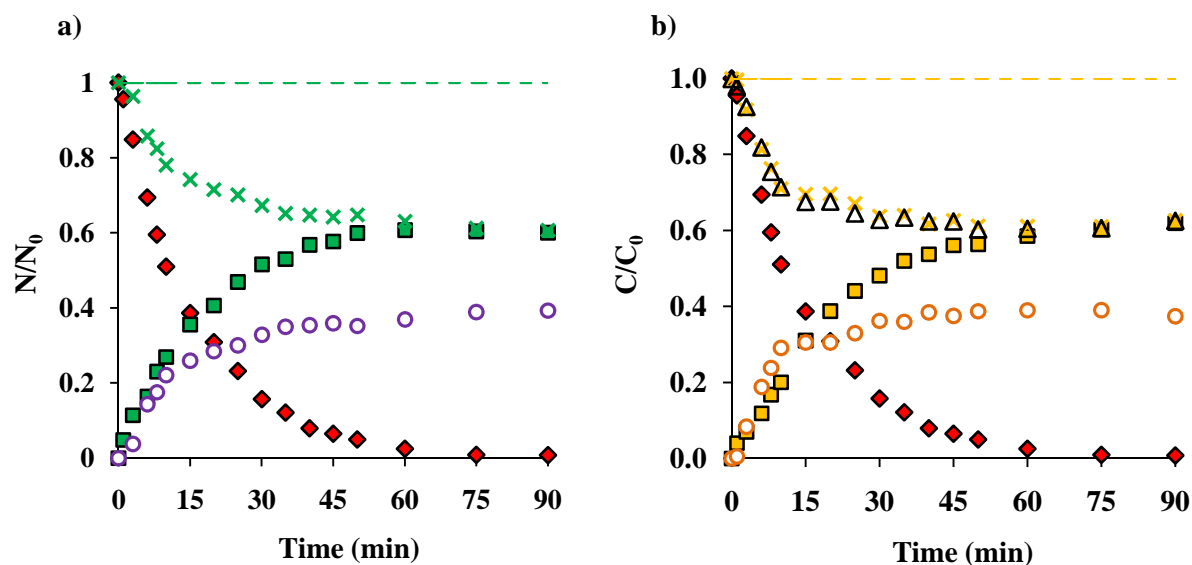
FIGURE 2

Figure 2. (a) Nitrogen elemental balance during the degradation of cyanide in presence of oxygen. ($\blacklozenge$) N as CN^-, ($\blacksquare$) N as NH_3, ($\times$) total measured N (NH_3 plus CN^-), ($\circ$) N as theoretical N_2. Dotted line indicates theoretical total nitrogen. (b) Carbon elemental balance during the degradation of cyanide in presence of oxygen. ($\blacklozenge$) C as CN^-, ($\blacksquare$) C as $HCOO^-$, ($\times$) total measured C ($HCOO^-$ plus CN^-), ($\circ$) C as theoretical CO_2, ($\triangle$) C as TOC. Dotted line indicates theoretical total carbon. Operating conditions: initial cyanide concentration = 3.85 mM, T=423 K, P=8.0 MPa and pH=11.
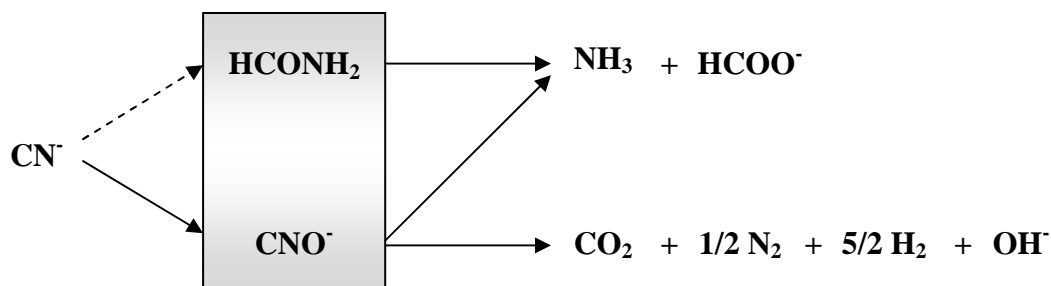
FIGURE 3

Figure 3. Reaction pathways proposed for the cyanide degradation in a basic medium by wet oxidation.

FIGURE 4
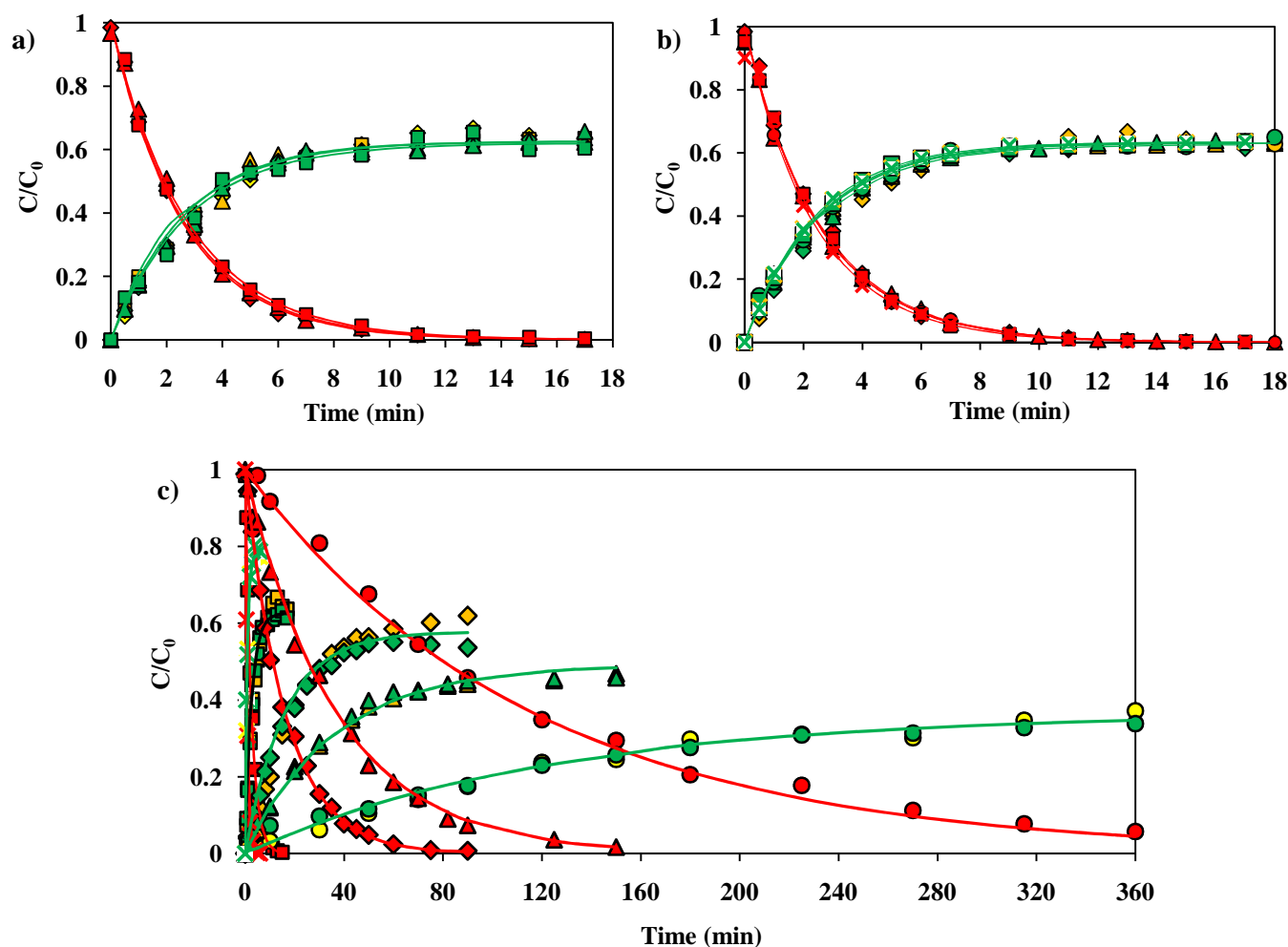
Figure 4. Concentration of cyanide (red symbols), ammonia (green symbols) and formate (yellow symbols) during the degradation conducted: a) At different pressures: (■,■,■) 2.0 MPa, (▲,▲,▲) 5.0 MPa, (◆,◆,◆) 8.0 MPa. Operating conditions: initial cyanide concentration = 3.85 mM, T=453 K, and pH=11. b) At different initial cyanide concentrations: (◆,◆,◆) 3.85 mM, (▲,▲,▲) 5.77 mM, (●,●,●) 7.69 mM, (■,■,■) 9.62 mM, (×,×,×) 25 mM. Operating conditions: T=453 K, P=8.0 MPa, and pH=11. c) At different temperatures: (●,●,●) 393 K, (▲,▲,▲) 408 K, (◆,◆,◆) 423 K, (■,■,■) 453 K, (×,×,×) 473 K. Operating conditions: initial cyanide concentration = 3.85 mM, P=8.0 MPa, and pH=11. In all cases, solid lines denote models according to Table 1.

TABLE

Table 1. Relevant kinetic data results for the degradation of cyanide at different operating conditions.

Effect of oxygen pressure

T(K)	453			
P(MPa)	2.0 (O_2)	5.0(O_2)	8.0 (O_2)	8.0 (N_2)
$C_{CN_0^-}$ (mM)	3.85±0.01	3.85±0.02	3.85±0.03	4.40±0.03
C_{O_2} (M)	1.0×10^{-2}	3.8×10^{-2}	6.7×10^{-2}	---
k_{ov}(s^{-1})	$(5.98±0.03) \times 10^{-3}$	$(6.27±0.07) \times 10^{-3}$	$(6.42±0.07) \times 10^{-3}$	$(6.32±0.03) \times 10^{-3}$
r^{2*}	0.9991	0.997	0.997	0.994
k_1 (s^{-1})	$(2.27±0.06) \times 10^{-3}$	$(2.35±0.16) \times 10^{-3}$	$(2.40±0.16) \times 10^{-3}$	$(2.10±0.07) \times 10^{-3}$
k_2 (s^{-1})	$(3.71±0.03) \times 10^{-3}$	$(3.92±0.09) \times 10^{-3}$	$(4.02±0.09) \times 10^{-3}$	$(4.22±0.04) \times 10^{-3}$
φ	0.620±0.002	0.626±0.003	0.626±0.006	0.667±0.002

Effect of temperature

P(MPa)	8.0				
T(K)	393	408	423	453	473
$C_{CN_0^-}$ (mM)	3.85±0.01	3.85±0.02	3.85±0.03	3.85±0.03	3.85±0.02
k_{ov} (s^{-1})	$(1.35±0.01) \times 10^{-4}$	$(4.53±0.05) \times 10^{-4}$	$(1.04±0.02) \times 10^{-3}$	$(6.42±0.07) \times 10^{-3}$	$(2.02±0.02) \times 10^{-2}$
r^{2*}	0.997	0.997	0.9992	0.997	0.998
k_1 (s^{-1})	$(8.57±0.02) \times 10^{-5}$	$(2.30±0.08) \times 10^{-4}$	$(4.37±0.03) \times 10^{-4}$	$(2.40±0.16) \times 10^{-3}$	$(4.50±0.5) \times 10^{-3}$
k_2 (s^{-1})	$(4.95±0.01) \times 10^{-5}$	$(2.23±0.03) \times 10^{-4}$	$(5.98±0.01) \times 10^{-4}$	$(4.02±0.09) \times 10^{-3}$	$(1.57±0.03) \times 10^{-2}$
φ	0.366±0.002	0.491±0.002	0.578±0.003	0.626±0.006	0.778±0.004

Effect of initial cyanide concentration

P(MPa)	8.0				
T(K)	453				
$C_{CN_0^-}$ (mM)	3.85±0.03	5.77±0.02	7.69±0.02	9.62±0.03	25±0.02
k_{ov} (s^{-1})	$(6.42±0.07) \times 10^{-3}$	$(6.55±0.10) \times 10^{-3}$	$(6.62±0.07) \times 10^{-3}$	$(6.68±0.07) \times 10^{-3}$	$(6.90±0.03) \times 10^{-3}$
r^{2*}	0.997	0.9991	0.998	0.997	0.998
k_1 (s^{-1})	$(2.40±0.16) \times 10^{-3}$	$(2.42±0.18) \times 10^{-3}$	$(2.44±0.13) \times 10^{-3}$	$(2.44±0.14) \times 10^{-3}$	$(2.52±0.06) \times 10^{-3}$
k_2 (s^{-1})	$(4.02±0.09) \times 10^{-3}$	$(4.13±0.08) \times 10^{-3}$	$(4.18±0.06) \times 10^{-3}$	$(4.24±0.07) \times 10^{-3}$	$(4.38±0.03) \times 10^{-3}$
φ	0.626±0.006	0.630±0.003	0.632±0.003	0.634±0.004	0.635±0.001

* referred to the goodness of the k_{ov} fitting

TOC/Abstract Art