



Catalytic wet oxidation of thiocyanate with homogeneous copper(II) sulphate catalyst

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ABSTRACT

The wet oxidation of thiocyanate has been investigated in a semi-batch reactor at temperatures between 423 and 473 K and pressures between 6.1×10^3 and 1.0×10^4 kPa in the presence of copper(II) sulphate as catalyst. The effects of copper concentration, initial thiocyanate concentration, pressure and temperature on the reaction rate were analyzed and the main products of reaction were identified. A kinetic model for the Cu-catalyzed reaction is here proposed, including temperature, oxygen concentration, and the reduction of Cu^{2+} to Cu^+ that gives an accurate prediction of the oxidation process under the assayed conditions. A mechanistic model based on the formation of a transition complex between a copper cation and two thiocyanate anions has been proposed for the catalytic wet oxidation.

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1. Introduction

Thiocyanate (SCN^-) is a linear, electronegative polyatomic ion that is used in a variety of industrial processes due to some of its rather unique properties [1]. Examples of these industrial processes are photofinishing, herbicide and insecticide production, dyeing, acrylic fiber production, manufacturing of thiourea, metal separation, and electroplating [2,3]. Moreover, thiocyanate is one of the major constituents of wastewater from factories for the gasification of coal, pyrolysis and in processes of gold and silver extraction [4]. These wastewaters need to be treated to meet local discharge standards because thiocyanate ions show several toxic effects towards vertebrates. Those toxicity effects include respiration problems or it can even provoke human death because of the formation of toxic gases from contact with acids [5].

Different degradation techniques have been proposed for the treatment of streams contaminated with thiocyanate [2,6–12]. Biological treatment results in some cases a simple solution and the most economical option. However, and despite of having been studied for decades, the application of biological treatment is limited to low concentrations of thiocyanate. Some other techniques, most of them based on redox reactions with chemicals, have been applied for higher concentrations. Thiocyanate chemical oxidation, which has received considerable attention in the past as an analytical tool for quantitative determination of thiocyanate, has further become

a quite promising alternative for the removal of such pollutant. Between the different oxidizing agents assayed, hydrogen peroxide has stood out as the most effective. However, these treatments are normally expensive.

Wet oxidation is an attractive method for the treatment of waste streams contaminated with thiocyanate which are too dilute to incinerate and yet too toxic to treat biologically. The advantages of this process include low operating costs and minimal air pollution discharges [13]. In previous works [14], the noncatalytic wet oxidation of thiocyanate was analyzed in a wide range of temperatures and pressures to make a preliminary analysis of the reaction mechanism. The results obtained were quite promising, however the industrial process could be too expensive because of the severe conditions required in some cases [15]. The cost of wet oxidation can be significantly reduced by the use of suitable catalysts capable of promoting the oxidation under milder operating conditions and shorter residence times [16,17]. The catalytic oxidation of organic compounds over various homogeneous and heterogeneous catalysts has, therefore, received a lot of attention. It has been reported a positive effect on the reaction rate and effectiveness of the wet oxidation of different compounds by using transition metal salts as homogeneous catalysts [13,18]. In fact, catalysts based on iron or copper are now being applied in several commercial wet air oxidations which are operating successfully to treat industrial effluents and sludges [19–22]. The addition of a homogeneous catalyst has the inherent disadvantage of the posterior metal removal from the treated effluent. In industrial applications of wet oxidations catalyzed by a Cu(II) salt (as the *Ciba Geigy* process), the catalyst is precipitated as copper sulphide in the reactor exit and recycled to

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Nomenclature

C_i	concentration of component i in the reaction mixture
C_{i0}	initial concentration of component i in the reaction mixture
D_{O_2}	oxygen diffusivity in water
E_a	activation energy
k	apparent reaction rate constant
k_L	mass transfer coefficient for oxygen in the liquid phase
K_1	formation constant of the complex $(CuSCN)^+$
K_2	formation constant of the complex $Cu(SCN)_2$
K^*	formation constant of the transition complex
Ha	Hatta number
P	pressure
r_i	reaction rate for the component i
R	gas constant
T	temperature
x, y	stoichiometric coefficients
α, β	reaction orders
ΔH^0	enthalpy of formation of the complex

the reactor [19]. The copper can be also precipitated as hydroxide due its slow solubility at basic pH (0.05 ppm at pH 8) [23].

To the best of our knowledge, there have been no studies dealing specifically with catalytic thiocyanate wet oxidation. After testing several transition metals as homogeneous catalysts, copper proved to have a highly positive effect. The aim of the present work is to analyze the effect of a copper catalyst on the wet oxidation of thiocyanate. A wide range of temperatures, pressures, copper concentrations and initial concentrations are here assayed, to obtain reliable kinetic data that allow to make a preliminary analysis of the possible reaction mechanisms and the applicability of this method for the degradation of real effluents.

2. Experimental section

2.1. Apparatus and procedure

Experiments were completed in a 1-L capacity reactor (Parr T316SS) equipped with two six bladed magnetically driven turbine agitators. The reactor was preceded by a 2-L stainless steel water reservoir. The loaded volume in each vessel is about the 70% of the total in order to ensure the safety conditions. The equipment, charged with the catalyst, was pressurized and preheated to the desired working conditions while the stirrer speed was adjusted to 500 rpm for all the experiments. The operating pressure was provided by bottled compressed oxygen, with the oxygen flow rate adjusted to $2.33 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$, and controlled by an electronic mass flow controller (Brooks). The oxygen was bubbled through the water reservoir in order to become saturated in water and then it was sparged into the reaction vessel. Once the equipment was pressurized and preheated up to the desired conditions, a predetermined volume of a thiocyanate concentrated solution (potassium thiocyanate) was injected into the reactor. The injection time was taken as the zero-time for the reaction. A valve and a coil fitted to the top of the vessel allowed the withdrawal of samples during the reaction. Reaction temperature and pressure were maintained during the course of each experimental. The pressure was kept constant by means of a back pressure controller located at the end of the gas line.

Two bubblers filled with a concentrated hydroxide solution were installed at the end of the gas line with the purpose of

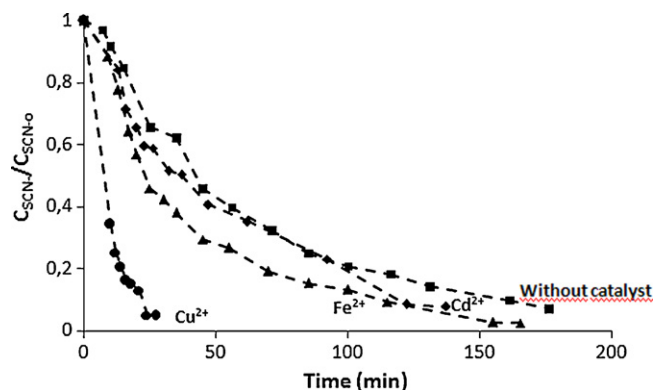


Fig. 1. Evolution of thiocyanate concentration during wet oxidation carried out in the presence of different sulphates: copper(II) (●), iron(II) (▲), cadmium (◆) and without metal (■). In all cases: initial concentration = 1.72 mM, metal concentration = 3.15 mM, $T = 473 \text{ K}$, $P = 1.0 \times 10^3 \text{ kPa}$.

absorbing the possible HCN formed. Nevertheless, no cyanide was detected in any case in the bubbler liquid.

To reduce hazards and corrosion problems during the experiments, metal sulphate salts were selected to be tested as catalysts. The assays with copper were carried out at acid pH (pH 5.3) in order to avoid copper precipitation (it was experimentally verified the absence of catalytic activity of the copper hydroxide formed at basic pH).

As in previous works [14], oxidations reported in this work were performed under kinetic control. Verification was done by calculating the Hatta number, Ha , which relations diffusion and reaction rates: $Ha = 1/k_L \sqrt{(2/(\beta + 1))k_r D_{O_2} C_{SAT,O_2}^{\beta-1} C_{SCN_0}^\alpha}$, being k_L the mass transfer coefficient for oxygen in the liquid phase, k_r the reaction constant, D_{O_2} the oxygen diffusivity in water and α, β reaction orders with respect to oxygen and thiocyanate, respectively. During all runs, Ha was lower than 10^{-5} . These small Hatta values ensure the absence of mass transfer limitations and the existence of a kinetic control. The diffusivity of oxygen was evaluated using the empirical expression proposed by Wilke [24], and the mass transfer coefficient was correlated according to an expression developed by Breman et al. [25].

2.2. Analytical methods

Concentrations of thiocyanate, cyanide and sulphate were monitored by using an ion exchange chromatograph (Dionex DX-120 Ion Chromatograph) and a suppressed conductivity detector (ASRS®-ULTRA Autosuppression Recycle Mode). The DX-120 is controlled remotely from a PeakNet workstation. The eluent employed is a solution 1.8 mM $Na_2CO_3/1.7 \text{ mM } NaHCO_3$, the flow rate 1.46 ml/min, the precolumn IonPac® AG4A-SC (4 mm × 50 mm), and the column IonPac® AS4A-SC (4 mm × 250 mm). Ammonium concentration was measured by the Nessler method.

3. Results and discussion

3.1. Previous catalysts test

A set of homogeneous transition metal sulphates has been tested as catalyst for the thiocyanate degradation (Fig. 2). As can be seen, the cadmium scarcely changed the rate of thiocyanate degradation. On the contrary, the catalytic effect of the iron(II) and the copper(II) is evident. Clearly, the copper showed the biggest catalytic activity of the metal sulphates assayed with 95% conversion in 30 min in front of the 3 h needed when the experiment was run without the metal sulphate. So, copper sulphate was selected as the most

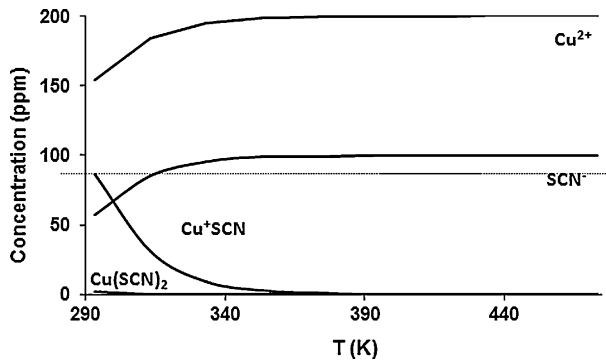
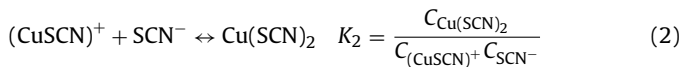
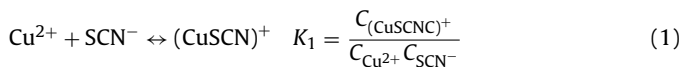


Fig. 2. Concentrations of Cu^{2+} , SCN^- , $\text{Cu}(\text{SCN})^+$, $\text{Cu}(\text{SCN})_2$ in solution at different temperatures. Initial concentrations of Cu^{2+} and SCN^- were 3.15 and 1.72 mM, respectively.

suitable salt to be used as homogeneous catalyst in thiocyanate oxidation. The effect of several operational variables on the catalytic oxidation is commented below.

3.2. Copper–thiocyanate complexes

Insofar as the catalytic potential of the copper or the copper–thiocyanate complexes is concerned, it is important to know the concentrations of the free ions and the complexes during the catalytic wet oxidation process. Copper ion interacts with thiocyanate anions by donating a pair of electrons, to form two coordination complexes [23]:



From K values at different temperatures [26] and assuming a temperature dependence of K according to expression (3), values of $a = 7418$ and $b = 19$ for Cu^+SCN and $a = 4424$ and $b = 12$ for $\text{Cu}(\text{SCN})_2$ were obtained

$$\ln K = \frac{\Delta H}{R} \frac{1}{T} - \frac{\Delta H}{R} \frac{1}{T_0} + \ln K_0 = a \frac{1}{T} - b \quad (3)$$

Using Eqs. (1)–(3) and with a mass balance to the copper and the thiocyanate, the distribution of the different compounds can be obtained. Fig. 1 shows that at high temperature, the free ions are the predominant species. For example, at 453 K, the concentrations of $\text{Cu}(\text{SCN})^+$ and $\text{Cu}(\text{SCN})_2$, are very low and the 99.99% of the initial copper is free. For all the runs of this work, it was verified that the amount of complexed copper can be despised and almost the total copper is free in solution during the oxidation processes.

3.3. Effect of the copper concentration

Fig. 3 compares the noncatalytic oxidation of a solution of thiocyanate (1.72 mM) with the catalytic oxidation with different concentrations of Cu^{2+} . The reaction was performed under 8.1×10^3 kPa of oxygen at 453 K and without initial pH adjustment (pH 5.3). As can be observed in the figure, the use of copper catalyst enhanced appreciably the degradation rate of thiocyanate. When working with 3.15 mM copper, a 95% conversion was reached in approximately 180 min. However, working without catalyst, similar reaction times were required to degrade only a 50% of the initial pollutant concentration. The oxidation rate is highly dependent on the catalyst concentration, which increases the rate of reaction, in special for low concentrations of copper. In fact, while thiocyanate nearly vanished during the first 300 min with 1.57 mM of Cu^{2+} , the

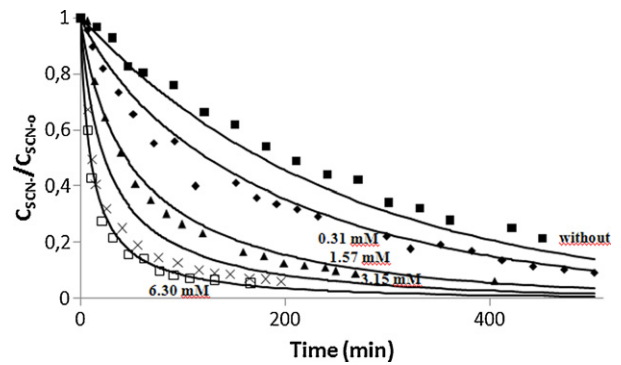


Fig. 3. Evolution of thiocyanate concentration during wet oxidation with different concentrations of Cu^{2+} : without (\blacksquare), 0.31 mM (\blacklozenge), 1.57 mM (\blacktriangle), 3.15 mM (\times) and 6.30 mM (\square). In all cases: initial concentration = 1.57 mM, $T = 453$ K, $P = 8.1 \times 10^3$ kPa. Solid lines denote model curves according to Eqs. (21) and (22).

maximum conversion achieved with 0.31 mM was 85% even after 500 min reaction. However, the beneficial effect of initial copper concentration decreased with the increase of the cupric ion concentration. In fact, the reaction rates for 3.15 and 6.30 mM were quite similar from a practical point of view. Moreover, the data reveals the effect of the copper addition in the apparent reaction order (Table 1). For the absence of copper or small copper concentrations (0.31 mM), the reaction was fitting to a pseudo-first order kinetic model ($r_{n=1}^2 > 0.99$) with respect to thiocyanate, but when the copper concentration increased ($C_{\text{Cu}^{2+}} \geq 1.57$ mM), the apparent order reaction for thiocyanate was 2. So, with 6.30 mM Cu^{2+} , the regression factors (r^2) were 0.88 for $n=1$ and 0.993 for $n=2$. This aspect will be discussed below.

3.4. Effect of oxygen pressure

Fig. 4 shows a plot of the evolution of the thiocyanate concentration for runs performed at 453 K, an initial thiocyanate concentration of 1.72 mM, a copper concentration of 3.15 mM and an oxygen pressure varying in the range 6.1×10^3 to 1.0×10^4 kPa. The flow rate of oxygen, $2.3 \text{ N m}^3 \text{ s}^{-1}$, provides an enough oxygen transfer rate to guarantee oxygen saturation during the reaction. The value of the concentration of oxygen varied from run to run as the oxygen pressure was changed.

Increments in the working pressure from run to run revealed the effect of the oxygen concentration. So, higher concentrations of oxygen in the liquid medium lead to higher reaction rates. For example, when working at 6.1×10^3 kPa, a 70% conversion was reached in approximately 100 min, but when the total pressure was

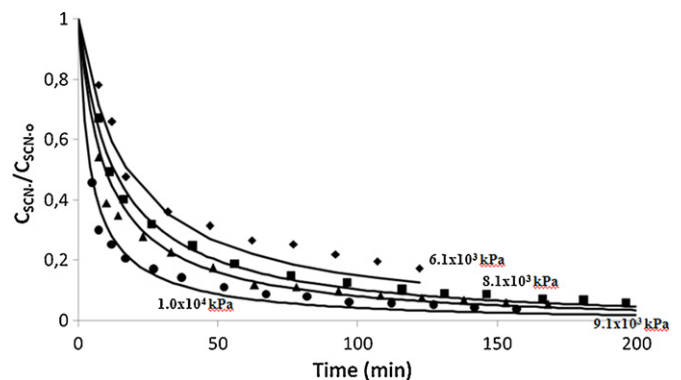


Fig. 4. Evolution of thiocyanate concentration during wet oxidation at different pressures: 6.1×10^3 kPa (\blacklozenge), 8.1×10^3 kPa (\blacksquare), 9.1×10^3 kPa (\blacktriangle) and 1.0×10^4 kPa (\bullet). In all cases: initial concentration = 1.72 mM, copper concentration = 3.15 mM, $T = 453$ K. Solid lines denote model curves according to Eqs. (21) and (22).

Table 1
Relevant kinetic data results for the catalytic wet oxidation of thiocyanate at different operating conditions.

<i>Copper concentration</i>						
T (K)	453					
P (kPa)	8.1×10^3					
$C_{Cu^{2+}}$ (mM)	0	0.31	1.57	3.15	6.30	
C_{SCN_0} (mM)	1.72					
C_{O_2} (M)	7.2×10^{-2}					
N	1	1	2	2	2	
k ($mM^{1-n} s^{-1}$)	5.5×10^{-5}	9.2×10^{-5}	4.9×10^{-4}	9.7×10^{-4}	1.2×10^{-3}	
r^2	0.995	0.990	0.996	0.995	0.993	
<i>Pressure</i>						
T (K)	453					
P (kPa)	6.1×10^3	8.1×10^3	9.1×10^3	1.0×10^4		
$C_{Cu^{2+}}$ (mM)	3.15					
C_{SCN_0} (mM)	1.72					
C_{O_2} (M)	5.2×10^{-2}	7.2×10^{-2}	8.3×10^{-2}	9.3×10^{-2}		
N	2	2	2	2		
k ($mM^{1-n} s^{-1}$)	7.3×10^{-4}	9.7×10^{-4}	1.1×10^{-3}	1.2×10^{-3}		
r^2	0.991	0.995	0.996	0.995		
<i>Temperature</i>						
T (K)	423	438	453	473		
P (kPa)	1.0×10^4					
$C_{Cu^{2+}}$ (mM)	3.15					
C_{SCN_0} (mM)	1.72					
C_{O_2} (M)	7.9×10^{-2}	8.5×10^{-2}	9.3×10^{-2}	1.0×10^{-1}		
N	2	2	2	2		
k ($mM^{1-n} s^{-1}$)	1.1×10^{-4}	3.6×10^{-4}	1.2×10^{-3}	4.6×10^{-3}		
r^2	0.993	0.991	0.995	0.98		
<i>Initial concentration</i>						
T (K)	453					
P (kPa)	8.1×10^3					
$C_{Cu^{2+}}$ (mM)	3.15					
C_{SCN_0} (mM)	1.72	3.45	6.90	12.07		
C_{O_2} (M)	7.2×10^{-2}					
N	2	2	1 ($t > 150$ min)	2 ($t < 150$ min)	1 ($t > 80$ min)	2 ($t < 80$ min)
k ($mM^{1-n} s^{-1}$)	9.7×10^{-4}	1.8×10^{-4}	6.7×10^{-5}	4.8×10^{-5}	6.7×10^{-5}	1.9×10^{-5}
r^2	0.996	0.995	0.991	0.991	0.992	0.98

1.0×10^4 kPa, less than 20 min were enough to achieve a similar conversion. In the range of pressures considered, the behaviour of the system properly was fitted to a pseudo-second order mechanism (Table 1).

3.5. Effect of temperature

The influence of temperature on thiocyanate degradation was studied in the range 423–473 K. Fig. 5 shows the result of a set of runs performed with an oxygen pressure of 1.0×10^4 kPa, a copper concentration of 3.15 mM and an initial thiocyanate concentration of 1.72 mM.

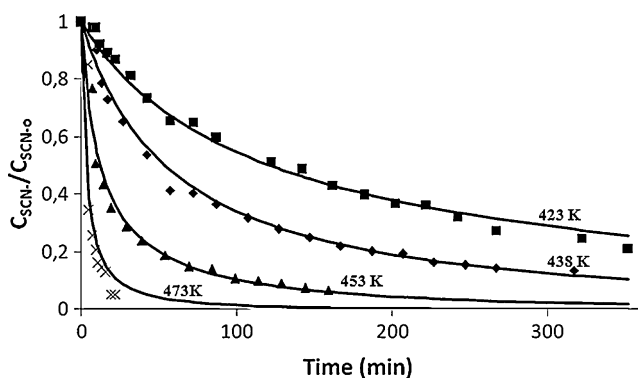


Fig. 5. Evolution of thiocyanate concentration during wet oxidation at different temperatures: 423 K (■), 438 K (◆), 453 K (▲) and 473 K (×). In all cases: initial concentration = 1.72 mM, copper concentration = 3.15 mM, $P = 8.1 \times 10^3$ kPa. Solid lines denote model curves according to Eqs. (21) and (22).

Results showed that an increase of few degrees implies a big increase in the reaction rate. For example, when the working temperature was 423 K, the time needed to reach a conversion over 70% was about 300 min, whereas only half-time was required to reach the same conversion when working at 438 K. When the temperature was set at 473 K, a 90% conversion was reached in only 15 min. In all cases a pseudo-second order kinetic could be assumed (Table 1).

3.6. Effect of initial thiocyanate concentration

A set of thiocyanate initial concentrations was selected in a range between 1.72 and 12.07 mM. Fig. 6 shows the effect of the initial thiocyanate concentration on the reaction rate. The time needed for a determined conversion was function of the initial concentration. As can be observed, the degradation rate was lower for higher initial concentrations of thiocyanate. A 80% conversion was reached in 40 min when the initial concentration was 1.72 mM, in 150 min when the initial concentration was twofold higher, in 230 min when the concentration was fourfold bigger and in 340 min when the experiment started with 12.07 mM.

The experiments with low initial concentrations were successfully fitted to a pseudo-second order kinetic. However, when the initial concentration increased, the degradation profiles cannot be fitted to a pseudo-first or pseudo-second kinetic model. In fact, the degradation curves for 3.45, 6.90 and 12.07 mM of thiocyanate seems to follow a pseudo-second kinetic order behavior during the first minutes of reaction, but the last data fit better to pseudo-first order (Table 1). This behavior and the negative dependence of the reaction rate with the initial concentration of thiocyanate will be further discussed.

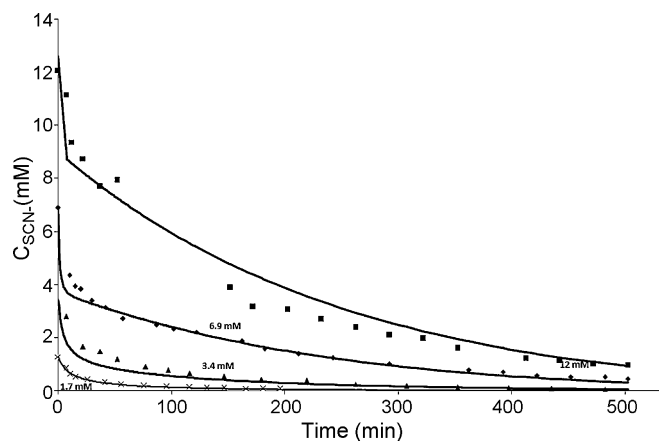


Fig. 6. Evolution of thiocyanate concentration during wet oxidation at different thiocyanate initial concentrations: 1.72 mM (x), 3.45 mM (▲), 6.90 mM (◆) and 12 mM (■). In all cases: copper concentration = 3.15 mM, $T=453$ K, $P=8.1 \times 10^3$ kPa. Solid lines denote model curves according to Eqs. (21) and (22).

3.7. Reaction products

As can be seen in Fig. 7, sulphate and ammonium were the main final products of the catalytic thiocyanate oxidation. A final yield of thiocyanate in sulphate of 1.69 mg SO_4^{2-} /mg SCN^- was obtained from the experimental data. This value, that it is similar to the maximum theoretical one (1.66), involves that the sulphate was the unique S-compound formed. The yield of thiocyanate in ammonium was 0.34 mg NH_4^+ /mg SCN^- , leading to a similar conclusion: ammonium is the principal N-compound formed, and the formation of another species as nitrates, nitrites or molecular nitrogen looks negligible in the assayed conditions. Similar behaviors were observed for the other operational conditions carried out in this work.

3.8. Reaction pathway

Taking into account the experimental results, reaction pathways for the catalytic oxidation process and kinetic models to describe it are here proposed. This knowledge, apart from giving a fundamental insight to the catalytic degradation of thiocyanate, could be used for improvements in the operation and design of wet oxidation units.

Fig. 8 shows the proposed reaction mechanism for the catalytic wet oxidation of thiocyanate in the presence of Cu(II) sulphate. The supposition for the catalytic process is the existence of a transition complex. The numerous collisions between thiocyanate and copper

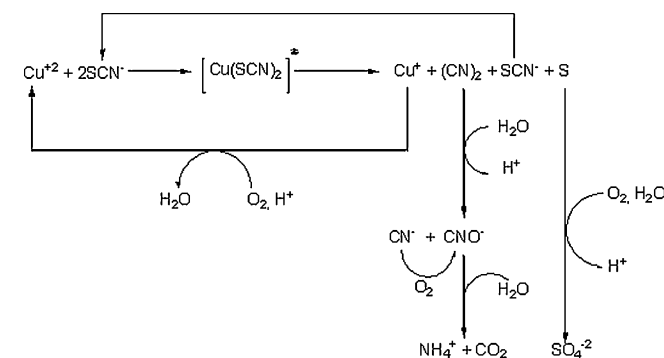
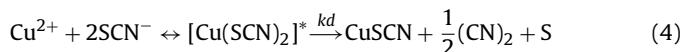


Fig. 8. Proposed reaction mechanisms for the wet oxidation of thiocyanate in the presence of copper(II) sulphate.

molecules may result in an unstable transition complex (TC), which can then give products, or return to the original molecules. The proposed formula for this transition complex was $[\text{Cu}(\text{SCN})_2]^*$.

This hypothetical transition complex presents the same stoichiometric formula than the real thiocyanate complex $\text{Cu}(\text{SCN})_2$. For this reason, it seemed adequate to suppose that both compounds have a similar chemical behaviour during their decomposition (Eq. (4)) [27]:



For the employed conditions, the CuSCN is unstable [26]:



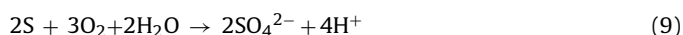
The formed cyanogen $(\text{CN})_2$ is fastly hydrolyzed according to [28]:



The last step of the mechanism is the cyanide oxidation (Eq. (7)) followed by the cyanate hydrolysis (Eq. (8)) [28,29]



In parallel with the cyanogens degradation, it is well-know that the sulphur formed during the decomposition of the transition complex is oxidized to sulphate by the dissolved oxygen at the severe operational conditions employed (Eq. (9)) [30]:



The Cu(I) formed in Eq. (8) is catalytically inactive for the oxidation of thiocyanate. However, the Cu(I) is re-oxidized to Cu(II)

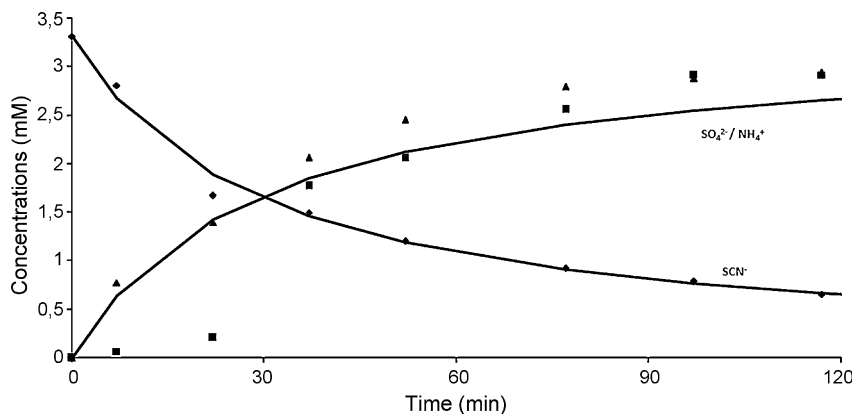


Fig. 7. Evolution of thiocyanate (◆), sulphate (▲) and ammonium (■) during the wet oxidation. Initial concentration = 3.45 mM, copper concentration = 3.15 mM, $T=453$ K, $P=8.1 \times 10^3$ kPa. Solid lines denote theoretical evolution of thiocyanate and products (if one mole of thiocyanate gives one mole of ammonium and one mole of sulphate).

in contact with the dissolved oxygen of the reaction media (Eqs. (10) and (11)) and then it is available for the formation of a new transition complex



The proposed pathway explains adequately the formation of the main products experimentally observed. The proposed intermediates (Cu^+ , $(\text{CN})_2$, $\text{Cu}(\text{SCN})_2$, S) are frequent in oxidation process of cyanide compounds, and their instability, specially in acid media with excess of oxygen and at high temperature, have been reported frequently in the bibliography. This fact explains why their presence was not tested in this work, where severe operational conditions are employed.

3.9. Reaction kinetics

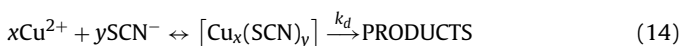
In the next section, the reaction kinetic model deduced from the reaction pathway is employed to fit the experimental data with the aim of verifying the validity of the proposed mechanism. The kinetic model here proposed includes the separated catalytic and noncatalytic wet oxidation reactions:

$$(-r_{\text{SCN}_0^-})_{\text{global}} = (-r_{\text{SCN}_0^-})_{\text{noncatalytic}} + (-r_{\text{SCN}_0^-})_{\text{catalytic}} \quad (12)$$

For the oxidation of thiocyanate in slightly acid media, the next kinetic model was obtained from previous experiments [31]:

$$(-r_{\text{SCN}_0^-})_{\text{noncatalytic}} = k_{\text{NC}} C_{\text{SCN}^-} C_{\text{O}_2}^{0.61} \quad (13)$$

The decomposition of the transition complex (TC) (Eq. (14)) has been selected as the rate limiting step. Initially, the formula of this complex was supposed unknown. Thus, for a generic complex:



$$(-r_{\text{SCN}_0^-})_{\text{catalytic}} = y(-r_{\text{TC}}) = yk_d C_{\text{TC}} \quad (15)$$

$$K^* = \frac{C_{\text{TC}}}{(C_{\text{Cu}^{2+}})^x (C_{\text{SCN}^-})^y} \quad (16)$$

$$(-r_{\text{SCN}^-})_{\text{catalytic}} = yk_d K^* C_{\text{Cu}^{2+}}^x C_{\text{SCN}^-}^y = k_C C_{\text{Cu}^{2+}}^x C_{\text{SCN}^-}^y \quad (17)$$

As can be seen in the previous section, a pseudo-second kinetic order has been generally observed for the thiocyanate at high copper concentrations. In these conditions, it is logical to think about catalytic reaction prevailed over the noncatalytic one, so y takes a value of 2. To obtain the value of x , experimental data of Fig. 3 were fitted to Eq. (18) and a value around of 1 was obtained. This is the reason of the selection of $[\text{Cu}(\text{SCN})_2]^*$ as molecular formula of the transition complex

$$(-r_{\text{SCN}^-})_{\text{global}} = k_{\text{NC}} C_{\text{SCN}^-} C_{\text{O}_2}^{0.61} + k_C C_{\text{Cu}^{2+}} C_{\text{SCN}^-}^2 \quad (18)$$

It can be appreciated that the formula of the transition complex deduced from the experimental data coincided with the formula of a real complex.

Eq. (18) fits the data when initial thiocyanate concentrations were low but it does not described adequately the behaviour of the system when the initial thiocyanate concentration was high (3.45, 6.90 and 12.07 mM of thiocyanate). This can be explained by the fact that not all the initial copper is as Cu^{2+} during the oxidation. The kinetic model can be completed taking into account the kinetic equation for the copper. If the amount of Cu forming part of the transition complex is negligible at any time, $C_{\text{Cu}^+} = C_{\text{Cu}_0} - C_{\text{Cu}^{2+}}$, being C_{Cu_0} the initial copper concentration. Then, the change in the

concentration of Cu^{2+} (catalytically active) in the medium can be described by the next equations (based on Eqs. (4), (5) and (10)):

$$(-r_{\text{Cu}^{2+}}) = (-r_{\text{SCN}^-})_{\text{catalytic}} - (-r_{\text{Cu}^+}) \quad (19)$$

$$(-r_{\text{Cu}^{2+}}) = k_C C_{\text{SCN}^-}^2 C_{\text{Cu}^{2+}} - k_{\text{OX}} [C_{\text{Cu}_0} - C_{\text{Cu}^{2+}}] \quad (20)$$

The effect of the operational pressure has been modeled under the supposition that the dissolved oxygen concentration remains constant along the reaction time (temperature and pressure were maintained constant). Based on the proposed mechanism (Fig. 8), only k_{NC} and k_{OX} are function of the oxygen concentration. The value of k_{NC} employed during the simulation was obtained in a work previously published by our research group [31]. The value for k_{OX} was taken from Papassiopi et al. [32]. These authors also proposed a value of 1 for the kinetic order of the oxygen during the oxidation of Cu(I).

Finally, the effect of the temperature has been incorporated in the kinetic model assuming an Arrhenius-type dependence. The activation energy for the noncatalytic reaction was 121 kJ/mol, a value obtained from experimental data (data not shown). For the oxidation of Cu^+ , it was taken the value of 25 kJ/mol proposed in the bibliography [32]. A value of 127 kJ/mol for the activation energy of k_C was obtained by fitting using the degradation curves at different temperatures showed in Fig. 5.

In conclusion, the kinetic model for the wet oxidation of thiocyanate in presence of copper(II) can be expressed through Eqs. (23) and (24) (time in seconds, concentrations in M, temperature in K).

$$r_{\text{SCN}^-} = -1.41 \times 10^{17} e^{-15269/T} C_{\text{SCN}^-}^2 - C_{\text{Cu}^{2+}} - 3.25 \times 10^{10} e^{-14561/T} C_{\text{SCN}^-} C_{\text{O}_2}^{0.61} \quad (21)$$

$$r_{\text{Cu}^{2+}} = -1.41 \times 10^{17} e^{-15269/T} C_{\text{SCN}^-}^2 - C_{\text{Cu}^{2+}} + 2.98 e^{-2964/T} [C_{\text{Cu}_0} - C_{\text{Cu}^{2+}}] C_{\text{O}_2} \quad (22)$$

All the experiments presented in this work were simulated using Eqs. (21) and (22) with a good degree of accordance (solid lines in Figs. 3–6), which confirms that the proposed mechanism is coherent with the experimental results.

4. Conclusions

Free copper(II) anion is a competent homogeneous catalyst in the wet oxidation of thiocyanate in acid media. However, no catalytic activity was observed in basic media due to copper precipitation. Effective thiocyanate degradation, higher than 95%, has been achieved in only 1 h using 3.15 mM of Cu(II) at 453 K and 8.1×10^3 kPa of oxygen pressure. The needed time in the absence of catalyst was 5 times higher.

A detailed reaction network has been proposed for the catalytic wet air oxidation of thiocyanate employing Cu(II). The model is based on the formation of a transition complex between a copper ion and two thiocyanate molecules. During the thiocyanate degradation, the catalytically active specie Cu(II) is reduced to Cu(I), which is reoxidized to copper(II) by the dissolved oxygen. The proposed mechanism pointed at sulphate, ammonium and carbonate as the main final products of the reaction, which is in agreement with the experimental observations. Based on this mechanism, the corresponding kinetic model with the differential equations that describes the change in the concentrations of Cu^{2+} and SCN^- fits properly the experimental results.

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References

- [1] E. Dizge, N. Demirbas, M. Kobia, Removal of thiocyanate from aqueous solutions by ion exchange, *J. Hazard. Mater.* 166 (2009) 1367–1376.
- [2] C. Hung, S. Pavlostathis, Aerobic biodegradation of thiocyanate, *Water Res.* 11 (1997) 2761–2770.
- [3] R.R. Dash, A. Gaur, C. Balomajumder, Cyanide in industrial wastewaters and its removal: a review on biotreatment, *J. Hazard. Mater.* 163 (2009) 1–11.
- [4] C.A. Papadimitriou, P. Samaras, G.P. Sakellaropoulos, Comparative study of phenol and cyanide containing wastewater in CSTR and SBR activated sludge reactors, *Biores. Technol.* 100 (2009) 31–37.
- [5] R.R. Dash, A. Gaur, C. Balomajumder, Removal of cyanide from water and wastewater using granular activated carbon, *J. Hazard. Mater.* 163 (2009) 1–11.
- [6] S. Ebbs, Biological degradation of cyanide compounds, *Biotechnology* 15 (2004) 231–236.
- [7] C. Staib, P. Lant, Thiocyanate degradation during activated sludge treatment of coke-ovens wastewater, *Biochem. Eng. J.* 34 (2007) 122–130.
- [8] J. Mishra, J. Joshi, Kinetics and mechanism of oxidation of thiocyanate ion with peroxomonophosphoric acid, *Indian J. Technol.* 31 (1992) 91–96.
- [9] J. Jensen, Y. Tuan, Chemical oxidation of thiocyanate ion by ozone, *Ozone Sci. Technol.* 15 (1993) 343–360.
- [10] V. Sharma, D. O'Connor, D. Cabelli, Oxidation of thiocyanate by iron(V) in alkaline medium, *Inorg. Chim. Acta* 357 (2004) 4587–4591.
- [11] A. Christy, P. Egeberg, Oxidation of thiocyanate by hydrogen peroxide—a reaction kinetic study by capillary electrophoresis, *Talanta* 51 (2000) 1049–1058.
- [12] I. Wilson, G. Harris, The oxidation of thiocyanate ion by hydrogen peroxide. I. The pH independent reaction, *JACS* 82 (1960) 4515–4517.
- [13] S. Bhargava, J. Tardio, J. Prasad, K. Foger, D. Akolekar, S. Grocott, Wet oxidation and catalytic wet oxidation, *Ind. Eng. Chem. Res.* 45 (2006) 1221–1258.
- [14] J. Vicente, M. Díaz, Thiocyanate wet oxidation, *Environ. Sci. Technol.* 37 (2003) 1452–1456.
- [15] H. Debellefontaine, J. Foussard, Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe, *Waste Manage.* 20 (2000) 15–25.
- [16] S. Imamura, Catalytic and non catalytic wet oxidation, *Ind. Eng. Chem. Res.* 38 (1999) 1743–1753.
- [17] L.F. Liotta, M. Gruttadauria, G. Di Carlo, G. Perrini, V. Librando, Heterogeneous catalytic degradation of phenolic substrates: catalysts activity, *J. Hazard. Mater.* 162 (2009) 588–606.
- [18] S. Bhaduri, D. Mukesh, Homogeneous Catalysis. Mechanism and Industrial Applications, third ed., Wiley Interscience, New York, 2000.
- [19] F. Luck, Wet air oxidation: past, present and future, *Catal. Today* 53 (1999) 81–91.
- [20] J. Vicente, R. Rosal, M. Díaz, Catalytic wet oxidation of phenol with homogeneous iron salts, *J. Chem. Technol. Biotechnol.* 80 (2005) 1031–1035.
- [21] S. Kolaczowski, P. Plucinski, F. Beltran, F. Rivas, D. McLurgh, Wet air oxidation: a review of process technologies and aspects in reactor design, *Chem. Eng. J.* 173 (1999) 143–160.
- [22] D. Karatza, M. Prisciandaro, A. Lancia, D. Musmarra, Reaction rate of sulfite oxidation catalyzed by cuprous ions, *Chem. Eng. J.* 145 (2008) 285–289.
- [23] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochman, *Advanced Inorganic Chemistry*, sixth ed., Wiley International, New York, 1999.
- [24] R.B. Bird, W.E. Stewart, E.N. Lighfoot, *Transport Phenomena*, second ed., Wiley International, New York, 2002.
- [25] B. Breman, A. Beenackers, M. Bouma, M. Van der Werf, The gas–liquid mass transfer coefficient ($k_{L,a}$) in the gas–liquid multi-stage agitated contactor (MAC), *Trans. IChemE* 74A (1996) 872.
- [26] L. Gunner Sillen, *Stability Constants of Metal Ion Complexes. Section I: Inorganics Ligands. Special Publication no. 17*, second ed., The Chemical Society London, London, 1964.
- [27] M. Sneed, J. Maynard, R. Brasted, *Comprehensive Inorganic Chemistry (vol. II): Copper, Gold and Silver*, first ed., D. Van Nostrand Company, New York, 1954.
- [28] N. Dahmo, Electrochemical oxidation of cyanide in the hydrocyclone cell, *Waste Manage.* 16 (4) (1996) 257–261.
- [29] J. Mishra, J. Joshi, Kinetics of reaction of cyanide at high temperatures, *Ind. J. Technol.* 25 (1988) 235–238.
- [30] W. Latimer, *Oxidation Potentials*, second ed., Prentice-Hall, New York, 1953.
- [31] S. Collado, A. Laca, M. Diaz, Wet oxidation of thiocyanate under different pH conditions. Kinetics and mechanistic analysis, *Ind. Eng. Chem. Res.* 48 (2009) 9902–9909.
- [32] N. Papassiopi, A. Gaunand, H. Renon, Oxidation of Cu(I) by oxygen in concentrated NaCl solutions I. Homogeneous kinetics of oxidation by molecular oxygen in solution, *Chem. Eng. Sci.* 40 (1985) 1527–1531.