



Simultaneous oxidation of cyanide and thiocyanate at high pressure and temperature



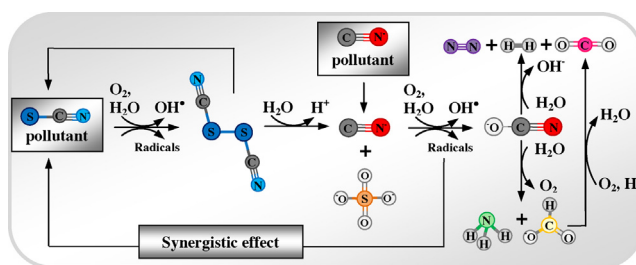
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HIGHLIGHTS

- The oxidation rate of SCN^- was greatly enhanced by the presence of CN^- .
- The degradation of mixtures was significantly affected by temperature and pressure.
- A free-radical pathway was proposed, CN^- and CNO^- being the reaction intermediates.
- The principal reaction products were found to be HCOO^- , NH_3 and SO_4^{2-} .
- One of the parallel routes gives the found products and the other N_2 , CO_2 and H_2 .

GRAPHICAL ABSTRACT



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ABSTRACT

Thiocyanate and cyanide are important contaminants that frequently appear mixed in industrial effluents. In this work the wet oxidation of mixtures of both compounds, simulating real compositions, was carried out in a semi-batch reactor at temperature between 393 K and 483 K and pressure in the range of 2.0–8.0 MPa. The presence of cyanide (3.85 mM) increased the kinetic constant of thiocyanate degradation by a factor of 1.6, in comparison to the value obtained for the individual degradation of thiocyanate, $(5.95 \pm 0.05) \times 10^{-5} \text{ s}^{-1}$. On the other hand, the addition of thiocyanate (0.98 mM) decreased the degradation rate of cyanide by 16%. This revealed the existence of synergistic and inhibitory phenomena between these two species. Additionally, cyanide was identified as an intermediate in the oxidation of thiocyanate, and formate, ammonia and sulfate were found to be the main reaction products. Taking into account the experimental data, a reaction pathway for the simultaneous wet oxidation of both pollutants was proposed. Two parallel reactions beginning from cyanate as intermediate were considered, one yielding ammonia and formate and the other giving carbon dioxide and nitrogen as final products.

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1. Introduction

According to the European Pollutant Release and Transfer Register (E-PRTR) of 2011, European annual emissions of total cyanide (free cyanide, cyanide complexes and thiocyanate) contained in industrial wastewaters are above 148 tons and Spain

is responsible for 6% of this amount [1]. The presence of cyanide in industrial effluents is an important environmental issue due to the acute toxicity of cyanide for living organisms, even at low concentrations [2,3]. Although thiocyanate is a less toxic form than cyanide, many harmful effects of thiocyanate on human health and the aquatic ecosystem have also been reported [4]. Moreover, several authors have reported that cyanide can be formed by the incomplete oxidation of thiocyanate [5,6].

Different biodegradation techniques have been proposed for the simultaneous treatment of these cyanide pollutants, including the use of bacterial co-culture, activated sludge and biofilm processes [7–10]. However, high concentrations of

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Nomenclature

C_i	concentration of component i in the reaction mixture (mM)
C_{i0}	initial concentration of component i in the reaction mixture (mM)
E_a	activation energy (kJ/mol)
k_i	apparent reaction rate constant (s^{-1})
k_1	reaction rate constant for the degradation of thiocyanate (s^{-1})
k_2	reaction rate constant for the degradation of cyanide (s^{-1})
k_3	reaction rate constant for the formation of formate and ammonia (s^{-1})
k_4	reaction rate constant for the formation of carbon dioxide and nitrogen (s^{-1})
k_5	reaction rate constant for the degradation of formate (s^{-1})
P	pressure (MPa)
r_i	reaction rate of component i (mol/Ls)
t	time (s)
T	temperature (K)

Greek symbols

α_i	oxygen reaction orders
α_1	oxygen reaction order for thiocyanate
α_2	oxygen reaction order for cyanide
α_3	oxygen reaction order for formate and ammonia
α_4	oxygen reaction order for carbon dioxide and nitrogen
β_i	reaction orders for initial concentration of thiocyanate
γ_i	reaction orders for initial concentration of cyanide

cyanide and thiocyanate and/or their simultaneous presence can cause inhibition of the biodegradation [9]. Hence, other treatments have been proposed, such as ferrate oxidation [5], hydrogen peroxide oxidation [11], photochemical oxidation [11], ozonation [12], coagulation–flocculation–sedimentation, Fenton oxidation and adsorption on activated carbon [13].

Wet oxidation is a well-established technique which involves the liquid-phase oxidation of organics and oxidizable inorganic compounds under high temperature (453–588 K) and pressure conditions (2.0–15.0 MPa) using a gaseous source of oxygen. The effectiveness of this technique for the treatment of wastewaters containing only cyanide [14–19], thiocyanate [20,21] or metal–cyanide complexes [22–24] has been proved. However, as far as we know, studies on the simultaneous wet oxidation of cyanide and thiocyanate do not exist, although these compounds are important pollutants in various industrial wastewaters and they commonly appear together. Besides, cyanide was proposed as an intermediate during thiocyanate oxidation [5]. The existence of synergistic and inhibitory effects is common in aqueous-phase oxidations, such as wet oxidation, and may affect the overall oxidation rate of the process significantly. Synergism involves the simultaneous reaction of two species, one being easily oxidized and the other more refractory to oxidation, with the easily oxidized component effectively increasing the oxidation rate of the refractory compound [25]. Hence, the values of the kinetic constants for the simultaneous degradation of thiocyanate and cyanide may be different from those obtained in the individual degradation of both pollutants. Moreover, the study of the simultaneous wet oxidation of these compounds could also be useful for clarifying the degradation pathway.

Consequently, the aim of this work was to investigate the kinetics that govern the wet oxidation of effluents containing a mixture of cyanide and thiocyanate and to propose a complete reaction pathway for the wet oxidation of these cyanide compounds, paying special attention to the synergistic and inhibitory effects. With this aim, a wide range of temperatures, pressures, initial concentrations of cyanide and thiocyanate were studied, and final reaction products and some intermediates were identified. This knowledge will allow a better evaluation of the applicability of this treatment for the oxidation of industrial cyanide wastewaters.

2. Experimental

2.1. Apparatus and procedure

Experiments were performed in a 1 L capacity semi-batch reactor (Parr T316SS) equipped with two six-bladed magnetically driven turbine agitators. A more detailed description of the experimental set up can be found in Oulego et al. [14]. In each run, the reactor was loaded with 0.7 L of distilled water and pH was adjusted to a suitable value using NaOH, so that after the addition of the cyanide and thiocyanate solution, the medium had a pH value of 11. This basic pH was used in order to prevent the formation of hydrocyanic acid ($pK_a = 9.21$ at 298 K) [26]. Once the desired conditions of pressure and temperature were achieved, 10 mL of a concentrated cyanide and thiocyanate solution (both sodium salts) was injected into the reactor. The concentration of this solution was calculated to give the desired concentration inside the reactor (in most cases 3.85 mM of cyanide and 2.20 mM of thiocyanate). These concentrations were selected taking into account the typical concentration of these pollutants in industrial effluents. Three bubblers filled with a concentrated sulfuric acid solution and two bubblers filled with a concentrated sodium hydroxide solution were installed at the end of the gas line with the purpose of absorbing ammonia and hydrocyanic acid, in case it was formed. All experiments were performed in triplicate.

2.2. Analytical methods

Concentrations of thiocyanate (SCN^-), sulfate (SO_4^{2-}), cyanate (CNO^-), formate ($HCOO^-$), nitrite (NO_2^-) and nitrate (NO_3^-), were monitored by using an ion exchange chromatograph (Dionex DX-120 Ion Chromatograph) and a suppressed conductivity detector (ASRS-ULTRA Autosuppression Recycle Mode). The eluent employed was a solution of 4.5 mM Na_2CO_3 and 0.8 mM $NaHCO_3$, with a flow rate of 1.04 mL/min; the precolumn was IonPac AG23 (4 mm \times 50 mm), and the column was IonPac AS23 (4 mm \times 250 mm). Cyanide concentration was measured by means of a cyanide ion-selective electrode (ISE Crison 9653) together with a double-junction reference electrode (Crison 5044) and an ISE-meter (Crison pH and Ion-Meter GLP 22). Total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) were measured using a TOC analyzer (Shimadzu TOC-V_{CSH}). Ammonia concentration was determined using the Nessler method [27] and pH was measured employing a selective electrode (pH Meter JENWAY 3510). All analytical measurements were made at least in triplicate, and the standard deviation was found to be below 5% in all cases. A portable gas detector (Gasman Crowcon detection) situated at the end of the gas line was used to determine the presence of hydrogen in the gas outflow.

3. Results and discussion

3.1. Simultaneous wet oxidation of cyanide and thiocyanate and reaction products

Fig. 1 compares the simultaneous wet oxidation of cyanide and thiocyanate with the individual wet oxidation of both pollutants. These runs were performed under 8.0 MPa of oxygen at 453 K, with an initial cyanide and thiocyanate concentration of 3.85 mM and 2.20 mM, respectively. The initial pH decreased as the reaction proceeded, its value being in the range of 11.0–10.6. This can be explained by the formation of protons (H^+) in the reaction medium as will be explained in Section 3.3. The same behavior was observed in all the experiments in this study. The concentration of thiocyanate and cyanide plotted in Fig. 1a and b are divided by the

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