Wet oxidation of real coke wastewater containing high thiocyanate concentration

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A B S T R A C T

Coke wastewaters, in particular those with high thiocyanate concentrations, represent an important environmental problem because of their very low biodegradability. In this work, the treatment by wet oxidation of real coke wastewaters containing concentrations of thiocyanate above 17 mM has been studied in a 1-L semi-batch reactor at temperatures between 453 and 493 K, with total oxygen pressures in the range of 2.0—8.0 MPa. A positive effect of the matrix of real coke wastewater was observed, resulting in faster thiocyanate degradation than was obtained with synthetic wastewaters. Besides, the effect of oxygen concentration and temperature on thiocyanate wet oxidation was more noticeable in real effluents than in synthetic wastewaters containing only thiocyanate. It was also observed that the degree of mineralization of the matrix organic compounds was higher when the initial thiocyanate concentration increased. Taking into account the experimental data, kinetic models were obtained, and a mechanism implying free radicals was proposed for thiocyanate oxidation in the matrix considered. In all cases, sulphate, carbonates and ammonium were identified as the main reaction products of thiocyanate wet oxidation.

1. Introduction

Iron and steel industries present a real environmental problem related to the existence of various heavily polluted effluents which must be treated before discharge into the environment. Most of these problematic wastewaters are generated in the coke-making process and contain significant amounts of toxic compounds, such as thiocyanate (SCN^-), phenolic compounds and cyanide (CN^-), as well as considerable concentrations of ammonium nitrogen (NH_4^+-N) and chlorides (Cl^-). Besides, lower concentrations of heavy metals, phosphorus, polyaromatic hydrocarbons and heterocyclic nitrogenous compounds are also common in these complex effluents (Chu et al., 2012).

Different biodegradation techniques have been proposed for the treatment of coke wastewaters, including the use of activated sludge in both single and multiple stage or biofilm processes (Staib and Lant, 2007). Depending on the characteristics of the stream being treated and the requirements of the output stream, various reactor types and configurations have been suggested: anoxic-aerobic reactors, anaerobic-anoxic-aerobic reactors, sequencing batch reactors, fix-bed biofilm reactors, fluidized bed reactors, membrane based reactors and moving bed biofilm reactors, among others (Jeong and Chung, 2006a; Sahariah and Chakraborty, 2011; Sirianuntapiboon et al., 2007; Zhao et al., 2009). Nevertheless, the coexistence of toxic compounds (CN^- and SCN^-) in the coke effluents can cause inhibitory effects on the biodegradation process (Jeong and Chung, 2006b). As a consequence, other treatments have been studied, such as adsorption, coagulation, ultrasonic irradiation and ozonation (Chang et al., 2008; Ning et al., 2005; Zhang et al., 2010a). However, these methods are either economically unfavourable or technically complicated, which make it difficult to use them in practice.

Wet oxidation has shown its effectiveness with several industrial effluents (Katsoni et al., 2008; Melero et al., 2009; Yang et al., 2010) and it seems to be an attractive method for the treatment of coke wastewaters as a previous stage to biological processes (Collado et al., 2012). This process implies the liquid-phase oxidation of toxic or poorly biodegradable compounds under high temperature (453—588 K) and pressure (2.0—15.0 MPa) conditions, using a gaseous source of oxygen.

Several authors have studied separately the wet oxidation of the main pollutants present in coke wastewaters, that is to say cyanide, phenol, thiocyanate and ammonia, the latter two being the most refractory to oxidation (Bhargava et al., 2006). However, very few works have studied the wet oxidation of real coke wastewaters. As far as we know, studies on the non-catalytic wet oxidation of real

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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
COD_{SCN^-}	chemical oxygen demand of thiocyanate
COD_m	chemical oxygen demand of the matrix
D_{O_2}	oxygen diffusivity in water
k_r	apparent reaction rate constant
k_L	mass-transfer coefficient for oxygen in the liquid phase
Ha	Hatta number
P	pressure
r_i	reaction rate for component i
R	gas constant
T	temperature
α, β	reaction orders

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coke wastewaters do not exist and only a few references focussing on the catalytic wet oxidation of these effluents have been found in the literature (Lei et al., 2005; Yang et al., 2007). These studies concentrated on the removal of chemical oxygen demand (COD) and ammonia, but did not analyze the oxidation of thiocyanate, which is one of the most problematic and toxic pollutants in coking effluents.

This contaminant has been successfully degraded in synthetic waters, but to determine the feasibility of applying this technique to coke effluents, it is necessary to study in depth the degradation of thiocyanate in the real matrix. Therefore, the first step is to establish the kinetics and mechanism by which the degradation occurs when real wastewaters are treated by non-catalytic wet oxidation. This knowledge will allow us to determine the potential of this technique under ideal operating conditions and also to establish the bases for the catalytic process.

Consequently, the aim of this work was to study the treatment of real coke wastewaters by non-catalytic wet oxidation processes, paying special attention to the effect of operating conditions on the degradation of thiocyanate and also the degree of mineralization achieved. In addition to this, the effect of the matrix on the performance of the thiocyanate degradation process was evaluated, and a kinetic model and mechanistic pathways were proposed on the basis of the experimental data.

2. Material and methods

2.1. Coke wastewater

The sample of coke wastewater used in the present work was supplied by a Spanish iron and steel plant and was stored at 277 K before experiments. It was deep brown in colour and had an unpleasant smell, pH being 9.0. The total organic matter measured as COD is 44 mM, this being biodegradable only around 14%. The main pollutants were ammonium (76.7 mM) and thiocyanate (20 mM). The concentrations of both free cyanide (CN^-) and weak acid dissociable (WAD) cyanide were negligible ($<1.9 \cdot 10^{-3}$ mM). A more detailed description of its composition is shown in Table S1 (see supplementary data).

2.2. Apparatus and procedure

Experiments were carried out in a 1-L capacity semi-batch 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 was about 70% of the total in order to ensure safe operating conditions. The equipment was charged with the coke wastewater, and in the experiments with different initial concentration ammonium thiocyanate was also added. Afterwards, the reactor was pressurized and heated up to the desired working conditions and the stirrer speed was adjusted to 500 rpm for all the experiments. The operating pressure was provided by bottled compressed oxygen, the oxygen flow rate being adjusted to 2.33×10^{-5} m^3/s and controlled by an electronic mass flow controller (Brooks). The oxygen was bubbled through the water reservoir in order to become saturated with water before being sparged into the reaction vessel. 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 experiment. The pressure was kept constant by means of a back pressure controller placed at the end of the gas line. One bubbler filled with concentrated sulphuric acid solution and two bubblers filled with concentrated sodium hydroxide solution were installed at the end of the gas line with the purpose of absorbing ammonia and/or hydrocyanic acid, if it was formed. Nevertheless, no cyanides were detected in any case in the bubbler liquid.

All oxidation assays reported in the present work were performed under kinetic control. The existence of this type of control was checked by means of the Hatta number (Ha), which relates diffusion and reaction rates (Equation (1)):

$$Ha = 1/k_L \sqrt{(2/\beta + 1)k_r D_{O_2} C_{SAT,O_2}^{\beta-1} C_{SCN_0^-}^{\alpha}} \qquad (1)$$

in which k_L is the mass transfer coefficient for oxygen in the liquid phase, k_r represents the reaction constant, D_{O_2} is the oxygen diffusivity in water and α and β are the reaction orders with respect to thiocyanate and oxygen respectively. During all runs, Ha ranged from 3.1×10^{-3} to 9.4×10^{-3}. These small Hatta number values ensure the absence of mass transfer limitations and the existence of kinetic control. Diffusivity of oxygen was calculated using the empirical expression proposed by Wilke (Bird et al., 2002) and the mass transfer coefficients were correlated according to an expression developed by Breman et al. (1996).

2.3. Analytical methods

The concentration of thiocyanate, phenolic compounds and COD were determined by colorimetric methods according to the Standard Methods (APHA et al., 1999). Thiocyanate was estimated using ferric nitrate at acidic pH at 460 nm. Phenolic compounds were measured by using the 4-aminoantipyrene method at 500 nm. COD was determined by the dichromate method at 600 nm. Thiocyanate was found experimentally to contribute to the total COD. Hence, $COD = COD_{SCN^-} + COD_m = 1.967 \times C_{SCN^-} + COD_m$, where COD is the total COD, COD_{SCN^-} is the COD of the thiocyanate, C_{SCN^-} is the concentration of thiocyanate and COD_m is the COD of the matrix (all compounds of the real wastewater except thiocyanate). The equipment employed for the spectrophotometric determinations was a UV/Vis spectrophotometer (Thermo Scientific, Heλios γ). Total nitrogen concentration was estimated by the Kjeldah method. pH was measured by means of a selective electrode (pHmeter ORION 9406 micro CM 2001).

The concentration of cyanide was determined potentiometrically, using a cyanide ion-selective electrode (ISE Crison 9653), in conjunction with a double-junction reference electrode (Crison 5044) and an ISE-meter (Crison pH & Ion-Meter GLP 22).