



Effect of the carboxylic substituent on the reactivity of the aromatic ring during the wet oxidation of phenolic acids

Sergio Collado, Adriana Laca, Mario Diaz*

Department of Chemical Engineering and Environmental Technology, University of Oviedo, E-33071 Oviedo, Spain

ARTICLE INFO

Article history:

Received 5 July 2010

Received in revised form

11 November 2010

Accepted 20 November 2010

Keywords:

Wet oxidation

Carboxylic group

Salicylic acid

p-Hydroxybenzoic acid

5-Hydroxyisophthalic acid

Electronic density

ABSTRACT

The wet oxidation of three phenolic acids that appear frequently in several industrial wastewaters (salicylic acid, *p*-hydroxybenzoic acid and 5-hydroxyisophthalic acid) was studied and compared with the wet air oxidation of phenol at 423 K, 1.0 MPa and pH 2. Results showed that the oxidation of salicylic acid and 5-hydroxyisophthalic acids was faster than phenol oxidation, with conversions of 100% and 90%, respectively after 200 min. The high reactivity of these compounds was attributed to the low electronic density of the aromatic ring, due to the ortho position of the substituents in the case of the salicylic acid and due to the presence of two carboxylic groups in the case of the 5-hydroxyisophthalic acid. On the other hand, *p*-hydroxybenzoic acid had a lower conversion rate and degree of mineralization than phenol, explained by the opposing effects on the electronic density of the aromatic ring of the substituents in the para position. In all cases, a maximum point in the colour of the reaction media (an indication of the accumulation of quinone-like compounds) was observed when the conversion of the phenolic compound was approximately 90%. Iron(II) changed the reactivity order of the phenolic compounds studied and, for any given conversion value, increased the degree of mineralization.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

For biotoxic organic pollutants (for which incineration is too costly or recovery is not profitable), wet oxidation is a promising route for pollution abatement and an alternative to other pre-treatment processes [1]. It avoids the regeneration of the adsorbent, necessary in the case of adsorption, and provides a more economically attractive process than chemical oxidation. This technique becomes of special interest when it is coupled with biological or physical–chemical final treatments [2–5].

At the high temperatures employed during the wet air oxidation processes, the form in which the oxygen participates in chemical reactions is quite complex. Elevated temperatures can lead to the formation of oxygen radicals O[•], which in turn can react with water and oxygen to form nucleophiles and electrophiles capable of participating in the first attack in the oxidation of the phenolic compound by means of a nucleophilic or electrophilic substitution [6]. The rate of attack of the nucleophile/electrophile to the aromatic ring depends on the degree of stabilization of the intermediate generated during the process. The free radical chain reaction mechanism that takes place during the wet air oxidation of pheno-

lic compounds suggests that the presence, number and position of different ring substituents may alter the reactivity of the phenolic compound [4]. The effect of the substituent on the aromatic ring is based on two factors: the inductive effects and the resonance effects [7]. The inductive effect of a substituent arises from the electrostatic interaction of the polarized substituent – ring bond whereas the resonance effect refers to the role of the substituent on the resonance stabilization of the intermediate. Except for halogens, resonance effects typically are stronger than inductive ones.

Most of the studies focused on the wet oxidation of phenolic compounds have been dedicated to phenol itself as a model pollutant, and only a few papers have investigated the oxidation of substituted phenols [4,8]. This is the case of the phenolic acids, which include benzoic acid derivatives such as hydroxybenzoic, gallic, vanillic, gentisic, protocatechuic or veratric acids. These compounds can be found in pharmaceutical and food processing wastewaters, incorporating into these effluents a significant contaminant load because of their high toxicity, refractory character and high stability in aqueous media.

In this work, salicylic, *p*-hydroxybenzoic and 5-hydroxyisophthalic acids have been selected as model pollutants to analyze the effect of the carboxylic group on the reactivity of the phenol-derivate (Table 1). These compounds are formed as by-products in the synthesis of salicylic acid or its derivatives, such as acetyl-salicylic acid, during the carboxylation of phenol with carbon dioxide. Their presence is frequent in pharmaceutical wastewaters, but also in wastewaters from cosmetic manufacture

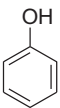
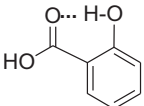
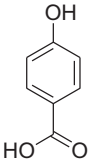
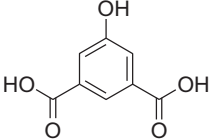
Abbreviations: 5HIA, 5-hydroxyisophthalic acid; A455 nm, absorbance at 455 nm; Ph, phenol; pHBA, *p*-hydroxybenzoic acid; SA, salicylic acid.

* Corresponding author. Tel.: +34 985103439; fax: +34 98103434.

E-mail address: mariodiaz@uniovi.es (M. Diaz).

Table 1

Structure of the compounds selected in this work (the formation of an intramolecular H-bond in the salicylic molecule is also showed).

Phenol (C ₆ H ₆ O) 94.1 g/mol	
Salicylic acid (C ₇ H ₆ O ₃) 138.1 g/mol	
<i>p</i> -Hydroxybenzoic acid (C ₇ H ₆ O ₃) 138.1 g/mol	
5-Hydroxyisophthalic acid (C ₈ H ₆ O ₅) 182.1 g/mol	

or the olive industry [9,10]. These compounds were selected for two reasons: their abundance in some real industrial wastewaters and the different position and number of the carboxylic groups in the aromatic ring (see Table 1), which allows the role of this group during the oxidation process to be analyzed.

The wet oxidation of salicylic acid, *p*-hydroxybenzoic acid or 5-hydroxyisophthalic acid has received little attention. Yang et al. [11] found that salicylic acid can be removed effectively at 413 K on perovskite-type oxide LaFeO₃. On the contrary, Tukac and Hanika [12] reported low conversions of salicylic acid (around 40%) during the wet oxidation of salicylic acid in a trickle bed reactor using activated carbon as catalyst. With respect to *p*-hydroxybenzoic acid, Creanga et al. [13] reported 80% conversions working at 2 bar and 413 K and employing activated carbon as catalyst. Pham Minh et al. [14] achieved a nearly total elimination of *p*-hydroxybenzoic acid within 7–8 h with a catalyst prepared on zirconia from Ru(NO)(NO₃)₃. In a recent work, Triki et al. [15] reported that Ru catalysts supported on Ce–Ti mixed oxides had good activity in the oxidation of *p*-hydroxybenzoic acid.

In this work, results obtained during the wet oxidation of the selected phenolic compounds were compared with those found in the case of phenol, which was taken as the reference compound, paying special attention to the effect of the carboxylic group on the reactivity, degree of mineralization and also the evolution of the colour of the media.

2. Materials and methods

A scheme of the semi-batch reactor used to conduct the wet oxidation experiments can be found in our previous work Collado et al. [16]. The reactor (Parr Model T316SS) had a capacity of 1 L and was equipped with two six-bladed magnetically driven turbine agitators. The reactor was preceded by a 2-L stainless steel water reservoir. In each run, the autoclave was loaded with 700 mL of distilled water and pH was adjusted to a suitable value using H₂SO₄, so that after the addition of the phenolic acid solution the medium had a pH value of 2 (pH 2.0 is the typical value found in real pharmaceutical wastewaters from aspirin synthesis). For catalytic oxidations, FeSO₄·7H₂O was dissolved in the water loaded in the reactor at the desired concentration. The autoclave was then sealed,

pressurized with oxygen to 1.0 MPa, and heated to 423 K. The stirrer speed was adjusted to 500 rpm for all the experiments. The operating pressure was provided by bottled compressed oxygen and controlled by an electronic mass flow controller (2.3×10^{-5} Nm³/s) and a backpressure controller located at the end of the gas line. The oxygen was bubbled through the water reservoir to become saturated with water vapour, and then it was introduced into the reaction vessel. Once the desired conditions were achieved, 2 mL of a concentrated phenolic compound solution was introduced into the reactor by an injection device. The phenolic compounds tested were phenol, salicylic acid, *p*-hydroxybenzoic acid and 5-hydroxyisophthalic acid. In the cases of salicylic, *p*-hydroxybenzoic and 5-hydroxyisophthalic acids, KOH was added to the solutions in order to dissolve these poorly soluble compounds. In all cases, concentrations of the solutions were calculated to give the desired concentration inside the reactor (5 mM). The moment of injection was taken as the starting time of the reaction. At pre-set reaction times, aliquots of the solution were withdrawn and analyzed for chemical oxygen demand (COD) and phenolic compound concentration.

The concentrations of phenolic compounds were determined by HPLC (Agilent Technologies 1200 Series) using a C18 reverse phase column. The mobile phase and detection wavelength were: methanol/water (40:60) and 254 nm for phenol; methanol/water (30:70) and 280 nm for salicylic acid; methanol/water (40:60) and 210 nm for *p*-hydroxybenzoic acid and methanol/water (30:70) and 240 nm for 5-hydroxyisophthalic acid. In the four cases, a flow rate 0.5 ml/min and an operation temperature of 298 K were selected. The COD was determined according to the Standard Methods for the Examination of Water and Wastewater [17]. Colour evolution was measured as absorbance of the media at 455 nm.

3. Results and discussion

Four phenolic pollutants with substituents sited in different positions (phenol (Ph), salicylic acid (SA), *p*-hydroxybenzoic acid (pHBA) and 5-hydroxyisophthalic acid (SHIA)) were oxidized at 423 K and 1.0 MPa, employing in each case an initial concentration of 5 mM. Initial pH was in all cases 2 and this value remained almost constant during the oxidation, only a slight decrease of around 0.1 pH units being detected.

3.1. Evolution of phenolic compound concentrations

Fig. 1 shows the evolution of the concentrations of the four compounds tested in this work.

As can be seen in Fig. 1, the four compounds were susceptible to degradation by non-catalytic wet oxidation. However, the number and position of the aromatic substituent clearly had an

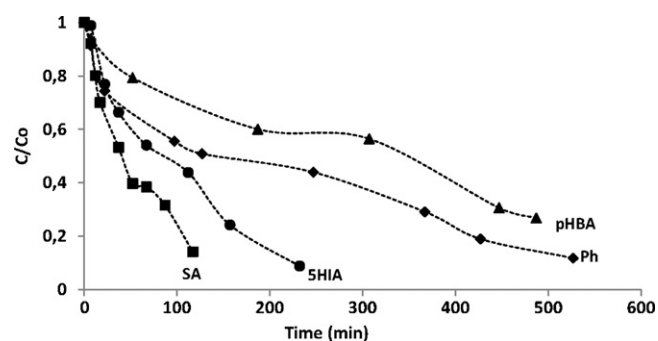


Fig. 1. Evolution of concentrations during the wet oxidation process: phenol (◆); salicylic acid (■), *p*-hydroxybenzoic acid (▲) and 5-hydroxyisophthalic acid (●). In all cases: $T = 423$ K; $P = 1.0$ MPa; initial concentration = 5 mM; pH = 2.

Download English Version:

<https://daneshyari.com/en/article/151472>

Download Persian Version:

<https://daneshyari.com/article/151472>

[Daneshyari.com](https://daneshyari.com)