



## Research article

## Wet air oxidation of resorcinol as a model treatment for refractory organics in wastewaters from the wood processing industry



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## ABSTRACT

Wastewater treatment systems are important tools to enhance sustainability in terms of reducing environmental impact and complying with sanitary requirements. This work addresses the wet air oxidation (WAO) process for pre-treatment of phenolic wastewater effluents. The aim was to increase biodegradability prior to a subsequent anaerobic stage. In WAO laboratory experiments using a micro-autoclave, the model compound resorcinol was degraded under different oxygen availability regimens within the temperature range 150 °C–270 °C. The activation energy was determined to be 51.5 kJ/mol. Analysis of the products revealed that after 3 h of reaction at 230 °C, 97.5% degradation of resorcinol was achieved. At 250 °C and the same reaction time complete removal of resorcinol was observed. In this case the total organic carbon content was reduced down to 29%, from 118.0 mg/L down to 34.4 mg/L. Under these process conditions, the pollutant was only partially mineralized and the ratio of the biological oxygen demand relative to the chemical oxygen demand, which is 0.07 for resorcinol, was increased to a value exceeding 0.5. The main by-product acetic acid, which is a preferred compound for methanogenic bacteria, was found to account for 33% of the total organic carbon.

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## 1. Introduction

Treatment of wastewater and potable water has become essential in modern societies. In practice, environmental compatibility and financial feasibility determine the methodology adopted for domestic and industrial water quality management (Balkema et al., 2001). Currently, efforts are being increasingly devoted to improving the energy efficiency of the processes employed. As a rule of thumb, an average input of 1.4 kWh to 3.2 kWh of electrical energy is necessary to remove 1 kg of biological oxygen demand (BOD), as reported in German wastewater treatment plants (Demoulin and Mervyn, 2003; Owen, 1982). Studies have indicated that the potential exists to decrease this energy input up to 50%

(Haber Kern et al., 2008; Olsson, 2012). One strategy is to rely upon scaled-up energy savings. However, small on-site treatment plants have a higher recycling potential (Bieker et al., 2010). Another strategy favours anaerobic treatment instead of energy-intensive aerobic processes (Diamantis et al., 2011; Descoins et al., 2012). For example treating industrial effluents anaerobically allows a saving of around 11.6 GJ in the form of biogas produced per Mg of COD degraded. Additionally it confers a lower electricity consumption of the order 1100 kWh since it removes the need for aeration (Speece, 1983; Svardal and Kroiss, 2011). Despite the progress that has been made in anaerobic digestion, a variety of recalcitrant compounds are still observed under anaerobic conditions (Sierra-Alvarez and Lettinga, 1991; Schonberg et al., 1997; Jonstrup et al., 2011). Anaerobically non-degradable pollutants, even with co-substrates, include *o*-cresol, benzene, 4-chlorophenol, alkylbenzenesulphonate, di-isopropyl ether (Kindziarski, 1991; Fedorak and Hruday, 1984; Bali and Sengül, 2003; Johnston et al., 1996). Degradation of such persistent substances can be enhanced by oxidative pre-treatment, giving rise to further

List of non standard abbreviations: DO, dissolved oxygen; HTC, hydrothermal carbonization; LTC, low temperature conversion; WAO, wet air oxidation.

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applications of efficient anaerobic technologies. Various technical processes have been applied: ozone oxidation, fenton oxidation, photo-fenton oxidation, photolysis/photocatalysis and wet air oxidation (WAO) (Suty et al., 2004; Vogelpohl, 2007; Gunten, 2007). The WAO process has a market share of 3–17% (Mantzavinos and Psillakis, 2004), since it is already a common practice in the pulp and paper industry (Maugans and Ellis, 2002; Luck, 1999), in the pre-treatment of landfill leachate and in the treatment of pharmaceutical wastewaters (Mishra et al., 1995). Process performance may be significantly enhanced when homogenous or heterogeneous catalysts are applied (Luck, 1999; Garg et al., 2010). An organic matter content above 10 g/L is characteristic for the application of WAO technology (Debellefontaine et al., 1996). However when these advanced aerobic treatment processes are used a variety of by-products are formed. The composition pattern of these by-products varies with temperature. Limiting the presence of oxygen favours the production of acetic acid (Li et al., 1991). This resembles the first three steps of classic anaerobic digestion. The subsequent biological anaerobic treatment produces biogas that is commonly used for the onsite generation of electricity with the possibility of waste heat recovery in the WAO process. As a consequence this kind of process combination does not need concentrations of organic matter over 4% to run the WAO process thermally autogenously (Baillod et al., 1985). The emerging practice of sequential exposure to wet air oxidation followed by anaerobic treatment is being exploited for the enhanced transformation of recalcitrant organics (Mantzavinos, 1999). Residual by-products have the potential to increase biogas yield in subsequent anaerobic digestion and show an improved biodegradability (Kacar et al., 2003; Kang et al., 2011).

One review in the literature reports the presence of phenolic substances in wastewaters from refineries, textile and resin industries and coal conversion plants (Veeresh et al., 2005). In addition, the emerging technologies of hydrothermal carbonisation (HTC), low-temperature conversion (LTC) and torrefaction of biomass (Stengl et al., 2012) produce complex wastewaters with inhibitory components in anaerobic consortia originating from the thermal degradation of lignocellulosic materials (Speece, 1999). Resorcinol is an aromatic compound that may be obtained either from nature or synthetically. It is a significant by-product in the manufacture of tires, diazo dyes and pharmaceuticals (Tschech and Schink, 1985). For example, in wastewater from a petroleum refinery Tyagi et al. detected resorcinol as one of the main constituents (Tyagi et al., 1993). One study classified resorcinol as very toxic after conducting a number of microbiotests (Kahru et al., 2000). Thus, these kinds of toxic effluents demand special attention. As a model component resorcinol has been shown to be slowly oxidized by HClO and NH<sub>2</sub>Cl (Cimetiere et al., 2009) and by periodate (Feifer et al., 1959). Other investigations report that resorcinol has been efficiently removed from water by electrochemical oxidation with boron-doped diamond electrodes requiring consumption of less than 30 Ah/dm<sup>3</sup> (Nasr et al., 2005); by ozone oxidation at 871 Pa partial pressure of ozone, 20 °C, neutral pH and high levels of turbulence within the reactor (Sotelo et al., 1990); by adsorption/oxidation with MnO<sub>2</sub> and KMnO<sub>4</sub> (Zhao et al., 2012); and by sono-photo-catalysis with H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub> at 0.75 g/L (Silva et al., 2007). In the present study, the process used was WAO, which has the advantage of using inexpensive air as oxidant and thermal energy that can provided by subsequent processing steps.

In laboratory-scale WAO experiments the degradation of initial resorcinol concentrations of 25 mg/L and 180 mg/L were investigated with respect to reaction time, temperature and the presence of dissolved oxygen. The formation of by-products is evaluated by UV/Vis analysis. Acetic acid concentrations were determined using an enzymatic method. Changes in biodegradability and the

remaining potential for anaerobic post-treatment were evaluated by TOC, COD and BOD analysis.

## 2. Material and methods

### 2.1. WAO treatment

The WAO treatment of resorcinol on the laboratory scale was performed in a tube reactor as shown in Fig. 1. The tube reactor consists of a laboratory grade stainless steel micro-autoclave equipped with a sodium calcium glass reaction tube with a volume of total 12 mL. The reaction tube was pre-treated with 2 mol/L hydrochloric acid solution overnight and washed with distilled water before use. Resorcinol (CAS-No. 108-4-63) was supplied by Sigma Aldrich. A stock solution with a concentration of 180 mg/L was prepared with distilled water and stored at 2 °C. The lower concentrations needed for the experiments were obtained by dilution. 7.5 mL of this aqueous solution of resorcinol of a known concentration was added to the reaction tube.

The dissolved oxygen concentration in the sample was adjusted in three different ways: a) Refrigeration overnight resulted in a dissolved oxygen concentration of approximately 7 mg/L due to the water solubility equilibrium. b) Bubbling pure oxygen into the bottom of the reaction tube for 5 min resulted in a dissolved oxygen concentration of 35 mg/L. After 5 min, the cap of the autoclave was closed immediately to maintain the oxygen concentration. In this case oxygen was also present in the gas phase. c) Bubbling of subliming CO<sub>2</sub> for 5 min at the base of the reaction tube eliminated nearly all of the oxygen from the system (residual oxygen concentration < 1 mg/L). The potential of oxidation capacity, X, referred to as the oxygen regime is expressed by the following equation:

$$X = \frac{c_{O_2}}{c_{COD}} \quad (1)$$

Here,  $c_{O_2}$  is the concentration of the dissolved oxygen, and  $c_{COD}$  is the theoretical chemical oxygen demand of the sample. Using concentrations of 25 mg/L and 180 mg/L of resorcinol (1 mg resorcinol = 1.89 mg COD<sub>theoretical</sub>) in the experiments, ratios of  $X = 0.75$  (25 mg/L resorcinol and oxygen); 0.1 (180 mg/L resorcinol and oxygen); 0.02 (180 mg/L resorcinol and air); and <0.003 (180 mg/L resorcinol and CO<sub>2</sub>) were investigated. Thus higher concentrations of resorcinol could not be investigated, because X is reduced proportionally. During the thermal treatment, limited oxygen transfer from the gas phase into the liquid is unavoidable.

After the autoclave was closed, it was placed into a laboratory

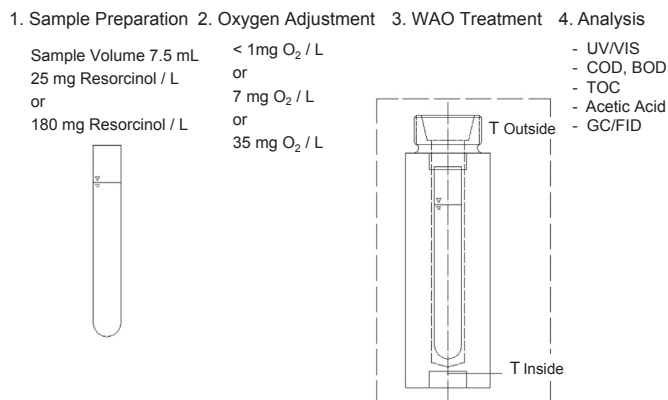


Fig. 1. Sketch of the sample preparation, wet air oxidation and analysis of products.

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