

Catalytic oxidation of industrial wastewaters - a comparison study using different analyzing methods

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Catalytic and non-catalytic wet air oxidation of industrial wastewaters was studied. Wastewaters originating from Finnish food industry were oxidized in a stainless steel autoclave at temperature of 150 °C and at pressure of 3.5 bar (air partial pressure). Ruthenium supported on Ce-Zr-mixed oxide was used as an oxidation catalyst. The progress of the oxidation processes were followed by sampling and analyzing water samples during the reactions. The changes in the composition of wastewaters (DOC, COD and manometric respirometric BOD) were determined as a function of time.

1. Introduction

The increased consumption of water, and therefore, the growing amounts of wastewaters force to find out more ecological and cost-efficient solutions to the wastewater treatment. Further, the legislation concerning the wastewater treatment and quality continuously become more restrictive.

The composition of wastewaters depends on the water source. Therefore, in the selection of the most suitable method for the specific effluent both the economics of the treatment as well as the feasibility of the process need to be considered. There are a number of different kinds of techniques available for the wastewater treatment such as chemical, physical and biological treatments and their combinations. All these technologies have their own application ranges depending on the composition and quantity of wastewaters produced. One available technique is wet air oxidation (WAO). WAO is a destructive wastewater treatment process where pollutants of the wastewater are oxidized with oxygen containing gas (typically air or oxygen) at elevated temperatures (125 °C - 300 °C) and pressures (0.5 - 20 MPa) to CO₂, water and also to intermediates which are usually carboxylic acids (Mishra et al. 1995). The enhanced solubility of oxygen in water at elevated temperatures and pressures provides a strong driving force for oxidation reaction (Kolaczowski et al. 1999). However, the energy-intensive WAO process may be quite too expensive for industrial use. The severe conditions (high temperature and pressure) of WAO can be reduced and the efficiency

of the process can be considerably improved by the use of heterogeneous catalysts (Levec and Pintar, 2007).

Catalytic wet air oxidation (CWAO) is a suitable technique for wastewaters with high COD value (Chemical Oxygen Demand) from 10 to 150 g L⁻¹. Hazardous wastes can also be treated and energy recovery is possible (Debellefontaine et al. 1996).

Supported noble metal (Pt, Ru, etc.) catalysts are developed and tested in order to improve the efficiency of the catalytic oxidation (Duprez et al. 1996, Oliviero et al. 2000). Ruthenium supported on ceria with high oxygen storage and exchanging capacity has shown to be a very effective catalyst in CWAO (Mikulová et al. 2007a, 2007b).

In this study, ruthenium catalyst supported on Ce_{0.85}Zr_{0.15}O₂ carrier was used to study the removal of organic impurities from food industry wastewaters. The high organic concentration is often a major problem in wastewaters from food industry, a reason why they are very suitable samples for CWAO.

The compositions of oxidized water samples were followed as a function of time. Organic concentrations were determined by DOC (Dissolved Organic Carbon) and by COD (Chemical Oxygen Demand) measurements. The BOD (Biological Oxygen Demand) was determined by the manometric respirometric BOD OxiTop[®] method. The different analyzing methods gave useful information about the wastewater samples, i.e. the compositions of these samples, after the oxidation. Combining the results, multifunctional data from the biodegradability of treated effluents was obtained.

2. Experimental

2.1 Catalyst preparation

The Ru catalyst (1.25 wt-%) was prepared by wet impregnation using Ce_{0.85}Zr_{0.15}O₂ as a support. 4.9 g of the support was stirred in vacuum for four hours with an aqueous solution of ruthenium chloride (Sigma Aldrich) containing 62.6 mg of the precursor salt. After the impregnation the catalyst was dried at 120 °C in air. The activation of the catalyst was made under hydrogen gas for 3 hours at 650 °C.

2.2 Oxidation reactions

Oxidation (catalytic and non-catalytic) of food industry wastewaters was investigated. The wastewater samples originated from the slaughterhouse and meat processing industry (initial DOC 800 mg L⁻¹, sample A) and from the potato and vegetable processing industry (initial DOC 7000 mg L⁻¹, sample B).

Oxidation reactions were carried out in a 2.4 L stainless steel autoclave equipped with a mechanical stirrer. Total oxidation times were between 90 to 180 minutes. The reaction temperature was 150 °C and the air partial pressure was 3.5 bar. Sample size was 500 mL and the catalyst load was 4 g L⁻¹. During the reaction water samples were taken periodically from the autoclave.

2.3 Analyzing methods

Organic concentrations of the wastewater samples were measured by DOC, COD and BOD₇. The wastewater samples were filtered before DOC and COD analysis in order to remove the suspended solids in the samples.

2.3.1. DOC

Dissolved organic carbon of the samples was measured by Sievers 900 Portable TOC analyzer. In this equipment the sample was first acidified by phosphoric acid and then the organic matter of the sample was oxidized by ammonium persulphate–UV-light combination to CO_2 . The concentration of the CO_2 was analyzed by electrical conductivity measurement and DOC of the sample was calculated automatically (GE Water and Process Technologies, 2006).

2.3.2. COD

COD of the wastewater samples was measured by Hach Lange DR 2800 spectrophotometer using Hach Lange cuvette tests (closed reflux dichromate method). In this method the organic matter of the sample reacts at high temperature ($148\text{ }^\circ\text{C}$) with potassium dichromate-sulfuric acid solution in the presence of silver sulphate as a catalyst. The green coloration of the Cr^{3+} was measured (Hach Lange, 2007).

2.3.3. BOD_7

BOD_7 was measured before and after the wet oxidation reactions (initial and terminal samples) using manometric respirometric BOD OxiTop[®] method. This test is based on the automatic pressure measurement in a closed bottle under constant temperature ($20.0 \pm 0.2\text{ }^\circ\text{C}$) (WTW, 2006). The organic matter of the sample consumes a certain amount of oxygen during the biodegradation. At the same time the formed CO_2 is bounded in an absorber (NaOH), i.e. the resulting pressure decline is a measure of the biological oxygen demand. The BOD value of the sample is measured automatically according to the ideal gas law modified for conditions in a closed space. Compared to common BOD determination methods, at the manometric respirometric BOD OxiTop[®] method the BOD value can be read continuously during the measurement. The measurement time can also vary between 30 min and 99 days. In this study the measurement time was seven days (WTW, 2006, Kuokkanen et al. 2004, Roppola et al. 2007).

3. Results and discussion

The DOC removal curves for catalytic and non-catalytic wet oxidation reactions of wastewaters A (slaughterhouse and meat processing industry) and B (potato and vegetable processing industry) are represented in figure 1.

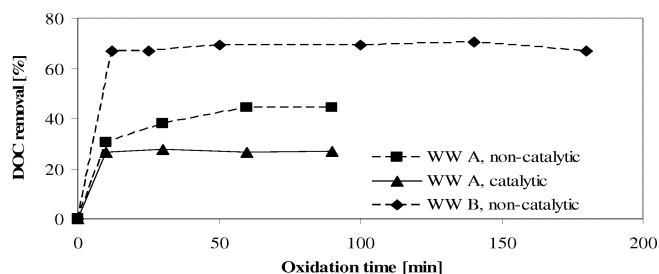


Figure 1. DOC removal efficiency as a function of time for the non-catalytic and catalytic wet air oxidation of food industry wastewaters. Operating conditions: temperature $150\text{ }^\circ\text{C}$, pressure 3.5 bar, catalyst $\text{Ru/Ce}_{0.85}\text{Zr}_{0.15}\text{O}_2$, catalyst load 4 g L^{-1} . WW A: wastewater from the slaughterhouse and meat processing industry, WW B: wastewater from the potato and vegetable processing industry.

DOC reduction efficiencies in the WAO were 45 % and 70 % for the wastewaters A and B, respectively. Accordingly, the initial DOC values were around 7000 mg L⁻¹ (wastewater B) and 800 mg L⁻¹ (wastewater A). Based on these results, it seems that when the initial DOC is higher the WAO is much more effective and the DOC removal is more considerable. Surprisingly, in the CWAO of the wastewater A the DOC removal was just around 30 %, i.e. Ru/Ce_{0.85}Zr_{0.15}O₂ catalyst did not have an influence on the reduction of the organic matter.

COD removal was around 40 % after WAO in both wastewaters A and B (figure 2). COD reductions in both WAO and CWAO treatment of wastewater A were equal with those of DOC removal efficiencies.

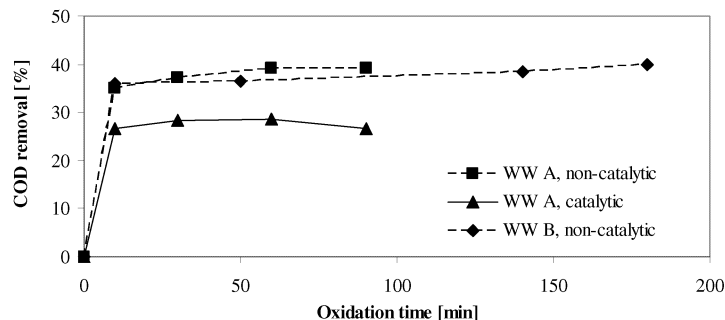


Figure 2. COD removal efficiency as a function of time for the non-catalytic and catalytic wet air oxidation of food industry wastewaters. Operating conditions: temperature 150 °C, pressure 3.5 bar, catalyst Ru/Ce_{0.85}Zr_{0.15}O₂, catalyst load 4 g L⁻¹. WW A: wastewater from the slaughterhouse and meat processing industry, WW B: wastewater from the potato and vegetable processing industry.

Obviously, organic compounds in the wastewater B were chemically more stable than in wastewater A, because the DOC removal in wastewater B was around 30 % larger than the COD reduction. The wastewater B was also quite acidic (pH around 4.3) which could also explain the lower COD removal efficiency.

The development of BOD values of the wastewater samples are described in figure 3. The great advantage of the manometric respirometric BOD OxiTop[®] test is that the BOD values can be read continuously during the measurement.

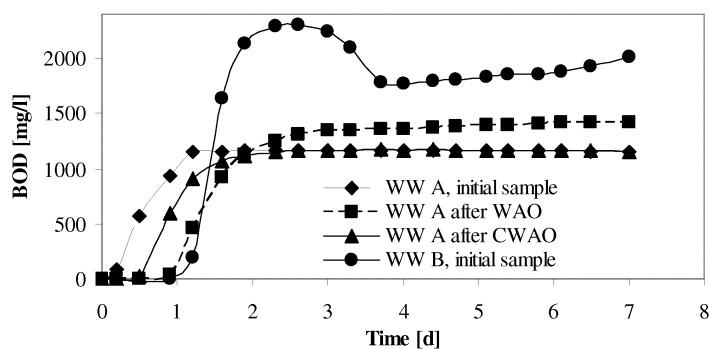


Figure 3. The development of BOD values of wastewater samples before and after the WAO and CWAO processes determined by respirometric BOD OxiTop[®] method at 20 °C.

After the incubation of the wastewater B, the biodegradation began only after 24 hours from starting of the measurement. After three days measurement the BOD value started to decrease. Evidently some other gases were formed causing the increase of the pressure and thus the BOD value decreases. The wastewater sample was quite well biodegradable and at the end of the measurement the BOD value seemed to steady.

The wet oxidation process did not have direct influence on the final BOD₇ value of the wastewater sample A. As a matter a fact, the BOD₇ was larger after WAO than in the initial sample and the CWAO did not change the BOD₇ value. However, in the beginning of the BOD measurement there was difference between initial and final samples: The initial sample started to biodegrade immediately but in the oxidized wastewater samples the biodegrading started until 12 - 24 hours after the BOD measurement began. Before the oxidation the pH of the wastewater sample A was around 6.5 but after WAO pH was 5.1 and after CWAO 5.3. The pH values and the inhibition step in the beginning of the BOD measurement refer to forming of intermediates like carboxylic acids. Although the catalyst (Ru/Ce_{0.85}Zr_{0.15}O₂) did not have direct influence on the removal of organic matter of the wastewater A it affected to its biodegrading: The inhibition step in the beginning of the BOD measurement was around half shorter than in the wastewater sample after WAO. Thus, the catalyst has promoted intermediates to oxidize further to final products, CO₂ and water. Also the wastewater sample transformed more biodegradable (BOD₇/COD value increased) during the CWAO.

4. Conclusions

The wet oxidation process decreased the organic concentrations of the food industry wastewaters. When the initial DOC was higher (wastewater B) the removal of organic compounds was more effective (DOC removal nearly 70 % during 3 hours experiment). Both DOC and COD reduction after WAO of the wastewater A was around 40 %. In this study the catalyst Ru/Ce_{0.85}Zr_{0.15}O₂ did not improve the removal of organic matter

of the wastewater A but after CWAO the wastewater was more biodegradable (BOD₇/COD value increased).

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