

Catalytic wet oxidation of *o*-chlorophenol at mild temperatures under alkaline conditions

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Abstract

Wet oxidation of a 100 ppm aqueous solution of *o*-chlorophenol (*o*-CP) was performed in a lab-scale batch reactor using 3% Ru/TiO₂ catalyst at 373 and 413 K, and a partial oxygen pressure of 0.1 MPa. The experiments were conducted by varying the initial pH values of *o*-CP solution from pH 6.3 to 9.8 and 11.8.

From the results, it was revealed that the catalytic decomposition of *o*-CP occurred most effectively at 413 K and at the initial pH of 9.8. Complete decomposition and dechlorination of *o*-CP were almost achieved within 1 h, and about 85% of TOC was removed in 3.0 h. On the other hand, the catalytic wet oxidation of *o*-CP at a higher pH value of 11.8 was not effective in the removal of TOC. The incomplete removal of TOC at the initial pH of 11.8 is likely attributed to a low p*K*_a of carboxylic acids formed during the wet oxidation of *o*-CP.

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1. Introduction

Industrial wastewater containing organic chloride compounds, which are highly toxic and harmful to humans, requires appropriate treatment before disposal. Biodegradation is one of the conventional treatment processes for wastewater contaminated with organic compounds. However, biodegradation of organic chlorides is not practical because of the low-decomposition rate for the treatment. Moreover, there are some concentration limits acceptable to bacteria for highly

toxic wastewater. The development of environmentally favorable techniques with high efficiency for the treatment of such organic wastewater has drawn considerable attention. Among several treatment techniques, the wet oxidation method has been attracting the interest of many researchers. In wet oxidation, the organic chloride contaminants dissolved in water are degraded by free radicals generated in the wet oxidation, to form biodegradable reaction products and inorganic compounds, with low-energy consumption at relatively low temperatures.

In the last decade, many researchers reported the decomposition behaviors of aromatic compounds (such as phenol and substituted phenols) and organic acids (such as acetic acid and formic acid) in aqueous solutions by conventional wet oxidation (Mishra et al.,

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1995; Luck, 1999). Joglekar et al. studied the kinetics of wet oxidation of phenol and substituted phenols in the temperature range of 423–453 K and oxygen partial pressure range of 0.3–1.5 MPa. They reported that there was an induction period for the wet oxidation of phenol and chlorophenol depending on the reaction temperature and the oxygen partial pressure (Joglekar et al., 1991). Keen and Baillod (1985) found that an aromatic compound underwent a ring-opening, resulting in the formation of maleic acid, oxalic acid, acetic acid, and formic acid in the wet oxidation of 5000 ppm aqueous phenol and substituted phenol solutions at 505 K and 5.2 MPa. In general, the wet oxidation of organic compounds was performed under high-total pressures (5–13 MPa) and at a higher temperature range (453–573 K). However, for the wet oxidation of organic chlorides, a serious corrosion problem arises at such high temperature and pressure, caused by HCl produced during the decomposition of organic chlorides. Therefore, it is preferable to operate at as low temperature as possible, for the decomposition of organic chlorides by wet oxidation. However, low temperature and pressure are unfavorable for effective degradation of organic compounds, in terms of reaction rate and reaction equilibrium (Qin et al., 2001). To make up for low efficiency of decomposition of organic compounds, it is effective to incorporate catalysts such as Ru/TiO₂ in the wet oxidation, thus increasing the rate of reaction by enhancing the activation of reactants. Many workers have reported decomposition studies on the catalytic wet oxidation of organic compounds in wastewater (Levec and Pintar, 1995; Mantzavinos et al., 1996; Matatov-Meytal and Sheintuch, 1998; Duprez et al., 1996). However, recent studies on the catalytic wet oxidation of organic chloride compounds at temperatures lower than 433 K are limited.

Alkaline agents such as NaOH are often used to neutralize the acids generated during the wet oxidation treatment of organic chloride compounds for the prevention of reactor corrosion by HCl. Besides, the addition of NaOH is considered either to promote or inhibit the degradation of organic compounds under the wet oxidation conditions. There are several reports about the effect of NaOH addition or pH on the decomposition of organic compounds in wet oxidation and catalytic wet oxidation at high temperatures (Keen and Baillod, 1985; Chang et al., 1995; Pintar and Levec, 1994a, b; Thomsen, 1998; Pintar et al., 2001a, b; Qin and Akita, 1998). However, there are few reports that explain clearly the effect of alkaline agent on the catalytic wet oxidation of organic chlorides. Pintar and Levec have reported that the conversion or decomposition of aqueous *p*-chlorophenol by catalytic liquid phase oxidation is markedly affected by pH (Pintar et al., 2001a, b). Yet, the pH-dependence on the dechlorination and removal of TOC during catalytic wet oxidation is still unclear.

The purpose of the present work is to study the catalytic wet oxidation of organic chloride at lower temperatures of 373 and 413 K by employing Ru/TiO₂ catalyst. The effect of initial pH on the catalytic wet oxidation of chlorophenol, one of the components of insecticides and herbicides, was investigated under alkaline conditions.

2. Experimental

2.1. Materials

Commercial grade *o*-chlorophenol from Waco Chemicals was employed as a model organic chloride sample. *o*-Chlorophenol was dissolved in distilled water to prepare 100 ppm aqueous solution. The initial pH was set in such a manner that the pH value of the solution after the wet oxidation of *o*-chlorophenol would be either acidic, neutral or alkaline condition. This initial pH was predetermined experimentally by adding NaOH to the solution. One gram of a ruthenium catalyst supported on TiO₂ (3% Ru/TiO₂) (Nikki Chemical Co. Ltd.) was added to 120 ml aqueous chlorophenol solution.

2.2. Experimental setup

Experiments were conducted using a commercial stainless-steel autoclave (OM Lab. Tech., Japan) with an inner volume of 200 ml schematically represented in Fig. 1. The reactor has an inner wall surface coated with Teflon to prevent it from corrosion by acid chlorides produced by the decomposition of *o*-chlorophenol. The reactor was equipped with a stirrer, a thermocouple, a sampling tube and a safety valve. The reaction temperature was kept at a prescribed constant temperature by controlling the electric power supply to an electric heater surrounding the outer wall of the reactor.

2.3. Experimental procedure

Prior to the wet oxidation experiment, 120 ml of *o*-chlorophenol aqueous solution of 100 ppm was charged into the reactor and the ruthenium catalyst was added. The reactor was purged by nitrogen (purity: 99.9%), until the reactor temperature was set at either 373 or 413 K. When the temperature of the reactor attained the prescribed temperature, pure oxygen was introduced into the reactor to adjust the initial O₂ partial pressure at 0.1 MPa. The amount of oxygen supplied to the reactor was sufficient for complete oxidation of all C and H molecules in *o*-chlorophenol to be converted to CO₂ and H₂O. The oxidation of *o*-chlorophenol was carried out for 0–24 h keeping a stirrer rotating at a speed of 150 rpm and temperature at 373 or 413 K. The reaction

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