

Short Communication

Wet air oxidation of nitrobenzene enhanced by phenol

Dongmei Fu, Jiping Chen, Xinmiao Liang *

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116011, China

Received 23 March 2004; received in revised form 21 October 2004; accepted 3 November 2004

Abstract

Simultaneous nitrobenzene and phenol wet air oxidation was investigated in a stainless autoclave at temperature range of 180–220 °C and 1.0 MPa oxygen partial pressure. Compared with the single oxidation of nitrobenzene under the same conditions, the presence of phenol in the reaction media greatly improved the removal efficiency of nitrobenzene. The effect of temperature on the reaction was studied. Phenol was considered as a type of initiator in the nitrobenzene oxidation.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Co-oxidation; Free radical; Promotion effect; Water treatment

1. Introduction

Nitrobenzene is a toxic and suspected carcinogenic compound that has been used by the industries for the production of aniline, aniline dyes, explosives, pesticides and drugs. It has also been used as a solvent in products like paints, shoes, floor metal polishes (Latifoglu and Gurol, 2003). Even at low concentrations, nitrobenzene may present high risks to environment (Bhatkhande et al., 2003). Since the degradation of nitrobenzene is very difficult to achieve, severe conditions were needed for its oxidation such as supercritical water oxidation (Arslan-Alaton and Ferry, 2002; Zhang and Hua, 2003). Other advanced oxidation processes like photocatalytic oxidation (Makarova et al., 2000; Rodriguez et al., 2002), sonolysis/ozonolysis (Weavers et al., 1998), ozonation and O₃/UV processes (Contreras et al., 2001), Fenton oxidation (Chamarro et al., 2001)

have been investigated for the same purpose. However, these methods are either expensive or ineffective for the treatment of nitrobenzene-containing wastewaters.

Wet air oxidation (WAO) is one of the promising technologies for wastewater treatment. In the process of WAO, the waste is oxidized to CO₂, H₂O and low molecule acids at elevated temperatures (150–325 °C) and pressures (0.5–20 MPa). With wastes of 2000 mg l⁻¹ COD or above, the process is self-sustaining, and it is suitable to treat hazardous and non-biodegradable wastes (Luck, 1999).

Numerous methods have been investigated to increase the oxidation rates and effectiveness of the WAO processes. Catalytic WAO processes received the attention since the 70s last century. Among them, the ones with homogeneous catalysts, especially Cu(II) salts, have the best effect to increase the overall reaction rate and catalyze the oxidation of small molecules and nitrophenols (Yoon et al., 2001). However, to overcome the problem of recovery/removal of the toxic catalysts from the final effluent, heterogeneous catalysts such as transition metal oxides, γ -alumina supported with CuO, copper, manganese, and lanthanum oxides on a

* Corresponding author. Tel.: +86 411 83699015; fax: +86 411 83606605.

E-mail address: liangxm@dicp.ac.cn (X. Liang).

zinc aluminate spinel, and multicomponent oxides $\text{CuO} \cdot \text{ZnO}$, Ru/Ce , Mn/Ce and Co/Bi have been developed (Imamura, 1999).

In recent years, WAO processes combined with other methods such as the use of hydrogen peroxide, ozone and ultrasonic technology have also been developed to increase the rate of waste oxidation (Andreozzi et al., 1999). Another way to increase oxidation rate is co-oxidation. It draws more and more attention of researchers. Willms et al. (1987) investigated the oxidation of *m*-xylene, and observed the promotion effect when the more easily oxidisable phenol was added to the system. Frederic (1998) observed that the presence of phenol moderately accelerated the degradation of nitrobenzene using $\text{H}_2\text{O}_2\text{-Fe}^{2+}$ catalyst in the WAO. Shende and Levec (1999) found that the conversion of formic acid was about 11% higher when it was mixed with equal molar of acetic acid under the same operating conditions. Similar evidence was found by Birchmeier et al. (2000), who added cellobiose or phenol to solutions containing recalcitrant products of incomplete oxidation and resulted in enhanced oxidation of the recalcitrant low molecular weight acids, and Mishra et al. (1995) experienced a similar trend when oxidizing diethanolamine and morpholine. Recently, Vicente and Diaz (2003) found that the degradation rate of thiocyanate was significantly enhanced when simultaneously oxidized together with phenol.

Since some compounds are very difficult to be oxidized under moderate reaction conditions, more easily oxidisable compounds may initiate the more difficultly oxidisable compounds. In this paper, phenol as an initiator to the nitrobenzene oxidation system was studied. The aim of the present work is to gain experimental information about the simultaneous nitrobenzene and phenol wet air oxidation.

2. Experimental

2.1. Wet air oxidation

The autoclave was made of stainless steel (SS316L) with inner volume of 400 ml. The reaction temperature was measured using a thermocouple and controlled by PID regulator.

The autoclave was charged with 200 ml aqueous solution, and the initial concentrations of nitrobenzene and phenol were 400 and 800 mg l^{-1} , respectively. The air in the reactor was purged with pure nitrogen for three times before nitrogen pressure of 3.0 MPa was maintained. Thereafter, the reactor was heated to the desired reaction temperature. Once the temperature was reached, pure oxygen of 1.0 MPa was supplied to the reactor and the reaction was considered to “zero”. The stirrer speed was set at 500 rpm to ensure vigorous mixing, and the oxidation rate was not controlled by mass transfer effect.

To compare with the co-oxidation of nitrobenzene and phenol, single nitrobenzene and single phenol oxidations were carried out, separately. Liquid samples were periodically withdrawn and analyzed for nitrobenzene and phenol contents. In the entire process, the system was kept under isobaric and isothermal conditions.

2.2. Analysis

The liquid samples were analyzed by HPLC with Waters 2487 double wave detector on a Kromasil C_{18} column (250×4.6 mm). The chromatography was calibrated with standard solutions. The mobile phase was water/methanol = 60/40 (v/v), with 265 nm as the detection wavelength for nitrobenzene analysis, and 270 nm for phenol.

3. Results and discussion

3.1. Single wet air oxidation of nitrobenzene

Single oxidation of nitrobenzene has been carried out at 180–260 °C. Nitrobenzene is very difficult to be oxidized at the temperatures studied. It only got 1%, 3%, 5% at 180, 200, 220 °C, respectively, after 3 h of oxidation. Even at 260 °C, it only got 14% of degradation. Ordinarily, it needs more severe conditions such as supercritical water oxidation (over 374.5 °C, and 22.1 MPa) to make it react rapidly.

3.2. Co-oxidation of nitrobenzene and phenol

Simultaneous wet oxidation of nitrobenzene and phenol was carried out at 220 °C. The initial concentrations were 400 mg l^{-1} of nitrobenzene and 800 mg l^{-1} of phenol. Under the co-oxidation conditions, the nitrobenzene reduction had a great improvement. It got only 5% in the single oxidation, while it turned to 30% in co-oxidation system.

3.2.1. Influence of temperature

The co-oxidation of nitrobenzene was further examined at four temperatures. Fig. 1(a) shows the removal efficiency of nitrobenzene versus time during co-oxidation experiments at different temperatures. As can be seen, there is an initiation period followed by a rapid degradation, which corresponds to the free radical reaction. Temperature has a great influence in the co-oxidation system. The initiation period is shortened when the temperature increases. At 180 °C, the addition of phenol has no promotion effect to nitrobenzene oxidation in the run time, but with the temperature increase, the promotion effect takes place. The removal of nitrobenzene is 1% at 190 °C in single oxidation experiment, while it reaches 23% in co-oxidation with phenol. The removal

Download English Version:

<https://daneshyari.com/en/article/9451698>

Download Persian Version:

<https://daneshyari.com/article/9451698>

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