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Oxidation of antipyrine by chlorine dioxide: reaction kinetics and degradation pathway

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Abstract:

Antipyrine (ANT, phenazone), a widely used anti-inflammatory analgesic in medical treatment, has been frequently detected in the aquatic environment. Chlorine disinfection process is thought as an efficient way to remove ANT, however, the potential risks of chlorine disinfection by-products (DBPs) such as trihalomethane (THMs) and haloacetic acids (HAAs) cannot be ignored. Chlorine dioxide (ClO_2) has been adopted as an effective alternative disinfectant of chlorine to reduce THMs and HAAs formation. In this work, the reaction kinetics and degradation pathway of ANT with ClO_2 were studied to investigate the feasibility of using ClO_2 as oxidant to degrade ANT. Experimental results demonstrated that ANT oxidation by ClO_2 followed second-order kinetics, and the second-order rate constant (k_{app}) was determined to be 4.8×10^{-1} $M^{-1}s^{-1}$ at neutral pH. Higher pH could accelerate the reaction when pH<9, while strong alkaline environment (pH>9) might significantly slow down the oxidation process. Structural change during the reaction was proposed with the assistance of fourier transform infrared spectroscopy (FT-IR), C=C and C-N bond of ANT were vulnerable under electrophilic attack of ClO_2. Degradation pathways of ANT with ClO_2 were suggested based on the main intermediate products. ANT was firstly transformed into ANT-Cl through single-electron-transfer (SET) and substitution reaction. Further oxidation of this intermediate product involved ring-opening reaction and de-carbonyl reaction.

Key words: antipyrine; chlorine dioxide; reaction kinetics; degradation pathway

1. Introduction

Pharmaceuticals are receiving increasing attention as potential bioactive chemicals in aquatic

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