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Degradation of octylphenol and nonylphenol by ozone – Part I: Direct reaction

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Abstract

This aqueous reaction between ozone and two alkylphenols (APs), namely octylphenol (OP) and nonylphenol (NP), has been investigated. Both compounds are important endocrine disrupting chemicals, which arise from the biodegradation of alkylphenol ethoxylates and are often found at relatively high concentrations in wastewater effluents. In this paper the results of an experimental study are presented which provide values for the reaction rate constants between molecular ozone and undissociated OP and NP, and overall reaction rate constants for the degradation of the two APs at pH values in the range of 7–9. The kinetic rate constants for OP and NP degradation by molecular ozone were $4.33(\pm 0.18) \times 10^4$ and $3.90(\pm 0.10) \times 10^4$ M^{-1} s^{-1}, and the reaction stoichiometry was similar in both cases and equal to approximately 1.3:1 ($[O_3]$:[AP]). The overall second order reaction rate constants for the two APs increased significantly with increasing pH, which is believed to be mainly due to the increasing influence of indirect radical reaction with increasing pH; this aspect is considered in more detail in a companion paper. A preliminary investigation of the reaction mechanism suggests that an initial product of ozonation is hydroxyl-alkyl phenol.

Keywords: Alkylphenol; Endocrine disrupting chemicals; Surfactant; Ozonation; Hydroxyl radical; Direct reaction

1. Introduction

Recently, a wide variety of chemicals have been identified which are capable of disrupting the endocrine systems of higher life forms, such as fish, wildlife and even humans; these have attracted considerable attention worldwide. The endocrine disrupting chemicals (EDCs) can be divided into two main categories: those that occur naturally and those that are synthetic. These EDCs may be released directly or indirectly to the aquatic environment, leading to alternations of normal hormone function and physiological status in wildlife and human (Butwell et al., 2002).

As one of the predominant EDCs, alkylphenol ethoxylates (APEOs) are the most widely used non-ionic surfactants, which comprise 6% of the total surfactant production in the world (Nimrod and Benson, 1996). They are widely used as cleaning products ($AP_{10–12}EOs$), detergents, emulsifiers ($AP_{n>20}EOs$), wetting agents ($AP_{8–9}EOs$) in domestic households, as dispersing agents in industry, and as pesticides ($AP_{n>15}EOs$) in agriculture (Planas et al., 2002; Ying et al., 2002). Consequently, a large quantity of APEOs is continually discharged to wastewater collection and treatment facilities, or directly released into the environment. One to one hundred repeating ethoxylate units (EO group) constitute the ethoxylate chain, and in general the longer the chain, the greater the water solubility of the compound (Ahel and Giger, 1993). In the UK, 16 000–19 000 ton of APEOs are consumed annually. Among this, it is estimated that 6500 ton are released to the aquatic environment (Butwell et al., 2002). Of all the APEO production, 80–85% is sold as nonylphenol ethoxylate and approximately 15% as octylphenol ethoxylate.

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In conventional biological wastewater treatment processes, the ethoxylate groups in the APEO molecule can be removed. This step is relatively fast, and the degradation products are alkylphenol (AP), alkylphenol monoethoxylate (AP_1EO), alkylphenol diethoxylate (AP_2EO), alkylphenol monocarboxylate (AP_1EC) and alkylphenol dicarboxylate (AP_2EC). The latter two compounds are generated by the oxidation of the hydroxyl group (–OH) to the carboxyl group (–COOH), which is summarised in Fig. 1. In anoxic conditions, these short chain APEOs or APECs can be further biodegraded to AP (Berryman et al., 2004). In general, the degradation of AP, AP_1EO and AP_2EO is relatively slow, which is partly due to the presence of the benzene ring in the molecules and their low solubility (Nimrod and Benson, 1996). As a result, the degradation of APEOs leads to the accumulation of AP, $AP_{1-3}EO$, and $AP_{1-3}EC$, which have potentially a greater toxicity and estrogenic activity than their parent compounds (White et al., 1994; Routledge and Sumpter, 1996; Mann and Boddy, 2000; Kanayama et al., 2003); thus, the main concern with APEOs is their biodegradation or metabolism during water and wastewater treatment (Lenz et al., 2004). It has been reported that their toxicity, persistence and estrogenic potency increase as the length of the ethoxylate chain decreases (Butwell et al., 2002). It has been shown that 4-*tert*-octylphenol has the greatest estrogenic potency of the APEO group of compounds (~1500 times less potent than 17β-estradiol), and 4-nonylphenol (4-NP) has the second greatest potency (~7000 less potent than 17β-estradiol) (Butwell et al., 2002). Although their estrogenic potency is three to six orders of magnitude lower than 17β-estradiol, their widespread use in industry led to a much higher concentrations in environment (more than 1000 times), which were not negligible (Villalobos et al., 1995).

Several technologies have been studied to further remove these short chain APEOs from the aquatic environment. In one study, two separate processes, membrane bioreactors and nanofiltration, were used to remove nonylphenol (NP), as reported by Wintgens et al. (2002). For the membrane bioreactor there was no significant removal of NP. With the nanofiltration process, they tested different nanofiltration membranes in the laboratory and found some removal of NP by molecular size exclusion. From their results, they expected higher removal efficiencies for other EDCs by nanofiltration since NP is one of the smallest EDCs in terms of molecular weight/size (Wintgens et al., 2002). Kuramitz et al. (2002) studied the electrochemical removal of NP from dilute solution using a carbon fibre anode by volta-metric techniques. The highest removal efficiency for NP was obtained when applying a potential at 0.7 V, and a complete removal from a 50 ml solution containing 5×10^{-6} M of NP was achieved in 10 min of oxidation. Furthermore, the result from this study also illustrated that the removal of NP from a wastewater could be successfully achieved through this method, even in the presence of other background organic substances with concentrations less than 10 mg l^{-1} (Kuramitz et al., 2002). In one study conducted by Goto et al. (2004), the degradation of $NP_{2-70}EO$ by UV irradiation was investigated. The EO side chain in $NP_{10}EO$ molecule was gradually degraded during UV irradiation, but the EO chain in $NP_{70}EO$ molecule was degraded near the benzene ring. The cleavage of benzene ring was observed, which was more effective in $NP_{70}EO$ than $NP_{10}EO$ molecule. The toxicity of the NPEOs with a smaller number of ethylene oxide unit was decreased by UV irradiation (Goto et al., 2004). Photodegradation (solar simulator irradiation) of APs was also performed by Kohtani et al. (2003). $BiVO_4$ was present as photocatalyst, which is suitable for the degradation of hydrophobic compounds, such as APs. Degradation rates were found to be increasing with increasing alkyl chain length. Half-life of NP was calculated at 18 min, which is approximately eight times shorter

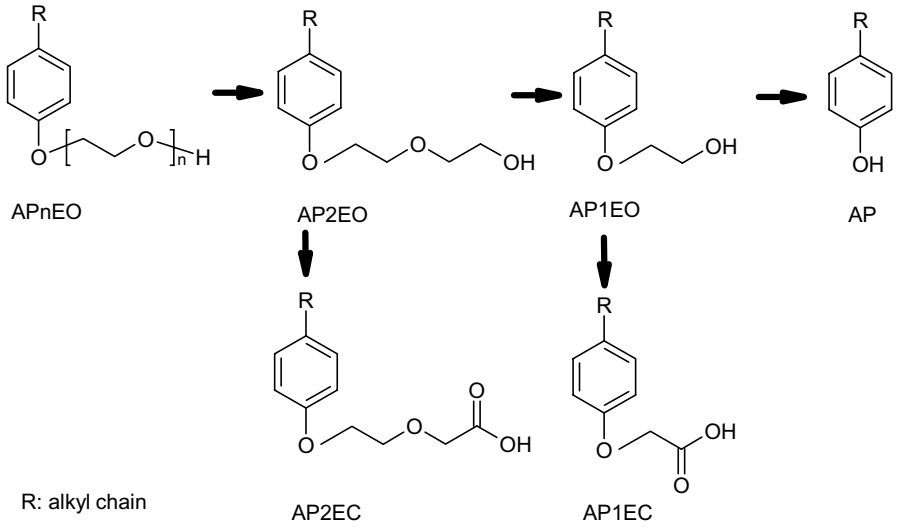

Fig. 1. Degradation pathway of AP_nEO compounds in conventional water and wastewater treatment processes.