

Chloride: A Menace to Advance Oxidation Processes (AOPs)

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A large amount of chloride ions in the real wastewater, ranging from 1.5 to 80 g/L, have been reported to scavenge hydroxyl radicals rapidly and therefore seriously deteriorate the overall treatment efficiency of advanced oxidation processes (AOPs) [1,2]. Most of previous studies have rather focused on the degradation kinetics of organic contaminants regarding Cl⁻ effect [3,4]. However, recent investigations revealed that the reactive chlorine species (Cl[•], Cl₂^{•-} and ClOH^{•-}) produced were capable of producing chlorinated intermediates [2,5,6]. Due to the high toxicity and potential carcinogenicity of these undesirable byproducts, it is urgent to elucidate their formation mechanism and fates in AOPs-based treatment before the large scale practical applications of AOPs are implemented. In this editorial, we will give some comments on the advance in AOPs-related saline wastewater treatment.

In the presence of chloride, Cl₂^{•-}/Cl[•] radicals generated may react with the organic molecules by one-electron oxidation, H-abstraction and addition to unsaturated C-C bonds, depending on the property of the substrates [7,8]. Addition to an aromatic ring takes place relatively slowly but various substituted aromatics can be efficiently oxidized by Cl₂^{•-}. Hydroxyl, methoxy and amino groups were observed to enhance the rate by one to two orders of magnitude, though their effect does not follow their Hammett's substituent constants [8]. A considerable inhibition is exerted by cyano and carboxyl groups when they are attached directly to the double bond. The greater selectivity for reactions of Cl₂^{•-} may be due to the lower C-Cl bond energy compared with C-H or C-OH [8]. Theoretically, Cl₂^{•-} is much less reactive than [•]OH. Therefore, the first step of chlorination may be [•]OH attack on aromatic ring, followed by chlorine radical reactions with substrate molecule and/or organic radicals as evidenced by the transformation of 1-naphthalenol to 4-chloro-1-naphthalenol in the previous study based on sulfate radicals [5]. Another important pathway may be related to the direct addition reaction on the double bond of organic compounds initiated by Cl[•] radical which are highly reactive compounds and readily take up an electron to complete its octet [5]. As a consequence, AOX (halogenated organic compounds adsorbable on activated carbon) formed in UV/TiO₂, UV/H₂O₂, Fenton, cobalt/peroxymonosulfate (Co/PMS) [5] and electrolytic oxidation systems [6] were reported recently by many researchers. The yield of AOX was found to increase with the initial content of chloride ions present in the wastewater [5,6].

It should be noted that many chlorinated aromatic pollutants are recalcitrant and have long half-lives. Some of them show a tendency to bioaccumulate due to their hydrophobicity and excellent ability to penetrate cell membranes while some are proven carcinogens and mutagens. If these byproducts are released into water bodies as a discharge effluent, it will pose a high toxicological risk to exposed humans and aquatic biota. Therefore, identification of these chlorinated byproducts and monitoring their further destruction processes seem more important to assess the safety of AOPs in the presence of Cl⁻. Until now, some researches have detected the chlorinated intermediates generated in Co/PMS system and UV/NaClO process [5]. 2,4-dichlorophenol, 2,5-dichlorohydroquinone, 2,4,6-trichlorophenol, 2,3,5,6-tetrachlorophenol and tetrachlorohydroquinone measured as the chlorinated byproducts of dye wastewater in Co/PMS system had high biological toxicities [5].

However, AOX detected and the chlorinated byproducts mainly detected by GC-MS instrument can just represent parts of the total

chlorinated compound (TOX). In addition, it is difficult to deduce degradation mechanisms of the organic contaminants involving chlorine radicals due to the limited knowledge of the chlorinated compounds formed at certain reaction time [5,6]. The authors propose to employ combined computational and experimental testing methods to evaluate the Cl⁻ effect on AOPs treatment. They are 3 systematic categories as following:

1. Developing a quantum-chemical calculation method to predict the reaction pathways of chlorinated organic compounds, based on the potential energy surfaces and activation energy of reactants, intermediates, transition states and possible products.
2. Selecting some representative organic molecules as models to analyze their intermediates and ultimate products during AOPs treatment in the absence and in the presence of chloride ions.
3. Evaluating their biological toxicities and biodegradabilities of the chlorinated byproducts, especially new identified products occurred in the recent studies. These results may provide useful information for predicting and assessing the safety of AOPs in the application of high salinity wastewater.

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