Kinetics and Thermodynamics of Hydroxyl Radical Reaction with Chloramines Under Advanced Oxidation Process Conditions

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The Orange County Water District (OCWD) in Fountain Valley, CA, utilizes a final Advanced Oxidation Process (AOP) after their primary, secondary, microfiltration (MF) and reverse osmosis (RO) processes in their treatment of wastewaters. This AOP utilizes a combination of UV light and hydrogen peroxide to generate the powerful oxidizing hydroxyl radical (\(\cdot \text{OH}\)) which can mineralize any remaining chemical contaminants. However, during the treatment, chloramines (\(\text{NH}_2\text{Cl}, \text{NHCl}_2, \text{and NCl}_3\)) are deliberately generated in the wastewater stream as an anti-biofouling agent for the RO membranes. The chloramines are produced by adding a 12.5% basic hypochlorite solution into the wastewater stream through a single-point feeder pipe. The reaction of hypochlorite with the natural ammonia in the water forms all three chloramines, initially favors trichloramine due to the high pH at the point of addition, but as the chloramines move through the system the pH shifts to 5.5 while the equilibrium becomes equal parts monochloramine and dichloramine with only trace amounts of trichloramine remaining. However, all three chloramines continue on into the AOP, which can significantly decrease the efficiency for the production and reactivity of \(\cdot \text{OH}\) with desired chemical contaminants. Understanding the impact of the chloramines in the AOP is essential for its optimal operation. In this study, the absolute second-order kinetics of these three chloramines with the \(\cdot \text{OH}\) radical have been quantified. Decreasing \(\cdot \text{OH}\) radical reactivity with increasing chlorine substitution was observed; however, all three chloramines reacted quickly (\(k = 1-5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}\)). Additionally, the temperature dependence of these reactions has been studied to determine their Arrhenius activation energies. These data will be combined with other performance factors to study the overall effects these chloramines have on the efficiency of the AOP.

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