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Concentration profiles of chlorine radicals and their significances in •OH-induced dye degradation: Kinetic modeling and reaction pathways

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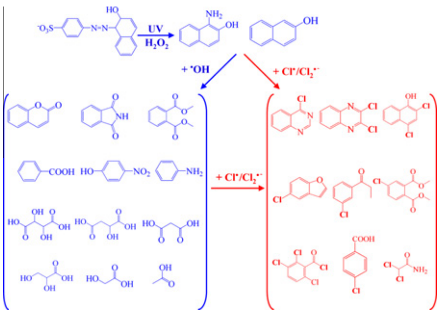
HIGHLIGHTS

- Concentration profiles of chlorine radicals were obtained by kinetic modeling.
- Several refractory halogenated byproducts were identified by GC–MS measurement.
- Possible reaction pathways involving hydroxyl/chlorine radicals were proposed.
- pH effect on chloride retardation in dye photobleaching was found.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to further understand the mechanism details during saline wastewater treatment by •OH-based advanced oxidation processes (AOPs), the degradation efficiency of an azo dye Acid Orange 7 (AO7) in UV/H_2O_2 process was investigated as a function of a wide range of salinity and pH. Kinetic modeling results demonstrated that the inhibitory effect of Cl^- on AO7 degradation observed in the laboratory experiments could be attributed to both scavenging effect of Cl^- on •OH and the much lower reactivity of chlorine radicals formed, although the chlorine radicals may be more abundant than •OH. Such retardation behavior was favored under acidic conditions due to a lower yield of •OH generated by the dissociation of $ClOH^{•-}$ to •OH and Cl^-. Traces of Br^- had a greater inhibitory effect on AO7 bleaching rate than Cl^-. AOX (halogenated organic compounds adsorbable on activated carbon) was found to increase with the increasing content of Cl^-. Based on the intermediate products and especially several toxic halogenated byproducts identified by GC–MS, the possible degradation pathways of saline dyeing wastewater were proposed.

1. Introduction

The chloride ions in industrial wastewaters have been found to scavenge hydroxyl radical (•OH) rapidly to form less reactive chlorine radicals ($Cl_2^{•-}$, $Cl^•$ and $ClOH^{•-}$), leading to significant influence on the degradation kinetics of organic contaminants during advanced oxidation processes (AOPs) [1–4]. Many researchers have observed the inhibitory effect of chloride ions on the oxidation degradation of various organic compounds [5–9]. For example, the decoloration rate of three dyes was found to decline significantly with the increasing concentration of sodium or potassium chloride [7].

Recently, a series of systematic investigations by our group have revealed a dual effect of chloride ions (i.e. inhibitory and accelerating effect) on azo dye degradation in UV/TiO_2 process and an emerging cobalt/peroxymonosulfate (Co/PMS) system over a wide range of salinity [1,3,10]. In the UV/TiO_2 system, Cl^- ions (0–200 mM) significantly enhanced the dye decoloration, but further addition of Cl^- apparently inhibited the dye degradation process [3]. For the Co/PMS system based on sulfate radical, the

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decoloration rate of dye was found to decrease significantly with lower chloride ion content (<5 mM), but higher content of chloride ions accelerated the dye bleaching rate [10]. Furthermore, several hazardous chlorinated byproducts, including 2,5-dichlorohydroquinone, 2,4,6-trichlorophenol and 2,3,5,6-tetrachlorophenol, were identified during the treatment of high salinity dyeing wastewater by both of these technologies. Though the possible degradation pathways of dye in the presence of Cl^- have been proposed by our previous studies [3,10], the exact mechanisms involving various chlorine radicals and their corresponding complicated reactions remain inadequately described. For radical-based chain reactions and the multiphase reaction pathways this can be attributed to difficulties in quantitatively detecting these chlorine radicals produced and limitations of reaction systems with unknown rate constants. In the heterogeneous UV/TiO_2 system, for instance, the chloride ions cannot only influence the dye adsorption on the catalyst surface, but also participate in the dye oxidation activated by reactions with both the photo-induced holes (h^+) and hydroxyl radical formed. These indeed complicated the kinetic analysis [3].

The homogenous photochemical process UV/H_2O_2 is relatively suitable for the detailed kinetic modeling analysis due to its simpler reaction conditions and the known reaction rate constants involved. Grebel et al. have tried to evaluate the importance of halogen and hydroxyl radical for organic degradation under neutral conditions [11]. Since the increase in pH may counteract the $^{\bullet}OH$ scavenging action of chloride ions, the effect of chloride was highly dependent on the solution pH [3]. Therefore, in this research, kinetic modeling based on radical reactions was implemented to examine the impact of both chloride ion concentrations and solution pH on the degradation efficiency of organic contaminant. A common nonbiodegradable azo dye Acid Orange 7 (AO7), widely used in industrial applications and laboratory studies, was chosen as the substrate, to compare the different dye degradation mechanisms in various AOPs under hypersaline environment. Laboratory experiments were carried out over a wide range of initial concentrations of chloride ions and solution pH. The experimental data were compared with the kinetic model to investigate the chlorine species responsible for dye degradation at different pH. Such kinetic modeling analysis can provide further understanding of the complex reaction mechanisms by identifying the important reaction pathways for dye degradation, which is difficult to be explained by other methods.

Besides chloride ion, bromide ion (Br^-) as the impurity of industrial salts was also investigated owing to its greater $^{\bullet}OH$ radicals scavenging ability and high cyto- or genotoxicity of brominated compounds possibly generated [11]. The effect of bromide ions on dye decoloration in aqueous solution was studied and the brominated intermediate products were examined based on GC–MS measurement. This work concerning the influence of halide ions on the kinetics of dye degradation and the formation of halogenated byproducts hopefully provides more insight into the degradation mechanism of high salinity wastewater.

2. Experimental

2.1. Materials

Acid Orange 7 (AO7: $C_{16}H_{11}N_2O_4SNa$) in the present work was obtained from Sigma–Aldrich Company. H_2O_2 (30%), NaCl and NaBr in the purest form were of analytical grade and used as received. The solution pH was adjusted by addition of sulfuric acid or sodium hydroxide, depending on the experimental conditions. The salinity was varied by addition of NaCl and NaBr. All sample solutions were prepared using deionized water from Barnstead UltraPure instrument.

2.2. Experimental procedures

The photodegradation of AO7 was conducted in an XPA-II type photochemical reactor (Nanjing Xujiang Electromechanical Plant, China). One 100 W medium-pressure mercury vapor lamp (λ_{max} = 365 nm) was used as the light source. The lamp is put into a hollow quartz hydrazine which is located in the middle of the reactor. Twelve holes which are used to put quartz tubes evenly distribute around the lamp and the distance between the lamp and each hole is equal. The light intensity at quartz tube positions was measured to be 12.7 mW/cm^2 by a UV-A irradiation meter (Photoelectric Instrument Factory of Beijing Normal University, China). The temperatures of reaction solutions were maintained at (25 ± 2) °C by a cooling water circulation. The solution was continuously stirred and aerated. The oxidation of AO7 by H_2O_2 was found to be negligible through dark control experiment.

The concentration of AO7 during degradation process was measured with UV–vis spectrophotometer (Hitachi U-2910) at 485 nm. Calibrations were performed at each tested pH in the present study to account for possible change in absorbance of AO7 at different pH values. The dye decoloration rates were described by pseudo-first-order model. TOC (total organic carbon) measurements at certain time intervals were carried out by a Shimazu TOC-V_{CPH} analyzer. According to our preliminary experiments, there is little interference of chloride ions on TOC measurement. The AOX determinations were carried out by instrumental analysis (AOX, multi X® 2000, Jena, Germany) after enrichment on activated carbon (European Standard EN 1485 H14, 1996). Dye degradation products in the presence of chloride ions were identified by GC–MS instrument (Agilent 7890A–5973N). Samples were pretreated by solid-phase extraction, liquid–liquid extraction and silylation methods to extract and concentrate compounds of different polarity and volatility. The GC–MS measurement conditions in details are available in our previous studies [3,10].

2.3. Kinetic modeling

Kinetic modeling of UV/H_2O_2 system was performed using chemical modeling software, Kintecus 4.40 [12]. Table S1 describes the reaction set used as input for the program. This reaction scheme based on radical reactions has been shown to effectively simulate the decomposition of H_2O_2 in homogeneous aqueous solutions under certain conditions [11,13]. In general the rate constants in Table S1 were cited from the previous literatures [11,14,15]. Optimization of unknown or poorly defined parameters was undertaken by use of a numerical routine incorporated into the Kintecus program to accurately simulate species profiles. The formation of hydroxyl radical, chlorine radicals and the corresponding degradation products of AO7 was finally modeled. To examine the sensitivity of the model to variation in a particular rate constant, the average normalized square of residuals between the original (control) model output and the perturbed model output was calculated, according to the method reported by Rose and Waite [16].

3. Results and discussion

3.1. Dye decoloration kinetics

A sharp decrease of the initial rate of dye decoloration was observed with the increasing concentration of sodium chloride or bromide (Fig. 1), which may be mainly attributed to $^{\bullet}OH$ radical scavenging by halide ions as discussed previously [5,17]. The higher scavenging effect of bromide ions (rate constant of $1.1 \times 10^{10}\ M^{-1}\ s^{-1}$) on $^{\bullet}OH$ radicals was reflected by the much