



Probing the radical chemistry in UV/persulfate-based saline wastewater treatment: Kinetics modeling and byproducts identification



Ruixia Yuan^{a,b}, Zhaohui Wang^{b,*}, Yin Hu^b, Baohui Wang^a, Simeng Gao^a

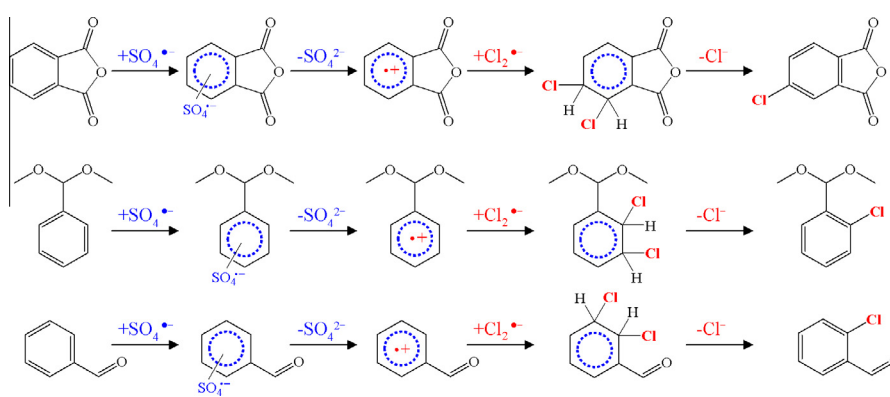
^a Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing 163318, China

^b College of Environmental Science and Engineering, Donghua University, Shanghai 201620, China

HIGHLIGHTS

- Concentration profiles of chlorine radicals in UV/S₂O₈²⁻ system were modelled.
- pH is a critical variable influencing chlorine radical chemistry in dye degradation.
- Several refractory chlorinated byproducts were identified by GC–MS measurement.
- Possible reaction pathways involving sulfate radical/chlorine radicals were proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 December 2013
 Received in revised form 6 March 2014
 Accepted 10 March 2014
 Available online 22 April 2014

Handling Editor: O. Hao

Keywords:

Sulfate radical
 Chloride ion
 Kinetic modeling
 Chlorinated byproducts

ABSTRACT

The effect of Cl⁻ on the oxidative degradation of Acid Orange 7 (AO7) was investigated in UV/S₂O₈²⁻ system to elucidate the chlorination pathways in saline wastewaters. Lower amount of Cl⁻ as well as Br⁻ enhanced the decoloration of AO7, but such promotion effect reduced gradually with the increasing halide ion dosage. The dye mineralization was found to be inhibited by Cl⁻, especially under acidic conditions. Results of kinetics modeling demonstrated that the fraction of different oxidizing radicals largely depended on the content of Cl⁻. At the initial pH of 6.5, Cl₂⁻ was much more abundant than SO₄⁻. The significance of Cl₂⁻ for AO7 degradation increased with the increasing Cl⁻ concentration and overwhelmed that of SO₄⁻ at [Cl⁻] > 1 mM. Without Cl⁻, SO₄⁻ was the predominant radical for AO7 degradation under acidic conditions, while ·OH prevailed gradually at higher pH. Under high salinity conditions, more ·OH can be formed and contributed to the dye degradation especially in alkaline medium, leading to higher destruction efficiency of AO7. Several chlorinated byproducts were detected in the presence of chloride ions, and SO₄⁻/Cl₂⁻-based degradation pathways of AO7 were proposed. This work provides further understanding of the complex reaction mechanisms for SO₄⁻-based advanced oxidation processes in chloride-rich environments.

© 2014 Elsevier Ltd. All rights reserved.

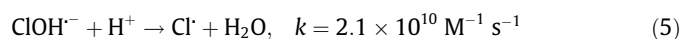
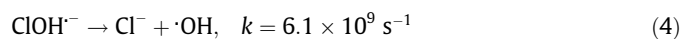
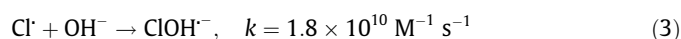
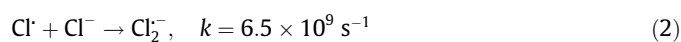
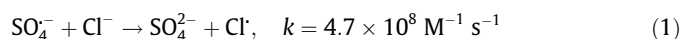
1. Introduction

Many kinds of industry wastewaters from dyeing, pesticide production, pharmacy, petroleum, agro-food and seafood processing contain large amounts of Cl⁻, ranging from 1.5 to 80 g L⁻¹

* Corresponding author. Tel.: +86 21 6779 2557; fax: +86 21 6779 2522.
 E-mail address: zhaohuiwang@dhu.edu.cn (Z. Wang).

(Table SM-1 in the Supplementary Materials). Recently the involvement of chloride in SO_4^- -based advanced oxidation processes (AOPs) has attracted great scientific interest in saline wastewater treatment (Anipsitakis et al., 2006; Chan and Chu, 2009; Wang et al., 2011; Yuan et al., 2011). However, the effects of Cl^- on the efficiency of SO_4^- -based AOPs remain obscure so far, even some conflicting conclusions have been drawn from different investigations. For instance, Anipsitakis et al. (2006) observed faster degradation kinetics of phenol and 2,4-dichlorophenol due to a small amount of Cl^- in cobalt/peroxymonosulfate (Co/PMS) system. Yang et al. (2010) reported that the destruction of an azo dye can be enhanced by Cl^- without catalyst, possibly resulting from the activation of PMS with unsymmetrical structure. In contrast, Chan and Chu (2009) found Cl^- exhibited significant inhibitory effect on the degradation of atrazine by PMS. In addition, dual effects of Cl^- (i.e. inhibitory and accelerating effect) on azo dye degradation in Co/PMS process have been reported by our group (Yuan et al., 2011). It should be noted that the formation of high toxic and refractory chlorinated byproducts was also observed during the transformation process of salinity wastewater (Anipsitakis et al., 2006; Yuan et al., 2011; Xu et al., 2013).

Furthermore, the kinetics and reaction mechanism are not well understood until now, mainly owing to the complicated reaction pathways involving various radicals and several unknown rate constants of catalytic reactions. For Co/PMS process, Cl^- can not only scavenge SO_4^- (2.5 V) to generate less reactive chlorine radicals (Cl_2^- , Cl^\cdot and ClOH^-), but also directly reduce PMS through two electron transfer, producing reactive halogens (e.g. Cl_2/HClO). These complicated the kinetic analysis and further efforts towards the degradation mechanisms involving the SO_4^- -based AOPs. Hence, it is necessary to probe the radical chemistry in a simpler system where Cl^- can be only activated by SO_4^- . As the result of high generation efficiency of SO_4^- by photolysis of $\text{S}_2\text{O}_8^{2-}$ and much lower oxidation reactivity of $\text{S}_2\text{O}_8^{2-}$, contaminants can be assumed to be degraded by mere SO_4^- . Therefore, it is assumed that Cl^- is only involved in the reactions of UV/ $\text{S}_2\text{O}_8^{2-}$ process through radical chain reactions (Eqs. (1)–(5)), making it possible to investigate the free radical chemistry in UV/ $\text{S}_2\text{O}_8^{2-}$ process.



In this study, the impact of both Cl^- concentration and solution pH on the degradation efficiency of an azo dye Acid Orange 7 (AO7) was examined. The experimental data were then compared and elucidated with the kinetic modeling results, to investigate the reactivity of various radicals with organic contaminant and their participation in chain propagation reactions under a chloride-rich environment. The possible formation of chlorinated byproducts was studied based on GC–MS measurement. Besides, the effect of Br^- , a common impurity in industrial NaCl (with 0.2–0.25% Br^- impurity) was also investigated.

2. Materials and methods

2.1. Materials

AO7 ($\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_4\text{SNa}$, 98%), $\text{K}_2\text{S}_2\text{O}_8$ (99%), dichloromethane (CH_2Cl_2 , 99.8%), anhydrous pyridine ($\text{C}_5\text{H}_5\text{N}$, 99%), hexamethyldisi-

lazane ($\text{C}_6\text{H}_{19}\text{NSi}_2$, 99%) and chlorotrimethylsilane ($\text{C}_3\text{H}_9\text{ClSi}$, 99%) were obtained from Sigma–Aldrich. NaCl (99.999%), NaBr (99.99%), NaOH (GR grade) and H_2SO_4 (GR grade) were purchased from Shanghai Jingchun Reagent. The salinity was varied by addition of NaCl (1 M) and NaBr (0.1 M). The initial pH value of AO7 solution was 6.5. The solution pH was adjusted by addition of H_2SO_4 or NaOH, depending on the experimental conditions. UltraPure water from Barnstead instrument was used to prepare the aqueous solutions.

2.2. Experimental procedures

Irradiation experiments were performed in an XPA-II type photochemical reactor, as shown in Text SM-1. The destruction of AO7 was monitored by UV–Vis spectrophotometer (Hitachi U-2910) at 485 nm. TOC measurements at certain time intervals were carried out by a Shimadzu TOC-V_{CPH} analyzer. Dye degradation products in the presence of Cl^- were detected by GC–MS instrument (Agilent 7890A-5973N). Samples were pretreated using 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 (Yuan et al., 2011, 2012a,b).

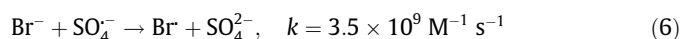
2.3. Kinetic modeling

Kinetic modeling of UV/ $\text{S}_2\text{O}_8^{2-}$ system was carried out using chemical modeling software, *Kintecus 4.55*. The reaction set based on radical reactions as shown in Table SM-2 was inputted into the program. The variations of SO_4^- , $\cdot\text{OH}$, chlorine radicals and the corresponding degradation products of AO7 were simulated (Text SM-2). Sensitivity of the model to certain reaction was investigated based on the average normalized square of residuals between the original model output, according to the method recommended by Rose and Waite (2002).

3. Results and discussion

3.1. Effect of halide ions on dye degradation

The removal rate of AO7 was significantly accelerated by the addition of Cl^- (1–100 mM) and Br^- (0.01–0.1 mM), but such enhancement reduced gradually with more halide ion present (Fig. 1a and Fig. SM-2). The mineralization process was not inhibited by lower content of Cl^- (1–100 mM). With higher amount of Cl^- (>100 mM) present in the solution, the TOC removal rate of AO7 decreased rapidly (Fig. 1b). The inhibition effect of Br^- above 0.5 mM may be ascribed to the higher scavenging reaction rate (Eq. (6)) and less reactive bromine radicals, e.g. $\text{Br}^\cdot/\text{Br}^-$ (2.00 V) < $\text{Cl}^\cdot/\text{Cl}^-$ (2.47 V).



The inconsistent results obtained by the previous studies regarding the effect of Cl^- (Text SM-3) on the oxidation efficiency by $\text{S}_2\text{O}_8^{2-}$ may be attributed to the complicated degradation pathways involving SO_4^- and various chlorine radicals (Bennedsen et al., 2012; Li et al., 2013; Lin et al., 2013; Tan et al., 2013). Therefore, the detailed mechanism of AO7 degradation using UV/ $\text{S}_2\text{O}_8^{2-}$ process was analyzed by means of kinetics modeling below.

3.2. Effect of the initial pH

Both decoloration rate and mineralization rate of AO7 was found to be enhanced by the increasing pH whether Cl^- was present or not (data not shown), which may be due to the conversion of

Download English Version:

<https://daneshyari.com/en/article/6309022>

Download Persian Version:

<https://daneshyari.com/article/6309022>

[Daneshyari.com](https://daneshyari.com)